Investigating cation-substituted metal vanadate photoanodes for solar water splitting

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**NANYANG
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SINGAPORE

**INVESTIGATING CATION-SUBSTITUTED METAL
VANADATE PHOTOANODES FOR SOLAR WATER
SPLITTING**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2019

INVESTIGATING CATION-SUBSTITUTED METAL VANADATE PHOTOANODES FOR SOLAR WATER SPLITTING

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

14 Feb 2019

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Date

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Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

14 Feb 2019

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A handwritten signature in black ink, appearing to read 'Lydia H. Wong', enclosed within a thin black rectangular border.

Lydia H. Wong

.....

Authorship Attribution Statement

This thesis contains material from papers published/in preparation in the following peer-reviewed journals where I was/will be the first author.

Chapter 4 is published as M. Zhang, R. P. Antony, S. Y. Chiam, F. F. Abdi and L. H. Wong. Understanding the Roles of NiO_x in Enhancing the Photoelectrochemical Performance of BiVO_4 Photoanodes for Solar Water Splitting. *ChemSusChem*. (2018) DOI:10.1002/cssc.201801780.

The contributions of the co-authors are as follows:

- Prof. L. H. Wong and Dr. F. F. Abdi and provided supervision on the project and revised the manuscript.
- Dr. R. P. Antony provided the initial idea and designed the experiments.
- I performed most of the laboratory work (except XPS, RSV and TRMC) at the School of Materials Science and Engineering. I also analyzed the data and drafted the manuscript.
- Dr. S. Y. Chiam carried out XPS measurements. Dr. R. P. Antony helped with XPS data analysis.
- Dr. F. F. Abdi performed RSV and TRMC measurements and analyzed the data.

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The contributions from co-authors are as follows:

- Prof. Lydia Wong supervised the project.
- I wrote the drafts of the manuscript. Prof. Lydia Wong and Dr. Fatwa Abdi edited the manuscript drafts.

- I performed most of the experimental work, including fabrication and characterizations. Khue Huu Pham performed part of the experiments. Dr. Yanan Fang helped with TEM measurements and image analysis. YF. Tay helped with XPS and UPS measurements.

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- Prof. Lydia Wong and Dr. Fatwa Abdi supervised the project.
- Prof. R. van de Krol, Prof. L. H. Wong, and Dr. F. F. Abdi edited the manuscript drafts.
- I wrote the drafts of the manuscript.
- I performed most of the experimental work, including fabrication and characterizations.
- Dr. Y. Ma and Dr. D. Friedrich helped in the data analysis of TRMC.

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Abstract

As a promising way to harvest solar energy, photoelectrochemical (PEC) water splitting has attracted intensive interest and attention in recent years. Some issues remain in the field of PEC water splitting and the choice of photoanode is an important problem. Recent decade has witnessed the rapid development of BiVO₄ as one of the most successful photoanodes. While it has achieved 90% of its theoretical photocurrent, further improvement is limited by its relatively large bandgap 2.4 eV. Hence, to find alternative photoanode candidates with lower bandgap and comparable charge transport properties is urgently needed.

This thesis aims to explore cation substituted metal vanadates which have lower bandgap than BiVO₄ and comparable charge transport properties. First, the properties of BiVO₄ and the role of catalyst have been explored to understand the limitation of BiVO₄ photoanode. Next, Fe was incorporated into BiVO₄ system to partially substitute Bi to create a mixture of BiVO₄ and FeVO₄. All the mixed metal vanadate photoanodes indeed have lower bandgap than BiVO₄. PEC measurements show that Bi/Fe in 1:1 ratio has the highest performance and the bandgap has lowered to 2.2 eV. The heterojunction between BiVO₄ and FeVO₄ is also confirmed to be beneficial to charge separation.

FeVO₄ has a near-optimal bandgap around 2.07 eV, but its photocurrent achieved has been an order lower than BiVO₄. The intrinsic properties of this compound are not available in the literature and hence limit its development as a potential photoanode. In this thesis, a series of characterizations have been carried out for the first time to determine the intrinsic properties and to understand the performance limiting factor. It is found that the performance of FeVO₄ is limited by its poor charge carrier separation. With the help of microwave conductivity measurements, the origin of inefficient charge separation is attributed to the low carrier mobility. Doping has been applied to improve the carrier concentration and mobility, but the absolute photocurrent increase is limited and separation efficiency still remains low.

To further enhance the charge separation, nanostructured FeVO_4 was fabricated by a facile two-step method. Interestingly, nanostructured FeVO_4 has an even lower bandgap of ~ 1.9 eV than the film. Substantial increase of photocurrent can be achieved as a result of enlarged absorption and surface area. It is demonstrated that nanostructure successfully boost the separation efficiency. Future investigations to optimize the crystalline quality and size of nanostructure may further improve the performance of FeVO_4 photoanodes.

In summary, this thesis succeeds in investigating novel cation substituted vanadates which has a smaller bandgap than BiVO_4 . FeVO_4 is identified as a promising photoanode material and found to be limited by poor charge separation. This thesis establishes for the first time its opto-electronic and photoelectrochemical properties and therefore recommends that, with optimized doping and nanostructuring, FeVO_4 has the potential as a photoanode for solar water splitting.

Lay Summary

Global warming has been widely acknowledged to be a pressing issue to sustain the long-term livability of the earth. It is proposed that reducing the usage of traditional fossil fuels while adopting renewable energy is the ultimate way to tackle the issue. Solar energy is considered unlimited compared with the lifespan of human life and is widely assessable. The intermittency problem of sunshine can be solved by storing solar energy into chemicals. Water is an abundant and accessible resource and it can be split into hydrogen and oxygen under certain conditions. Therefore, it is an exciting way to utilize solar energy to split water into hydrogen fuels.

Photoactive semiconductors are a kind of materials used in solar water splitting to realize the water splitting reaction. The semiconductors that are producing oxygen are called photoanodes. Their maximum ability to generate oxygen is related to the bandgap of semiconductor. One photoanode that has been well explored is bismuth vanadate with a bandgap of 2.4 eV. To generate more oxygen during water splitting and to make this technology more affordable, a lower bandgap is needed.

This thesis addresses the problem of finding a novel photoanode by incorporating other metal into bismuth vanadate. The newly identified material iron vanadate has a lower bandgap than bismuth vanadate and has the potential to absorb more sunlight. The thesis investigates the properties of iron vanadate and employs several techniques to improve its performance.

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Abbreviations

ALD	Atomic Layer Deposition
CB	Conduction Band
CBM	Conduction Band Minimum
DFT	Density Functional Theory
DOS	Density of States
ECSA	Electrochemical Active Surface Area
EDX	Energy Dispersive X-ray
EIS	Electrochemical Impedance Spectroscopy
EQE	External Quantum Efficiency
FESEM	Field Emission Scanning Electron Microscopy
FFT	Fast-Fourier Transform
FTIR	Fourier Transform Infrared Spectroscopy
FTO	Fluorine-doped Tin Oxide
HRTEM	High Resolution Transmission Electron Microscopy
IMPS	Intensity Modulated Photocurrent Spectroscopy
IPCE	Incident Photon-to-Current Conversion Efficiency
LSV	Linear Sweep Voltammetry
MS	Mott-Schottky
NR	Nanorod
OCP	Open Circuit Potential
OER	Oxygen Evolution Catalyst
PEC	Photoelectrochemical
PMOD	Photochemical Metal Organic Deposition
PVP	Polyvinyl Pyrrolidone
RSV	Rapid Scan Voltammetry
SDC	Scanning Droplet Cell
SECM	Scanning Electrochemical Microscopy
SEI	Secondary Electron Images
SEM	Scanning Electron Microscopy

STH	Solar-to-Hydrogen
TEM	Transmission Electron Microscopy
TRMC	Time-resolved Microwave Conductivity
UPS	Ultraviolet Photoelectron Spectroscopy
VB	Valence Band
VBM	Valence Band Maximum
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

Chapter 1

Introduction

The thesis overview is presented in the first chapter. After the brief introduction of project background, the hypothesis is described to substitute Bi^{3+} in bismuth vanadate with other metal cations to form novel complex metal oxides. On the basis of hypothesis proposed, objective and scope of the thesis are elaborated, followed by a brief introduction to the content of each chapter. The purpose of the thesis is to investigate cation substituted metal vanadates with enlarged optical absorption than bismuth vanadate but with comparable electronic properties. Research findings on the properties of novel metal vanadates like iron vanadate and modification techniques are highlighted in the last part.

1.1 Hypothesis/Problem Statement

The operation of modern society relies on the consumption of various energy resources. At present, the world population reaches 7.6 billion and it is accompanied by massive usage of energies (15 TW) to meet the needs of such a giant population. However, till 2015, more than 85% of total world energy consumptions is still using fossil fuel.^[1] It is estimated that by 2050 the world population will reach 9.7 billion and by then the predicted world energy consumption will be 30 TW.^[2-3] Easy and affordable access to energy resources would be a huge challenge worldwide, especially to less developed countries. The dual effect of fossil fuels depletion and greenhouse gas emission has alerted people to reduce the dependency on fossil fuels and develop alternative energy resources. Among all other energy resources, solar energy is considered the most abundant, cheap and accessible energy. It is estimated that if 0.16% of the earth surface is covered with 10% efficiency solar cells, it would be sufficient to fulfill the current energy needs.^[2]

The utilization of sunlight faces the problem of energy storage as the intermittent nature of sunlight. Photoelectrochemical (PEC) water splitting would be a potential way to storage solar energy into fuel (hydrogen) to overcome the issue. The key part in PEC water splitting is semiconductors, which can absorb incident photons and generate electron-hole pairs to split water. The process mechanism in alkaline electrolyte can be written in two half reactions (**Figure 1.1**):

In acidic electrolyte, the reaction process can be described as:

Combing the two half-reactions, overall water splitting reaction under illumination can be written as:

Figure 1.1 Schematic tandem cell with illumination on photoanode and photocathode. Enlarged is the band alignment of photoelectrodes and carrier transport mechanism during solar water splitting process.^[4]

The water oxidation reaction (Equation 1.2) involves multiple charge carrier transfer process, making it the rate-limiting step in the whole reaction. In PEC water splitting, semiconductor in the water oxidation side is called photoanode, while the water reduction side photocathode. The sluggish water oxidation reaction has attracted considerable research efforts in search of an appropriate photoanode material. The ideal photoanode material should satisfy some necessary requirements, including proper band alignments, decent charge carrier properties, good absorption and a long lifetime in aqueous environments. Although it is hard for one material to meet all the requirements, there are a few semiconductors identified as potential photoanodes such as titanium dioxide (TiO_2), hematite (Fe_2O_3), tungsten oxide (WO_3) and bismuth vanadate (BiVO_4). The recent decade has witnessed the successful development of BiVO_4 , whose photocurrent increases from $\sim 0.1 \text{ mA cm}^{-2}$ to approaching the theoretical limit of 6.72 mA cm^{-2} .^[5-6] Ideally, BiVO_4 photoanode can achieve 9% solar-to-hydrogen (STH) efficiency. Further efficiency improvement on BiVO_4 is limited by the bandgap of BiVO_4 (2.4 eV), which confines the utilization of sunlight below 520 nm.

It is calculated that in an ideal tandem cell, matching a photoanode with bandgap of 1.7-1.9 eV and a small bandgap bottom photocathode (1.0-1.3 eV) can reach 20% STH efficiency.^[7-10] In view of the photoanodes mentioned above, the choice for a good

photoanode in the tandem cell is still unclear. Therefore, looking for novel photoanode materials around the optimal bandgap range is the new research focus. Reducing the bandgap of BiVO_4 is a logical approach to begin with as various studies on BiVO_4 photoanodes provide rich experience and knowledge probably transferrable to other photoanodes. Density of states (DOS) calculations of monoclinic BiVO_4 by density functional theory (DFT) and experimental measurements have confirmed near-bandgap orbitals.^[11-13] Valence band maximum (VBM) is composed of O 2p and Bi 6s hybrid orbitals and conduction band minimum (CBM) is mainly contributed by V 3d orbital (Figure 1.2).

Figure 1.2 Illustrated electronic structure of monoclinic BiVO_4 in energy level diagram. Experimental data are shown on the right part of the figure.^[13]

The position of the conduction band (CB) of BiVO_4 is already close to the hydrogen evolution potential. The scaffold of $[\text{VO}_4]$ in BiVO_4 allows the formation of V 3d orbitals at CBM and O 2p orbitals at VBM.^[14] Reducing the bandgap by lowering the conduction band is therefore not preferred, since it would be reflected in a more positive onset potential (undesired). It is therefore our interest to remain on metal vanadates. Choi and coworkers investigated the possibility of replacing V by W or Mo but the bandgaps of Bi_2WO_6 and $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ are 2.8 and 3.0 eV, respectively, making them not favorable for use in solar water splitting.^[15]

Since the valence band maximum of BiVO_4 is mainly contributed from O 2p orbitals, incorporation of nitrogen or sulfur could possibly push up the valence band (VB). Initial results performed by nitrogen or sulfur doping of BiVO_4 successfully showed reduced bandgap, however the fabrication conditions and PEC stability poses some issues.^[16] Hybridized Bi 6s orbitals in VBM suggest that the addition of other metal cation is likely to lift valence band position.

The **hypothesis**, therefore, is to either partially or fully substitute Bi^{3+} with other metal cations to form novel complex (ternary, quaternary) metal oxides. The introduction of new cation orbitals would couple with O 2p orbitals to bring the valence band position up, while the conduction band is still controlled by V 3d orbitals. As a result, the bandgap of new complex metal oxides can be smaller than that of BiVO_4 and as a result the theoretical STH of the new metal vanadate can be enlarged. Substitution of Bi cation with other metal elements may also cause challenges such as unfavourable d-d transition (transition metal d orbital to V 3d orbital). Several recent publications on combinatorial synthesis and calculations have indirectly supported this hypothesis. For example, Neaton and coworkers provided evidence of smaller bandgap after cation substitution theoretically and experimentally, by calculating the density of states and measuring bandgap of different metal vanadates by UV-Vis spectroscopy. They proposed that manganese vanadate^[17] ($\text{Mn}_2\text{V}_2\text{O}_7$, bandgap 1.75 eV) can be used as an excellent light absorber, and copper vanadates^[18] ($\text{CuO-V}_2\text{O}_5$ system, bandgap below 2.0 eV) as promising solar fuels photoanodes.

1.2 Objectives and Scope

Based on the hypothesis discussed above, the **objective of this thesis** is to investigate cation substituted metal vanadates which have lower bandgap than BiVO_4 and comparable and/or superior electrical properties. The novel metal vanadate would enable enlarged visible light absorption and higher theoretical photocurrent. Initial stage of literature review confines the selection of cation substituted vanadate in this thesis to iron vanadate (FeVO_4) (reason for the choice and description on other metal vanadates to be seen in the next

chapter).

To fulfill the objective, the **scope** of the thesis includes:

- (1) Understanding the mechanism for better PEC performance of NiO_x catalyst modified BiVO_4 photoanodes. The project provides necessary understanding of vanadate photoanodes and serves as a starting point for the following investigations on novel vanadate systems.
- (2) Developing new metal vanadate photoanodes (cation substituted BiVO_4 , $\text{Bi}_x\text{Fe}_{1-x}\text{VO}_4$ and FeVO_4).
- (3) Assessing and understanding the limitations of FeVO_4 as a photoanode material for PEC water splitting. Both common and advanced characterizations are applied to obtain its physical, electrical and photoelectrochemical properties.
- (4) Modifying FeVO_4 photoanodes according to the limitations detected from various characterizations. The modification techniques include doping, catalyst loading and nanostructuring.

1.3 Dissertation Overview

The thesis addresses investigations of metal vanadates as photoanode materials (BiVO_4 , $\text{Bi}_x\text{Fe}_{1-x}\text{VO}_4$ and FeVO_4). Fe substituted BiVO_4 ($\text{Bi}_x\text{Fe}_{1-x}\text{VO}_4$ and FeVO_4) with smaller bandgap are assessed as photoanodes for PEC water splitting. The outline of this thesis is given as:

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

Chapter 2 reviews the literature concerning the development of BiVO_4 and other cation substituted metal vanadates. Specifically, common modification methods on BiVO_4 photoanodes are introduced. The justification for choosing Fe as a cation substitute is also given.

Chapter 3 discusses the principles underlying the fabrication methods and characterization

techniques employed. Detailed reasons for the chosen methods are given in the chapter.

Chapter 4 elaborates the functions of amorphous nickel oxide (NiO_x) loaded onto Mo-doped BiVO_4 . Deposition of NiO_x led to both enhanced charge separation and charge transfer efficiencies, which can be assigned to larger band bending and efficient hole injection at BiVO_4 surface respectively.

Chapter 5 elaborates the performances of partially-substituted Fe into BiVO_4 ($\text{Bi}_x\text{Fe}_{1-x}\text{VO}_4$, $0 \leq x \leq 1$) photoanodes. The combination of Fe and Bi vanadates showed higher charge carrier efficiency and enlarged visible light absorption. $\text{Fe}_{0.5}\text{Bi}_{0.5}\text{VO}_4$ composition demonstrated highest PEC performance. It is found that $\text{BiVO}_4/\text{FeVO}_4$ heterojunction is responsible for better charge separation, while the enlarged absorption is attributed to the lowered bandgap of $\text{BiVO}_4/\text{FeVO}_4$ mixture.

Chapter 6 elaborates the opto-electronic and photoelectrochemical properties of FeVO_4 photoanodes. FeVO_4 thin films were fabricated by spray pyrolysis and examined as a potential photoanode material. FeVO_4 was characterized to be limited by low carrier mobility and molybdenum doping was successfully adopted to enhance its mobility, lifetime, and carrier concentration to achieve better PEC performance.

Chapter 7 elaborates the fabrication of nanostructured FeVO_4 photoanodes. Physical and photoelectrochemical characterizations have been performed to demonstrate the improvement of nanostructured FeVO_4 compared with planar film. Doping of Mo in the nanostructure can further enhance the overall performance. Surprisingly, the nanostructured film exhibits a lowered bandgap, which extends visible light utilization further than planar film.

Chapter 8 summarizes the whole thesis and sheds light on the reconnaissance work which can be carried out in the future. Extended ideas based on the hypothesis and experimental results are also included.

1.4 Findings and Outcomes/Originality

This research led to several novel outcomes by:

1. Understanding the role of NiO_x catalyst on metal vanadate system for the first time. Higher charge separation is due to enlarged band bending after NiO_x deposited at the surface of BiVO_4 , as evidenced by higher photocurrent in the hole scavenger and open-circuit potential. Rapid scan voltammetry and time-resolved microwave conductivity measurements help to determine the role of NiO_x in swift hole transport. The easy and robust deposition method for both Mo doped BiVO_4 film and NiO_x layer presents an alternative route for large scale photoanode fabrication.
2. Fabricating mixed phase iron bismuth vanadate compound ($\text{Bi}_x\text{Fe}_{1-x}\text{VO}_4$) and investigating the optimal Bi/Fe ratio. The mixed phase compound $\text{Fe}_{0.5}\text{Bi}_{0.5}\text{VO}_4$ with 2.2 eV bandgap has an enlarged absorption than BiVO_4 . Charge separation efficiency was enhanced owing to the formation of $\text{BiVO}_4/\text{FeVO}_4$ heterojunction. The findings demonstrate a simple method to engineer the bandgap of BiVO_4 by forming vanadate mixture.
3. Fabricating triclinic FeVO_4 thin films by spray pyrolysis and assessing it as a potential photoanode material for solar water oxidation. This is the first reported measurement of FeVO_4 by time-resolved microwave conductivity measurements which reveals that its poor charge separation efficiency originates from the low carrier mobility. Molybdenum doping is found to be effective in significantly improving its carrier concentration, carrier mobility, carrier lifetime and diffusion length. The findings provide clear pathways by nanostructuring or heterojunction formation to improve charge separation in the bulk of FeVO_4 .
4. Fabricating nanostructured FeVO_4 photoanodes. FeVO_4 is first fabricated as nanorod shaped structure, which gives higher surface area than film structure. The nanostructured photoanode demonstrated much better PEC performance (in hole scavenger) and elemental doping assists higher charge separation efficiency. Another exciting finding is that nanostructured FeVO_4 photoanode can absorb more visible spectrum than pristine film one. These findings set a good foundation for next step investigations optimization of fabrication conditions. All findings above

contribute greatly to minimize the gap between theoretical limit of FeVO₄ and practical performances.

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Chapter 2

Literature Review

This chapter outlines the development of BiVO_4 photoanodes in the last two decades. The properties of BiVO_4 and modification techniques applied to tackle its limitations are explained in detail. Recent trials to find novel photoanodes beyond BiVO_4 are also summarized, with emphasis on the advancement of novel metal vanadates, MVO_4 , where $M = \text{Cu}, \text{Mn}, \text{Fe}$.

2.1 Development of BiVO₄ photoanodes

This section presents advancement of bismuth vanadate as a photoanode material in the recent decade. It also includes the techniques applied to tackle major limitations of bismuth vanadate.

2.1.1 BiVO₄ as a photoanode

BiVO₄ prepared in the laboratory usually present the scheelite structure although it has three polymorphs.^[1-2] The monoclinic scheelite crystal structure (space group $C2/c$, $a = 7.247 \text{ \AA}$, $b = 11.697 \text{ \AA}$, $c = 5.09 \text{ \AA}$, and $\beta = 134.226^\circ$) is usually prepared in the laboratory and utilized in photoelectrochemical applications, while a slightly different tetragonal structured BiVO₄ is also reported as space group $I2/b$ with $a = 5.1935 \text{ \AA}$, $b = 5.0898 \text{ \AA}$, $c = 11.6972 \text{ \AA}$, and $\beta = 90.387^\circ$.^[1, 3-4] The layered monoclinic BiVO₄ crystal is composed of [VO₄] and [BiO₈] units. [VO₄] tetrahedra and [BiO₈] dodecahedra are connected with edge-sharing O atoms.^[3] The Bi and V atoms surrounding O are slightly distorted in the monoclinic structure, which is reported to be favorable to photocatalytic applications.^[5]

Figure 2.1 (a) Illustration of crystal structure of monoclinic scheelite BiVO₄. (b) The side view taken along c -axis.^[2]

Monoclinic scheelite BiVO_4 is reported to have a bandgap of 2.4-2.5 eV and tetragonal BiVO_4 2.9 eV.^[6-7] The electronic structure of BiVO_4 has a strong relationship with its crystal and optical properties. Both theoretical calculations (DFT calculations) and experimental investigations have confirmed that scheelite BiVO_4 has a smaller bandgap (~2.4 eV), which is due to the Bi 6s + O 2p state hybridization at VBM.^[4, 6-9] Despite there has been a controversy regarding the optical transition in BiVO_4 ,^[8-11] recent studies combining DFT calculations with experiments have eliminated the confusion. Cooper and coworkers revealed BiVO_4 has an indirect optical transition while the direct one is occurring closely (only 0.2 eV above the indirect transition).^[12-13]

BiVO_4 was first investigated by Kudo et al. in 1998 for generating oxygen under visible light illumination in Ag^+ aqueous solution (Ag^+ as an electron scavenger).^[14] In the early stage, BiVO_4 was studied in the form of particulates as a heterogeneous photocatalyst.^[6, 15-17] Following studies of BiVO_4 fabricated as thin film photoanodes emerged, but the photocurrents reported were rather low (in the range of hundreds of $\mu\text{A cm}^{-2}$).^[18-20] The moderate photocurrents were limited by the poor understanding of its electrochemical and photoelectrochemical properties. The major PEC performance limiting factors have been identified, including sluggish carrier transport to the electrolyte, poor electrical conductivity and severe electron-hole recombination.^[1-2] For each limitation, corresponding techniques have been developed and great advancements have been achieved.

2.1.2 Strategies to improve BiVO_4 performance

(1) Catalyst loading or surface passivation

The first limitation of BiVO_4 has been attributed to its slow transfer of photogenerated holes to the electrolyte. Such a major limitation is evidenced by various reports using hole scavengers (hydrogen peroxide, sulfites, or methanol).^[19, 21-23] Without the presence of hole scavengers, surface modification composites have to be applied on the surface of BiVO_4 to tackle surface recombination.

After initial applications of precious metal catalysts such as PdO_x and IrO_x ,^[24-26] efforts have been shifted to earth-abundant and cost-effective catalysts like cobalt phosphate (Co-Pi), cobalt and nickel borate (Co-Bi and Ni-Bi), NiO_x , CoO_x , FeOOH , NiOOH .^[10, 21-22, 27-37] Co-Pi has been commonly used as top layer on BiVO_4 among all catalysts listed above. The structure and mechanism of Co-Pi is out of the scope the thesis and can be found elsewhere.^[38-39] Almost complete surface suppression was achieved by Zhong et al. after loading Co-Pi on W doped BiVO_4 , showing a catalytic oxidation efficiency over 80% through overall potential range and near 100% at 1.5 V vs. RHE.^[23] A remarkable cathodic onset potential shift (440 mV) was also achieved upon loading Co-Pi.^[21] Similar results were obtained on Co-Pi catalyzed W doped BiVO_4 by Abdi and coworkers. From 1.23 V vs. RHE onwards, catalytic efficiency of catalyzed film was beyond 90%. The deposition of Co-Pi was reported to enhance the photocurrent value especially at low bias, shift the onset potential cathodically, and improve the stability.^[22-23, 29-30, 40-42] The function of Co-Pi on BiVO_4 has been first considered as catalyst, while recent investigations using intensity modulated photocurrent spectroscopy (IMPS) revealed that surface modification with Co-Pi can reduce the surface recombination rate to one order lower than pristine BiVO_4 .^[43] It elucidates well that Co-Pi only passivate the surface through reducing surface recombination instead of enhancing water oxidation kinetics, which is quite surprising.

Figure 2.2 Schematic diagram of photocurrent increase and onset potential shift under the influence of catalyst (oxidation catalyst, OC).^[42]

Some other catalysts like CoO_x and NiO_x also obtain benefits in BiVO_4 photoanode PEC performance as they can form heterojunction with BiVO_4 . Ni doped CoO_x was deposited by spray pyrolysis on BiVO_4 photoanodes with superior catalytic efficiency.^[44] The improvement was attributed to increased surface band bending by Ni doped CoO_x layer reducing the Fermi level position. Charge separation efficiency can be also enhanced by depositing p-type Co_3O_4 onto BiVO_4 surface.^[33] The bulk separation efficiency can reach up to 77% at 1.23 V vs. RHE, which is the result of forming p-n Co_3O_4 - BiVO_4 junction.

Dual catalyst loading can demonstrate higher performance on BiVO_4 photoanodes compared with single catalyst. While NiOOH and FeOOH can both be oxygen evolution reaction (OER) catalyst on BiVO_4 , $\text{NiOOH}/\text{FeOOH}$ dual layer catalyst demonstrated even higher photocurrent when deposited on nanoporous BiVO_4 .^[31] The deposition sequence, however, plays an important role in affecting PEC performance. The reverse sequence $\text{FeOOH}/\text{NiOOH}/\text{BiVO}_4$ photoanode showed worst photocurrent in comparison with $\text{FeOOH}/\text{BiVO}_4$, $\text{NiOOH}/\text{BiVO}_4$, and $\text{NiOOH}/\text{FeOOH}/\text{BiVO}_4$ photoanodes. Such a sequence implied that minimum recombination can be obtained on $\text{FeOOH}/\text{BiVO}_4$ interface in combination with NiOOH top layer OER catalyst. There is a similar layered catalyst structure loaded on crystalline BiVO_4 particles. An ultrathin layer of p-type NiO was deposited by atomic layer deposition (ALD) on $\text{CoO}_x/\text{BiVO}_4$.^[32] Apart from forming p-n junction, the ultrathin NiO layer was able to in situ transform into NiOOH layer. The sequence of catalysts is consistent with the aforementioned reports that NiOOH was favorable for water oxidation and NiO/BiVO_4 p-n junction can offer additional band bending for better charge separation.^[31, 33] Owing to the synergic effect, BiVO_4 photoanodes loaded with dual catalysts demonstrated a low onset potential as well as a high photocurrent ($> 2 \text{ mA cm}^{-2}$) at 0.6 V vs. RHE.^[31-32, 45] The sluggish surface carrier transfer to the electrolyte, therefore, can be tackled with surface modification by loading passivation layers or catalysts.

(2) Doping

Compared with ZnO and WO₃, BiVO₄ has a relatively small carrier mobility which is more than 2 orders lower than that of ZnO (100 - 300 cm² V⁻¹ s⁻¹) and WO₃ (~10 cm² V⁻¹ s⁻¹).^[46-47] Pristine polycrystalline BiVO₄ is reported with a mobility of 0.02 cm² V⁻¹ s⁻¹ by time-resolved measurements and the mobility of single crystal BiVO₄ from AC Hall measurements is only ~0.2 cm² V⁻¹ s⁻¹.^[48-49] The low carrier mobility has been recently revealed to originate from polaron conduction mechanism as evidenced by THz spectroscopy results.^[50] As a result, poor carrier transport in BiVO₄ would inhibit the PEC performance.

Elemental doping has been widely applied to compensate for its poor carrier properties. By purposely introducing very small amount of other elements into BiVO₄, the carrier concentration will increase and thereby the electrical conductivity will also increase.^[2] A rapid screening study using scanning electrochemical microscopy (SECM) was performed to pick out the appropriate dopants.^[51] A third element was added into bismuth vanadate by different ratio in arrays to test its photoelectrochemical ability in this study. The additional elements include W, Fe, B, Cu, Zn, etc. Among these elements W doping exhibited obvious enhancement in photocurrent and 5% W doping had the highest photocurrent. The doped and pristine samples were analyzed by electrochemical impedance spectroscopy and it was found W doped sample had higher charge carrier levels and lower resistance. Further studies investigated other elemental doping and confirmed Mo and W as two most effective doping elements in BiVO₄.^[29, 34, 52] Upon Mo⁶⁺ or W⁶⁺ replaces V⁵⁺, the doping element functions as an electron donor in n-type BiVO₄. Dual doping of Mo and W behaved even better performance than single Mo or W doping.^[53-54] Apart from experimental confirmation, the first principles calculation and modeling results assuming the positional substitution of V by Mo and W proved to increase carrier density in BiVO₄.^[54-57] The discovery of synergistic effect adds insight into understanding of doped Bi-V-O system.

The space charge layer would be shortened when the carrier concentration increases after doping, which is not good for charge separation. A facile method to solve the problem was to construct n^+-n homojunction.^[58] Unlike uniformly doped BiVO_4 film, gradually doped BiVO_4 film obtained an internal electric field to facilitate charge separation (**Figure 2.3**). The separation efficiency at 1.23 V vs. RHE increased from 38% to over 60% after constructing the dopant gradient. Several other reports which have adopted the idea of gradient structure also achieved enhanced performance.^[59-61] Overall, doping has been proved to be an effective way to improve carrier mobility.^[1-2, 62-63]

Figure 2.3 Energy band diagram showing the extent of band bending for uniformly doped BiVO_4 film and gradient-doped one.

(3) Nanostructuring

BiVO_4 has found to have much shorter diffusion length (~ 70 nm) than its light absorption depth.^[48] The limitation of high recombination rate remains challenging, although low carrier densities can be increased by doping, and poor charge separation and transport could be facilitated by forming junctions or loading co-catalysts. In order for charge carriers successfully reach electrode surface before they are recombined, the morphology and structure should be carefully engineered to enable main dimensions smaller than diffusion length.

Creating a nanoporous structure is thereby desirable. A two-step fabrication method of nanoparticles (average particle size ~ 76 nm) was developed through BiOI electrodeposition and then apply vanadium source.^[31] After annealing the particles correlate into a three dimensional network (**Figure 2.4**). The calculated charge separation efficiency reached 70% and 90% at 0.6 V and 1.2 V vs. RHE, exceeding the common value of 30%. A recent report synthesized Mo-doped textured nanoporous BiVO_4 photoanode (particle size ~ 60 nm) and achieved similarly high photocurrent and efficiency with good stability for 14 h.^[64] The reduced particle size proved to be an ideal way in diminishing carrier recombination.

Figure 2.4 Cross-section image of microscopic images of a nanoporous BiVO_4 photoanode.^[31]

Constructing a core-shell structure is shot as an alternative design. Progresses have been made since the first trial of BiVO_4 on WO_3 nanowires. The host-guest structure (**Figure 2.5**) is introduced in the former part and WO_3 is chosen due to its appropriate band alignment and good electron conductivity as mentioned above.^[65] A highly transparent uniform $\text{WO}_3/\text{BiVO}_4$ photoanode was fabricated using thin layer BiVO_4 to coat mesoporous WO_3 nano-network with dual layer of $\text{FeOOH}/\text{NiOOH}$ catalysts.^[66] The photoanode was employed in a wireless $\text{WO}_3/\text{BiVO}_4/\text{DSSC}$ tandem cell, generating 5.7% STH water splitting efficiency without bias. However, the relatively low photocurrent density (3.1 mA cm^{-2} by Rao et al., 4.2 mA cm^{-2} by Shi et al.) compared with maximum 7.5 mA cm^{-2} showed the drawback of imperfect WO_3 nanostructure and non-optimal BiVO_4 thickness.^[65-66] The increase of surface area might bring about more defects and grain boundaries to become new recombination sites. The fabrication of WO_3 nanowire arrays and tuning optimal absorbing layer thickness should be very careful in this concern.

Once optimized, the highest photocurrent achieved adopting this structure is to be analyzed right in the next section.

Figure 2.5 Illustration of a core-shell BiVO₄/WO₃ structure.

2.1.3 Performance limitation of bismuth vanadate and outlook

BiVO₄ photoanodes now can be fabricated with confidence after identifying the main limitations and developing according techniques. Combined methods are generally utilized in modification to cope with the different problems. Photocurrent of BiVO₄ photoanode now can achieve close to its theoretical maximum value (7.5 mA cm^{-2}) if most of the problems solved properly.

Pihosh et al. noticed the pitfalls in others' publication which adopted the core-shell structure with a 5.35 mA cm^{-2} photocurrent.^[67-68] Pihosh optimized the length of WO₃ nanorods to $2.5 \mu\text{m}$ and thickness of absorbing layer Co-Pi/BiVO₄ to around 25 nm. The optimal thickness 25 nm, which is far less than the measured BiVO₄ diffusion length ($\sim 80 \text{ nm}$), achieved a tradeoff between light absorption and bulk carrier recombination. The fabrication procedure is shown in **Figure 2.6**. It was further evidenced by 90% IPCE under 480 nm and over 90% separation efficiency. The combinational effect of WO₃ heterojunction, conformal morphology, optimal film thickness and catalyst loading eventually gave a record photocurrent density of 6.72 mA cm^{-2} at 1.23 V vs. RHE under AM 1.5 simulated sunlight, i.e., 90% of the theoretical current. It should also be noted that the onset of photocurrent is only 0 V vs. RHE.

There remain some unresolved issues of BiVO_4 and one problem is the stability. For pristine BiVO_4 photocurrent drops quickly in electrolyte, owing to the dissolution of V^{5+} .^[69] Mechanism of BiVO_4 photocorrosion has been studied and trials of protection layers have been reported.^[70-72]

Figure 2.6 Illustration of fabrication procedure of the photoanode and water splitting diagram.^[67]

The relatively large bandgap, which limits the maximum photocurrent and STH efficiency, is the second challenge for BiVO_4 . Efforts into replacing V by W or Mo unexpectedly broadened the bandgaps of Bi_2WO_6 and $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ to 2.8 and 3.0 eV respectively, going in an opposite direction.^[73] Sb-alloyed BiVO_4 was explored to tune its bandgap ($\text{BiV}_{1-x}\text{Sb}_x\text{O}_4$ formula) but resulted in inferior PEC performance.^[74] A new promising strategy is to substitute Bi using other metal elements, fabricating cation-substituted bismuth vanadate with smaller bandgap. The idea of cation substitution has been well elaborated in **Chapter 1**.

2.2 Novel metal vanadates

To date there has been considerably very few reports on novel vanadates. **Section 2.2** introduces novel metal vanadates, MVO_4 (or other stoichiometries), where $\text{M} = \text{Mn}$, Cu and Fe, which are potentially promising in future photoelectrochemical applications.

2.2.1 Manganese vanadate

Some vanadates have been reconsidered or revealed recently as photoanode materials.^[75-77] Manganese vanadate is originally studied as a magnetic material and later considered to be used in the lithium ion battery anode due to its good capacity and stability.^[78-80] Manganese vanadate is normally synthesized in $\text{Mn}_2\text{V}_2\text{O}_6$ and $\text{Mn}_2\text{V}_2\text{O}_7$ formula with different Mn/V atomic ratio. MnV_2O_6 is in monoclinic crystal structure comprised of $[\text{MnO}_6]$ octahedra and $[\text{VO}_4]$ tetrahedral.^[79] While $\text{Mn}_2\text{V}_2\text{O}_7$ has two phases, namely monoclinic β -phase at high temperature, and triclinic low-temperature phase (α -phase) with a transition temperature at 16 K.^[77]

With the help of theoretical calculations, J. B. Neaton's group proposed β - $\text{Mn}_2\text{V}_2\text{O}_7$ as a promising light absorber, finding it has an ideal bandgap close to 1.8 eV theoretically and experimentally.^[77] From calculation, the band positions and density of states (DOS) clearly explained Mn 3d lift the valence band position, thus resulted in smaller bandgap of manganese vanadate. A small photocurrent ($\sim 0.1 \text{ mA cm}^{-2}$) was detected under chopped illumination in 0.1 M NaOH solution with $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple in a scanning droplet cell (SDC).^[77] However, without redox couple no photocurrent has been reported for water oxidation, which suggests itself may not be suitable as a photoanode material.^[2] It may be caused by the small overpotential ($\sim 0.3 \text{ V}$) as its the VBM is close to oxygen evolution potential, which suggests it may not be a good photoanode candidate.

2.2.2 Copper vanadate

Another cluster material investigated through both DFT calculations and high-throughput experiments is copper vanadate system. Analogous to FeVO_4 and $\text{Mn}_2\text{V}_2\text{O}_7$, copper vanadates before were only considered as battery materials or other applications.^[81-84] Copper vanadate system is taken into account for water splitting more recently. $\text{Cu}_3\text{V}_2\text{O}_8$ is the first copper vanadate reported systematically as a photoanode for water splitting.^[85] It has an indirect bandgap of 2.05 eV and is tested to be stable in pH 9.2. The photocurrent remains very low ($< 0.04 \text{ mA cm}^{-2}$ at 1.6 V vs, RHE) in potassium borate with a high onset

potential (> 0.7 V vs. RHE). By carrying out water oxidation in sulfite, the problem of $\text{Cu}_3\text{V}_3\text{O}_8$ was identified as fast bulk recombination. Mo doping dramatically changed its electronic structure by increasing electron diffusion length from 110 nm to 420 nm. This report provided a primary understanding of copper vanadate, shedding light to the unique features to motivate further investigations.

Larger scale of combinational experiments was later operated by J. B. Neaton and J. M. Gregoire groups.^[76, 86-87] A series of candidate copper vanadates were sorted out, enclosing $\alpha\text{-CuV}_2\text{O}_6$, $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$, $\beta\text{-Cu}_2\text{V}_2\text{O}_7$, $\gamma\text{-Cu}_3\text{V}_2\text{O}_8$, $\text{Cu}_{11}\text{V}_6\text{O}_{26}$. The cluster has desirable bandgaps located around 1.8 eV–2.0 eV, as summarized below in **Table 2.1**.

Table 2.1 Bandgaps obtained by experimental UV-vis measurements and band structure calculations.

	Phase	Optical bandgap (eV)	Computational bandgap (eV)	Reference
1	$\text{Cu}_{11}\text{V}_6\text{O}_{26}$	1.8 ± 0.1	2.01	[76]
2	$\alpha\text{-Cu}_2\text{V}_2\text{O}_7$	1.9 ± 0.1	2.26	[76]
3	$\beta\text{-Cu}_2\text{V}_2\text{O}_7$	2.0 ± 0.2	2.23	[76]
4	$\gamma\text{-Cu}_3\text{V}_2\text{O}_8$	1.8 ± 0.1	2.05	[76]
5	$\alpha\text{-CuV}_2\text{O}_6$	1.95	-	[88]

The retaining low conduction band edge is already known in vanadates due to the V states. The bandgap reduction, if compare with BiVO_4 , is attributed to the lifting of valence band edge affected by the hybridization of O 2p orbitals with open-shell cation Cu 3d states.^[76] These findings agree well with the hypothesis proposed in **Chapter 1**.

Initial studies of copper vanadates focused on material synthesis, bandgap and structure confirmation, scanning droplet cell PEC measurements and band structure calculations, intending to establish a structure-property relationship library. $\alpha\text{-CuV}_2\text{O}_6$, $\alpha\text{-CuV}_2\text{O}_7$,

$\text{Cu}_3\text{V}_2\text{O}_8$ and $\text{Cu}_{11}\text{V}_6\text{O}_{26}$ are stable in the electrolyte and demonstrated reasonable photoresponse. These materials still need further studies to meet the stringent requirements for use in solar fuel applications, including accurate measurement of flatband potential, carrier mobility, diffusion length and carrier lifetime. The photovoltage achieved may be limited by its band alignments, which prevents copper vanadate to be a promising photoanode.

2.2.3 Iron vanadate

Iron vanadate has been identified as an effective catalyst for photocatalytic degradation, gas sensing and NO_x conversion.^[89-92] Early combinatorial studies into different elemental compositions identified that Fe-V composite was photoactive and Fe/V in 1:1 ratio (corresponding to FeVO_4) obtained highest current response.^[93] Heterojunction of FeVO_4 with BiVO_4 , Fe_2O_3 , g- C_3N_4 , and Bi_2O_3 has been published as photocatalysts for efficient organic pollutant degradation.^[94-99] The stable and inexpensive material also attracts interest for photoelectrochemical water splitting due to their suitable bandgap of $\text{Fe}_2\text{V}_4\text{O}_{13}$ is 1.8 eV and FeVO_4 ~2.0 – 2.1 eV (Figure 2.10).^[100-101] Iron(II) vanadate was first systematically investigated by Craig D. Morton et al. as thin film photoanodes.^[101-102] In his dissertation FeVO_4 thin film was fabricated using precipitated particles suspension and sol-gel drop casting method. Photoanodes made by the two methods were characterized to give a bandgap of 2.0 eV. However, the photocurrent was only ~0.12 mA cm^{-2} and can not last long in aqueous solution.

Figure 2.7 UV-vis absorption measurement indicates FeVO_4 can absorb up to ~600 nm in the visible region.^[103]

W doped FeVO₄ photoanode was produced via layer-by-layer spin coating.^[103] Similar as BiVO₄, the introduction of W increased the photocurrent, which was almost doubled after doping. Nanoporous FeVO₄ photoanodes were fabricated by drop casting and self-doping of Fe³⁺ or Fe²⁺ was realized by immersing FeVO₄ into H₂O₂ or NaBH₄ solution.^[104] The nanoporous structure and effective doping resulted in improved PEC performance. Despite all the modifications, the photocurrents reported till now remain quite low.

Despite the increasing number of publications recently, disagreement between the publications should be noted. The optimal atomic ration of Fe/V in iron vanadate was first found to be 1 using a high-throughput screening system.^[93] The chemical composition can be tuned and photocurrent was evaluated automatically by the system. Another study showed that the highest photocurrent was achieved by FeV₂O₄, compared with Fe₂O₃, FeVO₄ and Fe₂VO₄.^[105] Discrepancies of the bandgap measured and band positions depicted are also observed.^[99, 105] There is, nevertheless, an agreement in most publications that iron vanadate with a proper bandgap would be a promising photoanode material. The variations fully reveal the inadequate knowledge of iron vanadate and necessity to further carry out systematic research into its intrinsic properties.

Table 2.2 Comparison of basic properties and PEC performances

Candidate materials	Crystal structure	E_g /eV	mobility	Band position	Stability	Photo-current*
Mn₂V₂O₇	thortveitite-like monoclinic	~1.75	***	Estimated VBM ~0.3 eV below H ₂ O/O ₂ potential	Stable in alkaline under illumination	N.A.
FeVO₄	triclinic	~2.07	?	?	Neutral to alkaline	In the order of 0.01-0.1 mA cm ⁻²
Cu_xV_yO_z	depends	1.8-2.1	?	depends	In pH=9.2 for 30 min	In the order of 0.01-0.1 mA cm ⁻²
BiVO₄	monoclinic	~2.4	0.2 cm ² V ⁻¹ s ⁻¹	VBM ~1 eV below H ₂ O/O ₂ potential	pH 3-11	~0.5-6.7 mA cm ⁻²

* Photocurrent values are summarized till Dec. 2016.

** Question mark indicates no reported value available till Dec. 2016.

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Chapter 3

Experimental Methodology

In this chapter, experimental methods to fabricate various photoanodes are listed including the rationale for selection. Prior to result chapters, the description of synthesis methods can provide initial understandings of the projects. Basic introduction to the characterizations is presented to give a broader view of the techniques applied.

3.1 Rationale for selection

The first project described in **Chapter 4** adopted a simple spin coating method to fabricate and drop casting to deposit NiO_x catalyst. Reasons to choose the fabrication methods are summarized below: (i) both spin coating and drop casting are low-cost fabrication methods; (ii) drop casting and spin coating are simple and efficient ways to fabricate thin film photoanodes; (iii) early work using spin coating has proved it to be a reliable fabrication method to produce high-quality BiVO_4 photoanodes.

In **Chapter 5**, electrospinning was used to deposit $\text{BiVO}_4/\text{FeVO}_4$ mixture. This method allows easy control on the film thickness and applied to all the compositions without altering fabrication parameters. In addition, the depositing process is efficient, flexible and tunable, making it suitable for multi-sample fabrication.

Spray pyrolysis was adopted in **Chapter 6** to fabricate thin film FeVO_4 photoanodes. The method has been verified by former results which show excellent BiVO_4 and CuBi_2O_4 photoelectrodes synthesized by spray pyrolysis. Spray pyrolysis has the advantage to construct high-quality and large-scale oxide layers but is also inexpensive. To study the basic properties of FeVO_4 , it is fitting and proper to use spray pyrolysis to produce a uniform thin film on either fluorine-doped tin oxide (FTO) or quartz substrates.

A two-step conversion method is applied to prepare nanostructured FeVO_4 in **Chapter 7**. One-step traditional methods mentioned above are hard to control the morphology despite the advantage of simplicity. The two-step method is composed of (i) preparing FeOOH nanorod and (ii) annealing with vanadium precursor. To fabricate FeOOH nanostructure template, hydrothermal is commonly used. The second step is carefully designed to incorporate V with facile control of temperature and annealing duration. This method is necessary to help maintain the nanostructure and is also simple and cost-effective.

Detailed descriptions on the steps of these fabrication methods are listed in the following section.

3.2 Experimental methods

3.2.1 Fabrication of graded Mo:BiVO₄ photoanodes

A simple synthesis strategy is adopted to fabricate bismuth vanadate, as reported in the previous studies.^[1-2] The precursor solution was prepared by mixing bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 98 %, Sigma Aldrich) and vanadium acetylacetonate ($\text{VO}(\text{C}_5\text{H}_7\text{O}_2)_2$, 98 %, Sigma Aldrich) in 1:1 ratio (0.3 mmol each). The solvent is a mixture of acetic acid (Sigma Aldrich), absolute ethanol and N,N dimethylformamide (Sigma Aldrich) taken in 1:1.25:1.25 ratio, respectively. 400 mg polyvinyl pyrrolidone (PVP, MW-130000, Sigma Aldrich) was then added into 3.5 mL of the precursor solution, which was further magnetically stirred at room temperature for 30 min to form a homogenous viscous solution. Molybdenum (Mo) doping was further achieved by adding ammonium molybdate tetrahydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, 99.98 % trace metal basis, Sigma Aldrich) into the precursor solution as mentioned above. The concentration of Mo doping was varied from 0 % to 2 % by adjusting the amount of ammonium molybdate tetrahydrate and vanadium acetyl acetate, resulting a final solution containing 1:1 molar ratio of Bi/(V+Mo). The graded samples were fabricated by a layer-by-layer spin-coating method (2000 rpm, 45 s) on a $1 \times 2 \text{ cm}^2$ cleaned FTO glass. All FTO substrates were sonicated successively in soap water, ethanol, acetone, deionized water (each step 20 min) and finally dried by nitrogen flow. The bottom layer consisted of 2 % Mo-doped BiVO₄, which was loaded through spin coating 60 μL precursor (containing 2 % Mo), and further annealed in air at 500 °C for 2 h with a heating rate 5° min^{-1} . Afterwards the second layer (1 % Mo-doped) was spin coated and annealed, so was the top layer (pure BiVO₄). The sequence of doping ratio is arranged to form a graded Mo doping.^[3] The prepared gradient Mo doped BiVO₄ (Mo:BiVO₄) samples were described as uncatalyzed BiVO₄ samples throughout the discussion. The schematic of the fabrication procedure is shown in **Figure 3.1**.

3.2.2 NiO_x catalyst deposition

PMOD method was employed to introduce NiO_x film on the as-prepared BiVO₄ samples. The method was previously demonstrated to be an effective technique to produce active transition metal based amorphous electrocatalyst for water oxidation.^[4-6] For this, PMOD precursor was prepared by dissolving 5 wt % (solution based) of Ni(II) 2-ethylhexanoate in hexane. Other concentrations have been explored, and 5 wt % was found to be an optimum concentration for maximizing performance. The Ni precursor was then spin coated over the uncatalyzed Mo:BiVO₄ thin film. Thereafter, the films were subjected to UV irradiation ($\lambda = 254$ nm, 15 W, Sankyo Denki) for 20 hours. To investigate the influence of annealing temperature, catalysts loaded BiVO₄ samples were annealed at 200 °C and 400 °C in a muffle furnace. The catalyst-loaded samples are named according to their Ni concentration and annealing temperature as follows: NiO_x-200 °C (coated with 5 wt % of Ni(II) precursor, annealed at 200 °C) and NiO_x-400 °C (5 wt % Ni(II) precursor, annealed at 400 °C).

Figure 3.1 Procedure adopted for fabricating NiO_x loaded porous gradient Mo:BiVO₄.

3.2.3 Preparation of Bi_xFe_{1-x}VO₄ films

All the films were fabricated by electrospinning in a similar procedure from the previous report.^[2] For one specific composition, Bi_xFe_{1-x}VO₄ ($0 \leq x \leq 1$), 0.06x mmol bismuth nitrate

pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 98%, Sigma Aldrich), 0.03(1-x) mmol iron(III) acetylacetonate ($\text{Fe}(\text{acac})_3$, 99.9%, Sigma Aldrich) and 0.03 mmol vanadium acetylacetonate ($\text{VO}(\text{acac})_2$, 98%, Sigma Aldrich) were mixed so that the (Bi+Fe)/V ratio equals to 1. The salt mixture was then dissolved in a mixed solvent containing 2 mL acetic acid (CH_3COOH , 99.7%, Sigma Aldrich), 2.5 mL absolute ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, 99.5%, Merck) and 2.5 mL N,N-Dimethylformamide ($\text{HCON}(\text{CH}_3)_2$, 99.8%, Sigma Aldrich). After adding 1200 mg Polyvinylpyrrolidone (PVP, $(\text{C}_6\text{H}_9\text{NO})_n$, $M_w \sim 1300000$, Sigma Aldrich), the solution was then kept at room temperature with magnetic stirring overnight to obtain a viscous and homogeneous solution. The addition of PVP was done to obtain a proper solution viscosity for electrospinning.

Figure 3.2 Illustration of the electrospinning setup in idle condition. During deposition, the needle moves along the slide to the center position.

The resulting solution was then used for the electrospinning deposition. 4 mL prepared solution was sucked into a 16 cm diameter syringe. The syringe and the electrospinning needle (20G, 13 mm length) were connected with a chemical resistant tubing (Tygon 2375, 1/16×3/16"). The setup is shown in **Figure 3.2**. Fluorine doped tin oxide (FTO) substrates ($14 \Omega/\text{cm}^2$, Nippon Sheet Glass) were subjected to a standard cleaning procedure (sonicated 20 min each in soap water, deionized water, acetone, deionized water and

ethanol). After drying by nitrogen flow, the FTO substrates were placed at the center of the electrospinning stage (collection plate) partially wrapped with an aluminum foil to allow contact between FTO conductive side and the stage. During the electrospinning process, a voltage of 25 kV was applied between the needle and the collection plate at a distance of 12 cm. The deposition rate was controlled at 1.5 mL/h by the syringe pump. The deposition was carried out at room temperature at different time intervals, i.e., 15, 30 and 45 min. All the films were finally annealed at 550 °C in air for 3h. The samples were denoted by the Bi content, for example $\text{Bi}_{0.3}\text{Fe}_{0.7}\text{VO}_4$ can be denoted as Bi30.

3.2.4 Fabrication of FeVO_4 thin films

The FeVO_4 films were fabricated using a simple spray pyrolysis method. The details of the spray setup and deposition process can be found in previous reports.^[7-8] The precursor solution was prepared by dissolving 20 mM $\text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_3$ (99.9%, Sigma Aldrich) and 20 mM $\text{VO}(\text{C}_5\text{H}_7\text{O}_2)_2$ (99%, Acros Organics) in absolute ethanol (Sigma Aldrich). For Mo doped samples, $\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)_2$ (Sigma Aldrich) was added into the precursor while keeping the molar ratio $\text{Fe}/(\text{V}+\text{Mo}) = 1$. The volume of precursor was adjusted according to the thickness of film to be deposited (e.g., 25 mL precursor for ~100 nm film). FTO substrates (TEC-7, Pilkington) were placed on the hot plate, which was heated to 450 °C before deposition. The spray rate was controlled to be ~1.5 mL/cycle, with each cycle containing 5 s spray time and 55 s rest time. The rest time was necessary to allow complete evaporation of the solvent and pyrolysis of acetylacetonate ligands. As-deposited films were then annealed at 650 °C for 2 min in technical air (20% O_2 , 80% N_2) with a ramp rate of 15 °C/min. For time-resolved microwave conductivity measurements, the films were deposited on quartz substrates ($2.5 \times 1.2 \text{ cm}^2$, Spectrosil 2000, Heraeus) using the same spray procedure.

3.2.5 Fabrication of nanostructured FeVO_4 photoanodes

Both FeVO_4 nanorod and film samples were fabricated from a simple conversion method modified from spinel ferrite fabrication reported before.^[9-11] $\beta\text{-FeOOH}$ nanorod film was

first grown on cleaned FTO (sonicated in soap water, ethanol, acetone, deionized water, and ethanol for 15 min each) by a typical hydrothermal method.^[12-13] 10 mL precursor containing 0.15 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (97%, Sigma Aldrich) and 1 M NaNO_3 (99%, Sigma Aldrich) was transferred to a clean Teflon lined autoclave. FTO substrates ($14 \Omega/\text{cm}^2$, Nippon Sheet Glass) were immersed into the precursor with conductive side facing downwards at an angle around 45° . Hydrothermal growth of FeOOH was set at 100°C for 4 h. The as-grown FeOOH film was thoroughly washed by deionized water and dried with nitrogen flow. Afterwards, 200 μL 40 mM NH_4VO_3 (99%, Sigma Aldrich) aqueous solution was drop cast onto FeOOH film surface, and the film with solution on top was transferred into a furnace that was already heated to 600°C . The treatment was 5 min to convert FeOOH into FeVO_4 nanorods and 20 min for film sample, followed by natural cooling down. The film surface was covered with a layer of vanadium oxide, which was later washed away by 0.1 M NaOH (97%, Sigma Aldrich) solution soaking for 15 min. No further annealing or post-treatment was carried out.

3.3 Characterizations

3.3.1 Scanning Electron Microscopy (SEM)

The morphology of photoanodes in Chapter 4, 5 and 7 was observed on field emission scanning electron microscopy (FESEM) JEOL-6340F and JEOL-7600F in SEI mode and for Chapter 6 a LEO GEMINI scanning electron microscope was used. Samples were cut into small pieces (e.g., $10 \text{ mm} \times 4 \text{ mm}$) and sputtered gold for 30 s before they were loaded onto the chamber. The SEM uses electrons to produce magnified images of samples with a resolution of around 1.5 – 3.0 nm. A beam of accelerated electrons is generated from the cathode, which is located at the top of SEM. The beam of electrons travels along the column in the vacuum, passing through condenser lens and objectives respectively. Under the force of magnetic and electrical fields, the electrons largely follow a vertical path to the sample surface. Once the electrons hit samples surface, a series of X-rays and electrons is ejected, as shown in **Figure 3.3**.

Figure 3.3 Interactions between incident electrons and the sample.^[14]

The interactions generate different kinds of electrons and X-rays, which can be used for sample observation and analysis. For sample imaging, the secondary electrons can show the morphology and topography of samples, while the backscattered electrons function to demonstrate the color contrast of different compositions. In this work photos were taken in SEI mode.

Energy-dispersive X-ray (EDX) spectroscopy was operated on FESEM to check the elemental dispersion on the sample surface or cross-section. X-rays are generated due to the inelastic collisions of electron beam and sample atoms. Each element has its characteristic X-rays, which can be distinguished by X-ray detector for element matching. Elemental mapping can be obtained from EDX measurements to confirm the existence of certain elements.

3.3.2 Transmission Electron Microscopy (TEM)

Different from SEM, transmission electron microscopy (TEM) can accelerate electrons at a much higher voltage up to 100 – 300 kV.^[15] A beam of higher energy, coherent electrons travel through the column condenser lens to the specimen. Part of the electrons can transmit through the sample to projector lens to form enlarged images. TEM can generate images with much higher resolution than SEM, enabling the observation of crystal parameters and

grain boundaries. Typical sample preparation to transfer and distribute a small amount of sample onto the copper grid. The thickness is normally controlled within 100 nm to ensure good electron transmission.

There are several modes to be chosen in TEM measurements, namely bright field, dark field, high-resolution TEM images (HRTEM) and diffraction mode. Both HRTEM images and diffraction pattern can offer information on crystal parameters to determine the crystal structure.

3.3.3 X-ray Diffraction (XRD)

Samples' crystal structure was checked and confirmed by X-ray diffraction (XRD) measurements by Shimadzu thin film X-ray diffractometer (for Chapter 4, 5 and 7) and Bruker D8 Advance X-ray diffractometer (for Chapter 6), where Cu K α radiation is used. The 2 θ configuration was taken for thin film measurements, with a tilt angle of 0.5° to 1° for better signals. XRD measurements take advantage of the scattering of incident parallel X-rays on crystal lattice. It is an effective analytical method for phase identification of prepared samples. A diffraction pattern is produced, offering information of the crystal structure (phase, lattice constants, etc.). The diffraction satisfies Bragg's law, i.e., $n\lambda = 2d \times \sin\theta$, where λ is the wavelength of incident X-ray, d is the inter-planar distance, and θ is the incident angle. For thin film measurements, it adopts the 2 θ configuration as shown in **Figure 3.4**. The angle of incoming X-ray is fixed and the sample is placed with a small tilt angle. The detector rotates around the sphere to receive signals from all directions. Match software was employed to identify the crystal structure after XRD measurements. TOPAS software was used to perform crystal structure refinement and composition calculation.

Figure 3.4 Schematic view of XRD operating positions.^[16]

3.3.4 X-ray Photoelectron Spectroscopy (XPS) and Ultraviolet Photoelectron Spectroscopy (UPS)

Surface elemental analysis was obtained by X-ray photoelectron spectroscopy (XPS) on a VG ESCALAB 220I-XL system (for Chapter 4 and 5). The source is a monochromatic Al K α (1486.6 eV) with a concentric hemispherical energy analyzer. Samples were cut in 10 mm $\times$ 10 mm dimensions. XPS is a quantitative technique that provide elemental compositions of the sample surface. According to photoelectric effect, when X-rays irradiate the sample, photoelectrons are generated and emit from sample surface (**Figure 3.5**). The detection depth is usually within 10 nm and the measurements are carried out in high vacuum. In addition to elemental identification and chemical states information, chemical composition at very surface can be calculated by analyzing elemental peak areas. In Chapter 6, XPS was carried out with a monochromatic Al K α X-ray source (1486.74 eV, Specs Focus 500 monochromator) and a hemispherical analyzer (Specs Phoibos 100) in an ultrahigh vacuum system (base pressure $\sim 10^{-8}$ mbar). Ultraviolet photoelectron spectroscopy (UPS) was conducted using He I source ($E = 21.218$ eV) with the same hemispherical analyzer as in the XPS measurement.

Figure 3.5 Photoelectric effect illustration in XPS.^[17]

In a typical measurement, a survey spectrum is first obtained to observe all the elements that exist on sample surface. Afterwards the high-resolution scan of main elements is performed. The fitting and analysis are done on XPSPEAK41 software.

3.3.5 UV-vis Absorption Spectroscopy

The UV-visible absorption studies were completed on an UV–vis–NIR spectrophotometer (PerkinElmer, Lambda 750S and 950), scanning from 300 nm to 800 nm in an integrating sphere setup. UV-Vis spectroscopy is a convenient method to acquire the semiconductor bandgap by measuring the electron transitions between VB and CB. Before loading samples to collect absorption or reflectance spectra, a baseline scan (reference scan, remove all samples) is performed. The nature (allowed or forbidden, direct or indirect) and value of bandgap can be determined after creating Tauc plots.

3.3.6 Photoelectrochemical measurements

Photoelectrochemical (PEC) measurements were completed on CHI 660D working station (CH Instruments, Inc.) for Chapter 4, 5 and 7. A three electrode configuration was normally used where samples served as the anode. Pt functioned as the counter electrode (surface area $\sim 3.6 \text{ cm}^2$), and Ag/AgCl (3M) was the reference electrode (**Figure 3.6**). Na_2SO_4 , KPi, NaOH or KOH were used as the electrolyte for various pH environment measurement. The

potential conversion between vs. 3M Ag/AgCl and vs. RHE was calculated by the following equations:

$$E (\text{vs. RHE}) = E (\text{vs. Ag/AgCl}) + E^{\circ}_{\text{Ag/AgCl}} (\text{reference}) + 0.0591 \times \text{pH} \quad (3.1)$$

$$\text{Where } E^{\circ}_{\text{Ag/AgCl}} (\text{reference}) = 0.21 \text{ vs. NHE at } 298\text{K} \quad (3.2)$$

The effective working electrode surface area was fixed at 0.125 cm^2 , determined by the PEC cell used. Before PEC measurements, the electrolyte was degassed with nitrogen for 15 minutes. Typical scan rate of voltammogram sweep was 20 mV s^{-1} .

Figure 3.6 Three electrode configuration in PEC measurements.

The simulated light source is a 150 W xenon solar simulator (67005, Newport Corp.). A solar filter (KG 3) is equipped and calibrated to have a measured light intensity equal to the standard AM 1.5G sunlight (100 mW cm^{-2}) shed on the samples.

For Chapter 6, PEC performances were measured on a potentiostat (EG&G PAR 273A) with a solar simulator (WACOM, type WXS-50S-5H, class AAA).

3.3.7 Incident Photon to Current Conversion Efficiency (IPCE) measurements

Incident photon to current conversion efficiency (IPCE) measurements were carried out from 350 to 650 nm at 1.23 V vs. RHE, with the combination of a xenon light source (MAX-302, Asahi Spectra Co. Ltd.) and a monochromator (CMS-100, Asahi Spectra Co.

Ltd.). The IPCE of samples were calculated with IPCE data of a Si photodiode (Bentham, DH-Si), which was already measured by a source meter (Keithley Instruments Inc., model no. 2400). At each specific wavelength, the IPCE was calculated using equation (3.3).

$$\text{IPCE (\%)} = \frac{1240 \text{ (V nm)} \times \text{Photocurrent density (mA cm}^{-2}\text{)}}{\text{Incident light power density (mW cm}^{-2}\text{)} \times \text{wavelength (nm)}} \quad (3.3)$$

IPCE is also referred as external quantum efficiency (EQE), which combines the charge separation efficiency, charge transport efficiency across the bulk and the interface. IPCE is measured as a function of wavelength, providing the ratio of incident photons and generated photocurrent. In Chapter 6, IPCE measurements utilized a 300 W xenon lamp (Oriol) connected with a grating monochromator (Acton Spectra Pro 2155).

3.3.8 Impedance and Mott-Schottky (MS) measurements

Similar to PEC measurements, electrochemical impedance spectroscopy (EIS) was implemented on an automated potentiostat (Metrohm-Autolab, AUT 83285) in Chapter 4 and a Zahner Elektrik potentiostat (Model IM6) in Chapter 6 using a three-electrode configuration. EIS is a perturbative characterization of internal and interfacial dynamics in an electrochemical system. The measured impedance data can be interpreted by equivalent circuits, which are explained elsewhere.^[18] Mott-Schottky is one of the electrochemical impedance spectroscopy technique, which tells the flat band potential and carrier density. However, Mott-Schottky is difficult to perform and there are many pitfalls to avoid. Therefore, it is sometimes used as a qualitative method. Mott-Schottky plots were obtained from the EIS measurements with a small voltage perturbation (around 10 mV) and varying frequency from 100 kHz to 0.1 Hz. All the samples were scanned from -0.6 to 0.8 V vs. Ag/AgCl in the dark. Among all the data a typical Mott-Schottky plot can be extracted at a specific frequency such as 1 kHz or 3 kHz. Carrier concentration is calculated by equation (3.4) and (3.5).

$$\frac{1}{C^2} = \left[\frac{2}{e\epsilon\epsilon_0 N_D} \right] \left[V_A - V_{Flat} - \frac{k_B T}{e} \right] \quad (3.4)$$

$$N_D = \left(\frac{2}{e\epsilon\epsilon_0} \right) \left[\frac{d(1/C^2)}{dV} \right]^{-1} \quad (3.5)$$

3.3.9 Time-resolved Microwave Conductivity (TRMC) measurements

The time-resolved microwave conductivity (TRMC) study was carried out to find the carrier mobility and carrier lifetime. For this, all samples were prepared on plain quartz plates. TRMC measurements were performed in a cavity cell using a frequency-tripled Q-switched Nd:YAG laser at a wavelength of 355 nm as the excitation source with a 7 ns pulse. Microwaves in the X-band region (8.4–8.7 GHz) were generated by a voltage-controlled oscillator (SiversIMA VO3262X). Further details of the TRMC measurement have been described elsewhere.^[19-22]

Figure 3.7 Illustration of BiVO₄ on quartz measured by TRMC setup.

3.3.10 Oxygen evolution measurements

A two-compartment electrochemical cell divided by ion exchange membrane was used for gas evolution test. The photoanode was subject to an applied potential (for example 1.5 V vs. RHE) under AM1.5 illumination. Each time, the same amount of gas (0.5 mL) in the anode chamber was collected by the micro-syringe and the amount of O₂ can be detected by a gas chromatograph (GC) (Agilent 7890A).

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Chapter 4*

Understanding NiO_x Catalyzed BiVO₄ Photoanodes

It is important to understand the properties and limitations of BiVO₄ photoanode before exploring cation-substituted vanadates. Catalyst loading on BiVO₄ is often used to tackle the limitations of charge recombination and sluggish kinetics. In this chapter, amorphous nickel oxide (NiO_x) is loaded on BiVO₄ by photochemical metal organic deposition method. The resulting NiO_x/Mo:BiVO₄ photoanodes demonstrates a 2-fold improvement of photocurrent density of 2.44 mA cm⁻² at 1.23 V vs. RHE as compared with uncatalyzed samples. After NiO_x modification, both the charge separation and the charge transfer efficiency significantly increase across the entire potential range. It is further elucidated by open circuit photovoltage, time-resolved microwave conductivity and rapid scan voltammetry measurements that NiO_x modification introduces larger band bending and promotes efficient charge transfer on the surface of BiVO₄. This chapter provides insights into designing other metal vanadate photoanodes using a simple surface modification route for efficient solar water oxidation.

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4.1 Introduction

It has been mentioned in **Chapter 2** that the photoelectrochemical performance of pristine BiVO₄ is hindered by poor charge separation^[1-2] and sluggish charge transfer kinetics.^[1, 3] To overcome these, various modification methods, such as doping,^[4-7] catalyst loading,^[8-11] nanostructuring,^[1, 9, 12] forming heterojunctions or composites,^[1, 13] have been widely applied.

Modification by loading earth-abundant catalysts, such as cobalt phosphate (Co-Pi),^[1-2] FeOOH,^[8-9] and CoO_x (CoO, Co₂O₃ or Co₃O₄),^[10-11, 14] has been utilized to achieve enhanced PEC performance and stability on BiVO₄. Typically, these catalysts only affect the surface charge transfer processes, either via increasing catalytic activity or suppressing surface recombination, which has been recently shown to greatly limit the performance of BiVO₄.^[15-16] In contrast, nickel oxide (NiO_x) catalysts may potentially provide further functionality; loading NiO_x onto BiVO₄ would construct a buried p-n junction, which can facilitate charge separation within BiVO₄ photoanode.^[10, 17-18] This is in addition to the profound catalytic ability and proper band alignment,^[19-21] suppression of surface recombination through passivation,^[12] and durable protection against corrosion.^[22] However, this expected multifunctionality is still not convincingly shown, since existing NiO_x/BiVO₄ systems either normally combine other catalysts to achieve high performance^[10, 23] or utilizes sub-optimal deposition leading to relatively low performance.^[12, 18]

In this chapter, a simple, inexpensive but effective photochemical metal organic deposition (PMOD) method is employed to deposit a thin layer of amorphous nickel oxide (NiO_x) on Molybdenum (Mo) gradient-doped BiVO₄ (Mo:BiVO₄). The graded Mo:BiVO₄ has been investigated in former studies to enhance the diffusion length and charge separation.^[24-25] Here, NiO_x catalyst modified photoanode offers superior performance than the unmodified one; it is shown that both bulk and surface recombination are reduced with the deposition of NiO_x as evident from the higher charge injection and charge transfer efficiencies. Through open circuit potential measurements, the enhancement in charge separation was mainly attributed to the enlarged band bending induced by NiO_x layer, which enables

efficient carrier transport. Time-resolved microwave conductivity (TRMC) measurements first employed in NiO_x-BiVO₄ system as well as rapid scan voltammetry (RSV) measurements also reveal the additional role of NiO_x in aiding efficient charge transfer at the BiVO₄ surface.

4.2 Results and Discussion

4.2.1 Physical characterizations

Figure 4.1 Side-view schematic illustration of NiO_x/Mo:BiVO₄ sample.

The schematic illustration of the NiO_x catalyst on BiVO₄ is shown in **Figure 4.1**. Fourier transform infra-red (FTIR) spectroscopy was first employed to confirm the complete removal of organic ligands from spin coated Ni(II) 2-ethylhexanoate films, and the spectra were recorded during different time intervals upon UV light irradiation. The intensity of absorption at $\sim 1600\text{ cm}^{-1}$ and from 2800 cm^{-1} to 2900 cm^{-1} weakened to almost zero after 16 hours of UV irradiation (shown in **Figure A2.1**); these absorption features can be assigned to the C=O and C-H vibrational stretching frequencies of the organic ligands, respectively.^[21, 26] The decline of the IR vibration signals associated with the organic ligands therefore revealed the complete decomposition of 2-ethylhexanoate precursor. The 20-hour UV light irradiation was followed by annealing in air at $400\text{ }^{\circ}\text{C}$ for 2 h to transform the deposited Ni(II) 2-ethylhexanoate into NiO_x. The decomposition process can be illustrated in the following reactions:^[27]

Amorphous metal oxide film fabricated by PMOD has been proven to possess higher catalytic activity than crystalline films,^[21] and contain minimal carbon contamination due to the complete removal of organic ligands under UV illumination.

The morphology of the photoanode was investigated using field emission scanning electron microscopy (FESEM), and the top-view and cross-section view of the samples are shown in **Figure 4.2**. In the case of uncatalyzed BiVO₄ sample, it is clear from the surface morphology (**Figure 4.2a**) that it is composed of interconnected particles, with grain size ranging from ~200–400 nm. This was successfully achieved by introducing PVP in the precursor as a sacrificial polymer, as reported previously.^[28] The introduction of porosity increases the number of catalytic sites and light absorption in BiVO₄.^[29-30] The existence of the NiO_x layer on top of the NiO_x-400 °C BiVO₄ sample can be clearly observed in **Figure 4.2b**. It is observed that the NiO_x film is cracked presumably during annealing, leading to the formation of fragments, leaving a small area of BiVO₄ surface uncovered. Differently, NiO_x-200 °C BiVO₄ sample has NiO_x covered almost the whole surface (**Figure 4.2c**). Based on the cross-section image (**Figure 4.2d**), the thicknesses of the tri-layer Mo:BiVO₄ and the NiO_x layer of NiO_x-400 °C samples are estimated to be ~750 nm and ~150 nm, respectively.

The UV-Vis absorption spectra (**Figure A2.2a**) reveal that the NiO_x loading has no significant effect on the absorption profile of the BiVO₄ films (minor differences are due to variation in films' reflectance after NiO_x loading). The band gap of BiVO₄ is unaffected with the NiO_x loading (indirect band gap 2.3 eV, direct band gap 2.6 eV for all films, see **Figure A2.2b-d**). This band gap is consistent with a typical band gap of the monoclinic scheelite phase of BiVO₄, which is further confirmed by the X-ray diffraction (XRD) patterns (peaks match JCPDS no. 014-0688, **Figure 4.3a**). The NiO_x layers both annealed at 200 °C and 400 °C are amorphous (**Figure A2.3**); no additional peak is observed in the XRD patterns of catalyst loaded Mo:BiVO₄ (**Figure 4.3a**), which is in agreement with literature results.^[21, 26]

Figure 4.2 FESEM images of (a) uncatalyzed Mo:BiVO₄ surface; (b) NiO_x-400 °C BiVO₄ surface; (c) NiO_x-200 °C BiVO₄ surface; (d) NiO_x-400 °C BiVO₄, cross-section view. The false color indicates different layers: green for NiO_x, yellow for BiVO₄, and blue for FTO.

4.2.2 PEC measurements and XPS analysis

Water oxidation performances of uncatalyzed, NiO_x-200 °C, and NiO_x-400 °C BiVO₄ photoanodes were evaluated in 0.5 M Na₂SO₄ (pH 6.8) solution, and the linear sweep voltammetry (LSV) under dark and illuminated conditions is shown in **Figure 4.3b**. Under simulated solar illumination (AM 1.5G, 100 mW cm⁻²), the NiO_x loaded photoanodes exhibit remarkable increase of photocurrent density as compared to the uncatalyzed graded Mo:BiVO₄. The photocurrent density of the NiO_x-200 °C and NiO_x-400 °C samples at 1.23 V vs. RHE reach 1.9 and 2.44 mA cm⁻², respectively. These photocurrents represent a significant ~2-fold improvement as compared to the 1.18 mA cm⁻² photocurrent of the uncatalyzed BiVO₄. The different PEC performance of NiO_x-200 °C and NiO_x-400 °C could be interpreted by the different chemical compositions of each NiO_x layers, as further described below.

Figure 4.3 (a) XRD patterns of the uncatalyzed and NiO_x loaded BiVO₄, (b) Current density - potential curve of uncatalyzed and NiO_x loaded samples under light and dark conditions. High resolution XPS spectra of (c and d) Ni 2p and (e and f) O 1s of NiO_x-200 °C and NiO_x-400 °C samples.

The chemical compositions of uncatalyzed and NiO_x/Mo:BiVO₄ samples were analyzed using X-ray photoelectron Spectroscopy (XPS). All expected elements (Bi, V, O, Ni and adventitious carbon) are observed, and there is no evidence for contamination of other species (**Figure A2.4**). The fitted Bi 4f_{7/2} and V 2p_{3/2} peaks correspond to binding energies at ~159.08 eV and ~516.70 eV, respectively. The Bi 4f peak at 159.08 eV is characteristic of Bi³⁺ oxidation state while the V 2p binding energy can be assigned to the oxidation state of V⁵⁺.^[31] No Mo peak is observed in the survey spectra as well as in the high resolution peak since the top layer consists of only undoped BiVO₄ and the concentration of Mo in measured films is at the edge of the resolution of XPS (see **Figure 4.1**). Moreover, in the case of NiO_x-200 °C sample, the Bi and V peaks are highly attenuated due to the near-

complete coverage of NiO_x layer (see from **Figure 4.2c**).

To have a better understanding on the catalytic effect of the NiO_x species, it is essential to identify the oxidation states of Ni. High resolution XPS Ni 2p spectra of both NiO_x-200 °C and NiO_x-400 °C samples are deconvoluted into different components as shown in **Figure 4.3c and d**. In both cases, the Ni 2p_{3/2} peaks are located at ~852 – 868 eV with a main peak and a satellite peak (~862 eV).^[32-33] The Ni 2p_{3/2} main peak is deconvoluted to three peaks. The peak appeared at ~857.3 eV is due to the presence of Ni³⁺ states and the peak at ~855 eV corresponds to NiO.^[10, 32-34] In the case of NiO_x-400 °C an additional small peak at ~854 eV is observed, which is also responsible for the Ni-O bonding in NiO.^[32, 35] The presence of NiOOH has been reported to be caused from the in-situ transformation of surface NiO.^[10] The high resolution O1s spectra (**Figure 4.3e and f**) corroborates with this explanation. For both, oxygen peak was observed due to surface adsorbed H₂O (~533 eV),^[36] hydroxyl oxygen from NiOOH (~532 eV)^[37] and oxygen corresponding to Ni-O bonds (~529 eV).^[10, 32] Higher NiO content is clearly observed in NiO_x-400 °C; the ratio of Ni²⁺ (i.e., NiO) to the total Ni content is calculated to be 84% in the NiO_x-400 °C sample and only 18% in the NiO_x-200 °C sample. In other words, NiOOH is the dominant phase in the NiO_x-200 °C sample and only traces of NiOOH is found in the NiO_x-400 °C sample (**Figure 4.3c and d**). This is also consistent with the higher surface adsorbed H₂O intensity for the NiO_x-200 °C sample, as a self-discharge reaction of the NiOOH (2NiOOH + H₂O → 2 Ni(OH)₂ + 1/2 O₂) has been reported to occur.^[38]

The different annealing temperatures therefore clearly result in two different samples with distinct compositions (NiOOH and NiO). Although a Ni²⁺/Ni³⁺ redox system is present in both cases for facilitating better catalytic water oxidation, the content of NiO in NiO_x-400 °C is much higher than that in NiO_x-200 °C sample. This possibly indicates that NiO has superior catalytic ability and/or better suppresses surface recombination on BiVO₄ than NiOOH. More detailed identification of this requires further studies, which is beyond the scope of this paper. Since the NiO_x-400 °C sample has the highest performance, from here onwards the discussion will be restricted to this sample in comparison to the uncatalyzed sample (graded Mo:BiVO₄).

Apart from the photocurrent density increase, a cathodic shift in the onset potential for water oxidation current is also observed for the catalyst modified photoanodes (**Figure 4.4a**). The onset potential is cathodically shifted ~70 mV to 0.35 V vs. RHE for the NiO_x-400 °C sample in comparison with the uncatalyzed one (0.42 V vs. RHE), further supporting the ability of NiO_x to reduce surface recombination.^[1] The stability of the uncatalyzed and NiO_x-400 °C samples was tested in 0.5 M Na₂SO₄ under simulated sunlight and applied potential of 1.23 V vs. RHE. The photocurrent densities of both samples remain stable up to 1000 s (**Figure 4.4b**). Despite some fluctuations (possibly due to bubbles accumulation), the photocurrent of the NiO_x-400 °C sample recovers to the initial level, showing no degradation of stability within 9000 s (2.5 h) (**Figure A2.5**). In contrast, the photocurrent of the uncatalyzed sample is degraded by ~30 % during this time-scale.

Incident photon-to-current conversion efficiencies (IPCE) measurements were carried out as shown in **Figure 4.4c**. The IPCE of NiO_x-400 °C correspond well with its enhanced water oxidation performance. The IPCE reaches a value of 53 % at wavelength of 360 nm (at 1.23 V vs. RHE), while that of uncatalyzed sample is only 20 %. All the samples absorb visible light up to ~540 nm, consistent with the bandgap of 2.3 eV. The photocurrent density integrated from IPCE spectra matches well with PEC measurement values (1.1 mA cm⁻² for uncatalyzed film, 2.4 mA cm⁻² for NiO_x-400 °C) by equation 4.3:

$$J = \frac{\int_{\lambda_1}^{\lambda_2} \lambda \text{ IPCE}(\lambda) E(\lambda) d\lambda}{1240} \quad (4.3)$$

where λ_1 and λ_2 define the integration wavelength range, $\text{IPCE}(\lambda)$ is the measured IPCE value as a function of wavelength λ at 1.23 V vs. RHE and $E(\lambda)$ is the solar spectral irradiance at one specific wavelength λ .

4.2.3 Role of NiO_x on BiVO₄

To examine the effect of NiO_x on the bulk charge separation and surface charge transfer of BiVO₄, photoelectrochemical measurements were carried out in Na₂SO₄ electrolyte containing Na₂SO₃ as hole scavenger (definition and calculation steps described in the

Appendix A). With hole scavenger, the photocurrent density of the NiO_x-400 °C sample is increased sharply (a factor of ~2) at potentials below 1.3 V vs. RHE (**Figure A2.6**). A photocurrent of ~4.2 mA cm⁻² is achieved for the NiO_x-400 °C sample at 1.23 V vs. RHE, which is 56 % of the theoretical photocurrent (7.5 mA cm⁻²) that can be achieved by BiVO₄. The charge transfer efficiency (η_{trans}) of this sample is overall higher than that of uncatalyzed, indicating the ability of NiO_x to suppress recombination on BiVO₄ surface and/or enhanced catalytic activity for OER (**Figure 4.4d**). Surprisingly, the charge separation efficiency (η_{sep}) increases considerably with NiO_x deposition, and this increase is even higher at more positive potentials (**Figure 4.4e**). At 1.23 V vs. RHE, η_{sep} of the NiO_x-400 °C sample is more than twice that of the uncatalyzed sample, which vividly shows improvement in charge separation due to NiO_x loading. This is particularly interesting since NiO_x layer, which is a surface modification layer on the BiVO₄, is typically not expected to affect transport of carriers to the surface. The observation therefore clearly shows that NiO_x truly has multi-functionality when deposited on these BiVO₄ photoanodes.

Figure 4.4 (a) Comparison of onset potential under chopped illumination, showing cathodic shift after catalyst loading. (b) Stability test for 1000 s. (c) IPCE of uncatalyzed and NiO_x-400 °C BiVO₄ samples at 1.23V vs. RHE. Calculated d) charge transfer efficiency and e) charge separation efficiency in the potential range 0.5 V to 1.3 V vs. RHE. All measurements shown are done under AM 1.5G illumination (100 mW cm⁻²) in 0.5 M Na₂SO₄ electrolyte (pH 6.8).

Figure 4.5 (a) Nyquist plots of uncatalyzed and NiO_x -400 $^\circ\text{C}$ BiVO_4 measured in 0.5 M Na_2SO_4 at 1.23 V vs. RHE under AM1.5 illumination. (b) Open circuit potential measurements in 0.5 M Na_2SO_4 ; The light turns on at 100 s and turns off at 400 s.

The charge transfer efficiency at the electrode/electrolyte interface was further analyzed by electrochemical impedance spectroscopy (EIS). **Figure 4.5a** shows the Nyquist plot of the uncatalyzed and NiO_x -400 $^\circ\text{C}$ samples under simulated solar light at 1.23 V vs. RHE in 0.5 M Na_2SO_4 . The radius of the semicircle is clearly decreased upon NiO_x loading. This parameter is typically assigned to the charge transfer resistance at the electrode/electrolyte interface; lower charge transfer resistance of the NiO_x -400 $^\circ\text{C}$ sample is in agreement with the better charge transfer efficiency observed in **Figure 4.4d** due to catalyst modification. It is time now to turn attention to the enhanced separation efficiency due to NiO_x modification. A possible explanation for this is that NiO_x forms a solid-solid junction on the surface of BiVO_4 , thereby modifying the band bending (i.e., extend of the space charge region). An enlarged band bending implies higher number of holes arriving at the interface, i.e., a higher $\eta_{\text{sep.}}$ ^[10, 18] This is supported by the significantly higher hole scavenger photocurrent of the NiO_x -400 $^\circ\text{C}$ sample as compared to the uncatalyzed sample (**Figure A2.6**). In the presence of hole scavenger, the surface loss mechanisms are typically assumed to be negligible; enhanced photocurrent therefore indicates more efficient hole arrival to the surface. To test this argument further, open circuit potential (OCP) measurements were performed under dark and illumination, as a simple method to obtain qualitative information about the Fermi level and band bending.^[39-40] OCP measurements were conducted in 0.5 M Na_2SO_4 in dark and AM 1.5 G illuminated conditions for

uncatalyzed and NiO_x-400 °C photoanodes. The open circuit potential difference between dark and light voltages directly reflects the extent of band bending in both samples. The OCP measured before and after illumination is shown in **Figure 4.5b** and it is evident that the NiO_x-400 °C sample has an enlarged Δ OCP value as compared to the uncatalyzed sample (~ 200 mV vs. ~ 100 mV). This is very well in agreement with the explanation above, and further supports the already observed enhanced separation efficiency. Interestingly, it can be noted that the difference of Δ OCP value between the NiO_x-400 °C and the uncatalyzed sample (~ 100 mV) is in very well agreement with the observed cathodic shift in the photocurrent onset potential (~ 70 mV, see **Figure 4.4a**), suggesting that this cathodic shift may be a result of higher generated photovoltage.^[41]

Figure 4.6 (a) Baseline-corrected capacitance vs. potential curves of uncatalyzed and NiO_x-400 °C BiVO₄, obtained from rapid scan voltammetry (RSV) performed at 1 V s^{-1} in dark. RSV curves are shown in Figure A2.8. (b) TRMC signal (fSm) as a function of time for uncatalyzed and NiO_x-400 °C samples. Carrier mobility can be obtained from the peak of the curve, and carrier lifetime can be obtained by fitting the curve with an exponential decay function. The solid red lines are the fit for each curve, resulting in a carrier lifetime value of $29.6 \pm 1.4 \text{ ns}$ for the uncatalyzed sample and $19.2 \pm 1.0 \text{ ns}$ for the NiO_x-400 °C sample.

To further reveal the role of NiO_x on BiVO₄ films, rapid scan voltammetry (RSV) measurements were performed. Here, the samples were conditioned at a positive potential of 2.1 V vs. RHE for 2 minutes and followed by a rapid (1 V s^{-1}) negative sweep of potential. By comparing the current-voltage curves, with and without conditioning (**Figure A2.8**), the surface capacitance indicating hole accumulation can be determined. **Figure 4.6a**

shows that the presence of NiO_x on the surface of BiVO₄ increases the capacitance by more than one order of magnitude, i.e., the number of holes being accumulated on the surface is significantly increased. This may be caused by efficient transfer of holes from the BiVO₄ to the NiO_x layer, where holes can be stored much longer, and electron-hole recombination can thus be avoided. Indeed, NiO has been used as a hole collector in solar cells.^[42-43] To confirm this, time-resolved microwave conductivity (TRMC) measurements were performed. Since carriers in NiO_x are immobile, they cannot be detected with TRMC; TRMC signals therefore only correspond to the charge carriers in BiVO₄. A more efficient transfer of holes from BiVO₄ to NiO_x would be depicted by decreased carrier mobility and/or lifetime. **Figure 4.6b** shows that the uncatalyzed BiVO₄ possess a carrier mobility of $5 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and a carrier lifetime of $29.6 \pm 1.4 \text{ ns}$. These values are smaller than the reported pristine undoped BiVO₄ film ($4 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and 40 ns, respectively) due to Mo doping in the film.^[44] Upon NiO_x loading, the carrier mobility slightly decreases to $4 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and the carrier lifetime is shortened to $19.2 \pm 1.0 \text{ ns}$. This supports the role of NiO_x in promoting efficient charge transfer and avoiding electron-hole recombination at the surface of BiVO₄.

Figure 4.7 Schematic diagram of band alignments and band bending for NiO_x loaded Mo:BiVO₄ in contact with electrolyte. For illustration purpose only, the band positions are not drawn to scale.

Figure 4.7 shows schematic band bending diagram of NiO_x loaded Mo:BiVO₄ photoanode

at the electrode-electrolyte interface. In the bulk of BiVO₄, there exists enlarged band bending due to Mo gradient. Band bending at the interface of NiO_x and BiVO₄ is also enlarged due to the p-n junction. Upon contact with electrolyte, generated holes can be collected more efficiently from BiVO₄ to NiO_x layer, and further transferred into electrolyte to oxidize water.

4.3 Conclusions

In summary, this chapter showed the multifunctional role of amorphous nickel oxide when deposited as a catalyst on graded Mo doped BiVO₄. The modified photoanode is shown to be stable and efficient for water oxidation, generating an AM1.5G photocurrent density of 2.44 mA cm⁻² at 1.23 V vs. RHE, which is a ~2-fold improvement as compared to the uncatalyzed film. The improved performance is attributed to both enhanced bulk charge separation efficiency and more efficient surface charge transfer upon deposition of the NiO_x layer. The enhanced charge separation is caused by the modification of band bending at the surface of BiVO₄, as supported by the higher hole scavenger photocurrent and enlarged open circuit potential for the NiO_x-modified BiVO₄. The role of NiO_x in promoting efficient charge transfer is further confirmed with the combination of RSV and TRMC measurements. Overall, the simplicity of the deposition, both for the graded Mo:BiVO₄ film as well as the PMOD of NiO_x, presents an alternative route for a scalable synthesis of high performing photoelectrode for water oxidation. While shown for BiVO₄ here, the insights from this chapter may be generally applied to other photoelectrode materials (including cation-substituted vanadates in the following chapters) and enable expedited developments of large scale and low-cost solar water splitting devices.

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Chapter 5

Synergistic Effect of Cation Mixing in Bi_xFe_{1-x}VO₄ Photoanodes

Mixed metal vanadates are interesting class of materials due to the favorable bandgap for visible light absorption and their catalytic activity. This chapter reports a novel Bi_xFe_{1-x}VO₄ mixture system fabricated by electrospinning, which is composed of triclinic FeVO₄ and monoclinic BiVO₄ phases after annealing. The mixture extended the optical absorption of BiVO₄ towards the visible range, which is also accompanied by an extended absorption range for its photoactivity as evident from the incident photon-to-current efficiency. In addition, the mixture with Bi/(Fe+Bi) ratio of 0.5 shows superior charge transfer and charge separation efficiency. The improved charge transfer efficiency can be attributed to the better catalytic activity of the mixed cation, while the presence of BiVO₄/FeVO₄ heterojunction enhances the charge separation. The formation of the heterojunction is verified through detailed microscopic investigations and revealed BiVO₄ particles intimately surrounded by FeVO₄. This chapter demonstrates the advantage of establishing a mixture of complex metal oxides in extending optical absorption and boosting the photoelectrochemical performance.

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5.1 Introduction

As has been discussed in **Chapter 1 and 2**, with recent progress and success of achieving 90% of its theoretical maximum photocurrent, it is clear that further improvement on the solar-to-hydrogen (STH) efficiency of bismuth vanadate (BiVO₄) is limited by its bandgap (2.4-2.5 eV).^[1-2] Numerous attempts have been reported on either lowering the bandgap of BiVO₄, or identifying novel narrow bandgap photoanode materials. Sulfurization or nitridation has been demonstrated to effectively reduce the bandgap of BiVO₄, but its PEC stability may be a concern.^[2-3] Some emerging materials, such as CuWO₄ (2.1 eV),^[4] SnWO₄ (2.1 eV),^[5-6] ZnFe₂O₄ (2.0 eV),^[7-8] Cu_xV_yO_z (1.8-2.0 eV),^[9-10] and FeVO₄ (2.06 eV)^[11-12], have been reported to be promising photoanode candidates. However, these novel complex metal oxides still show much lower performance than expected, and further developments on a relatively longer timescale are necessary. As an alternative, the bandgap of BiVO₄ can be modified by incorporating another metal cation to form a metal vanadate mixture. The combination of the new metal cation – if chosen properly - could possibly raise the valence band of BiVO₄ without much effect on the conduction band, or form a favorable heterojunction with extended light absorption. The effective bandgap, as a result, will be reduced.

Studies on mixed metal vanadates have been reported from a decade ago for photocatalytic applications (e.g., BiCu₂VO₆, BiZn₂VO₆).^[13-18] Combining two metal vanadates (Cu and Bi) into a solid solution to lower the bandgap of BiVO₄ has been experimentally demonstrated.^[13, 15] The absorption of BiCu₂VO₆ extends to 600 nm, which is 80 nm longer than BiVO₄. It was proposed that the bandgap reduction is due to band modulation through the incorporation of two metal cations. Also, Bi_{0.75}Fe_{0.25}VO₄ mixture demonstrated higher photocatalytic efficiency in the degradation of methylene blue than FeVO₄ or BiVO₄.^[19] However, detailed mechanism on why mixed vanadates can offer higher catalytic activity or improved photoelectrochemical performance is not well understood. In addition, high performance mixed vanadate photoanode has not been reported in the literature.

In the previous report, a series of Bi_xFe_{1-x}VO₄ (0 ≤ x ≤ 1) films were fabricated by spray

pyrolysis.^[20] Initial results indicated the possibility of maintaining good mobility of BiVO₄ and extending visible light absorption by mixing FeVO₄ with BiVO₄. The present study adopted electrospinning to deposit the mixed vanadate films and higher annealing temperature to improve the crystallinity. The combination of Fe and Bi vanadate showed higher catalytic efficiency and enlarged visible light absorption; in particular, the Fe_{0.5}Bi_{0.5}VO₄ composition demonstrated the highest PEC performance. Microscopic observations showed that the Fe_{0.5}Bi_{0.5}VO₄ consists of adjacent FeVO₄ and BiVO₄ nanoparticles, which resulted in a favorable heterojunction to facilitate charge separation. The chapter presents the synergistic effect of Bi/Fe vanadate mixture and gives insights to further improve the performance of vanadate-based photoanodes.

5.2 Results and Discussion

5.2.1 Physical characterizations and chemical compositions

A series of Bi_xFe_{1-x}VO₄ ($0 \leq x \leq 1$) films were prepared by electrospinning (**Figure 3.2**) (The expression Bi_xFe_{1-x}VO₄ here is determined by the composition of precursors, and does not necessarily indicate the formation of a solid solution). For brevity, the different films are designated by the percentage amount of Bi in each film, i.e., Bi0 corresponds to a FeVO₄ film, Bi50 corresponds to Bi_{0.5}Fe_{0.5}VO₄, and Bi100 corresponds to BiVO₄. Prior to other measurements, EDX spectroscopy was used to confirm that the Fe and Bi ratio follows the initial amount added into the precursor (**Figure 5.1a**). EDX mapping confirms the uniform distribution of Fe and Bi throughout the film (**Figure B1.1**). **Figure 5.1b** shows the x-ray diffraction (XRD) patterns of the various Bi_xFe_{1-x}VO₄ films. At each extreme of the composition (i.e., Bi0 and Bi100), a pure phase of triclinic FeVO₄ and monoclinic BiVO₄ were obtained, respectively. For the mixed vanadate, both FeVO₄ and BiVO₄ peaks were detected from Bi5 to Bi50. From Bi65 and above, the FeVO₄ phase can no longer be detected by XRD, but no obvious BiVO₄ peak shift was observed (**Figure B1.2**). This may be caused by the relatively small amount of FeVO₄ phase in the films. Further investigations on the crystal structure by transmission electron microscopy are discussed later in the paper. Compared with the peak intensity of BiVO₄, the FeVO₄ peak intensity is

relatively lower. This is due to the fact that the films were annealed at 550 °C; annealing temperature of 650 °C is typically required to obtain good crystallinity of FeVO₄.^[11, 20] This lower temperature was chosen as a compromise because V loss occurs at temperature above 450 °C.^[21] **Figure B1.3** indeed shows that all of the films are slightly V-poor. The effect of V loss has been discussed elsewhere, and not the focus of this report.^[21]

The chemical composition and oxidation states in the films were analyzed by XPS. All the spectra were calibrated using the adventitious carbon peak at 284.8 eV. Fe, Bi, V and O core level XPS spectra of FeVO₄, Bi50 and BiVO₄ films are shown in **Figure B1.4**. Peaks at 710 – 714 eV can be observed in FeVO₄ and Bi50 films, which can be assigned to Fe 2p_{3/2} multiplets with an oxidation state of 3+.^[22-23] The peak at 716 eV, which is present for all films, corresponds to the Sn 3p_{3/2} core level, which is caused by the exposed FTO.^[24] XPS peaks at 158.7 eV and 164.1 eV confirm the existence of Bi³⁺ in Bi50 and BiVO₄.^[25-26] The vanadium is present as V⁵⁺ in all films, as evident from the V 2p_{3/2} peak at ~516.9 eV.^[27-28] The binding energy of O 1s at 530 eV matches with the oxygen lattice peak in the oxide.^[27] The peak positions do not shift for all films, suggesting that the chemical environment of the mixture remains unchanged.

Figure 5.1 (a) Bi ratio in the annealed films calculated from EDX results compared with Bi ratio in the precursor. (b) XRD patterns of all compositions annealed at 550 °C in air.

Figure 5.2 (a) and (b) Absorption spectra, (c) Calculated direct and indirect bandgap for all films with various Bi ratio.

Gradual color change from orange (FeVO₄) to bright yellow (BiVO₄) can be observed from the visual appearance of the films (**Figure B1.5**), similar to the previous report.^[20] The porous appearance of the films is due to the addition of PVP in the electrospinning precursor. The absorption spectra of the mixed vanadate films obtained from UV-vis spectroscopy are shown in **Figure 5.2a and b**. Other than the pure BiVO₄ film, the absorption edge of the mixed vanadate films extends beyond 520 nm (absorption edge of BiVO₄), validating the effect of Fe incorporation on increasing the visible light absorption range. For Bi10 to Bi50 films, higher Bi ratio increases the absorption at around 480 nm (which is a characteristic absorption shoulder of BiVO₄) while keeping the absorption edge similar at ~ 600 nm (**Figure 5.2a**). Beyond this Bi concentration (i.e., 50% and above), visible light absorption at 520-600 nm range decreases with more Bi content (**Figure 5.2b**), possibly due to the difference of absorption coefficients of BiVO₄ and FeVO₄.^[20, 29] Although the films were detected to be mixtures of BiVO₄ and FeVO₄, the ‘apparent

bandgap' of the mixture, instead of the actual bandgap, can still be determined. The direct and indirect bandgaps of all the films can be calculated using Tauc analysis; the results are shown in **Figure 5.2c**. The direct bandgap only shows minor differences for all compositions (2.45-2.5eV), but the indirect bandgap increases with increasing Bi content.

This chapter's results clearly show that higher Fe content leads to larger visible absorption range. However, the appearance of the absorption shoulder at 480 nm and the varying absorption spectra at ~ 520-600 nm suggest an optimal Bi/Fe ratio may exist in order to achieve the maximum total absorption. By integrating all the absorption spectra with the AM1.5 photons, the theoretical absorbed photocurrent density (J_{abs}) can be readily calculated for each composition and shown in **Figure B1.6**. As expected, a maximum is observed for the Bi10 film, with J_{abs} of ~4 mA cm⁻².

5.2.2 Improved charge carrier efficiencies

AM1.5 photocurrent density of all films was measured in 0.1 M phosphate buffer (KPi, pH = 7). Most films show higher photocurrent under backside illumination as compared to front illumination (**Figure B1.7**). 30 min deposition time (electrospinning) is found to be optimal to ensure sufficient film thickness and avoid peeling off of the films during annealing. As the PEC performance is similar for 30 min and 45 min deposited films (**Figure B1.8**), only films electrospun for 30 minutes will be discussed below. As shown in **Figure 5.3a**, the photocurrent of pristine FeVO₄ and BiVO₄ is quite comparable to the previously reported sprayed FeVO₄ and electrospun BiVO₄.^[20, 27] Among all the compositions, Bi50 film demonstrates the highest photocurrent (0.47 mAcm⁻² at 1.23 V vs. RHE). The peak photocurrent trend at Bi 50% ratio is even more obvious at higher potential, while other Bi rich or Fe rich composition films only generate moderate photocurrents. From Bi0 to Bi50, the photocurrent increases almost linearly with increasing Bi content; for Bi50 to Bi100, the photocurrent instead decreases. To exclude any surface limitation (due to slow charge transfer or surface recombination), the photocurrent was also measured in KPi with added H₂O₂ as a hole scavenger. The hole scavenger photocurrent trend is

similar to that in KPi (**Figure 5.3b**), with Bi50 film showing the highest photocurrent up to 1.82 mA cm⁻² at 1.23 V vs. RHE.

Figure 5.3 Photocurrent as a function of Bi ratio for all compositions, measured in 0.1 M KPi buffer (pH = 7) (a) and in 0.5M H₂O₂ + 0.1 M KPi (b) under backside illumination. (c) Charge transfer efficiency (η_{trans}) and separation efficiency (η_{sep}) at 1.23 V vs. RHE as a function of Bi ratio. (d) Onset potential taken from chopped current-voltage curves in KPi buffer.

The charge transfer and separation efficiencies can be readily calculated from the photocurrent density with and without hole scavenger (definition and calculation steps are stated in **Appendix A**). The transfer efficiency (η_{trans}) of all compositions are shown in **Figure B1.9** and the overall trend at 1.23 V vs. RHE is shown in **Figure 5.3c**. It is interesting to note that the charge transfer efficiencies of all Bi/Fe mixed vanadate films are more or less constant and higher than pure FeVO₄ and BiVO₄ over the whole potential range. This is in good agreement with the observation that mixed vanadates have higher catalytic activity than a single metal vanadate for particulate oxygen photoevolution or dye

degradation.^[15, 17, 19] In addition, a closer look at the trend shows that the η_{trans} of the films with higher Fe content (Bi5 to Bi50) are slightly higher than those of the Bi rich films (Bi65 to Bi100). This is attributed to the higher catalytic activity of Fe sites for oxygen evolution as compared to Bi. Indeed, the dark current of FeVO₄ and Bi50 films are higher than that of BiVO₄ (**Figure B1.10**).

Since J_{abs} of all films are relatively close with each other (**Figure B1.6**), the charge carrier separation efficiency (η_{sep}) (**Figure 5.3c** and **Figure B1.11**) follows a similar trend as the hole scavenger photocurrent. The incorporation of Bi/Fe around 1:1 ratio (i.e., Bi50) results in an optimal charge separation. The η_{sep} of Bi50 at 1.23 V vs. RHE is 10-fold and 1.7-fold higher as compared to that of FeVO₄ and BiVO₄, respectively. It is therefore clear that the main reason behind the photocurrent improvement of the mixed Bi-Fe-vanadate films is due to more efficient charge carrier separation.

The much higher η_{sep} can be explained by the formation of FeVO₄ and BiVO₄ heterojunction with favorable band alignment to facilitate efficient charge carrier separation.^[23] As the two vanadates are homogeneously distributed, indeed the 1:1 ratio is expected to be optimal to ensure enhanced charge separation at all parts of the film. A BiVO₄/FeVO₄ heterojunction in 1:1 ratio has also been reported to obtain the highest photocatalytic activity for pollutant degradation,^[30] which agrees very well with current results and interpretation.

The heterojunction explanation is also supported by the trend in the onset potential as a function of Bi ratio. The addition of BiVO₄ into FeVO₄ leads to a dramatic onset potential drop from 0.94 V vs. RHE (Bi0, FeVO₄) to ~0.4 V vs. RHE (Bi80-Bi95) (**Figure 5.3d**). Cathodic onset potential shift is a typical effect of heterojunction, which has been reported on TiO₂, Fe₂O₃, and BiVO₄ photoanodes.^[31-35] While surface passivation can also induce a cathodic onset potential shift, effect of surface passivation has been ruled out and the mixed vanadates show similar surface charge transfer efficiency (**Figure B1.9**). Further observations by SEM show that all films are composed of nanoparticles with similar morphology (**Figure B1.12**). Capacitive current measurements show no apparent trend of

the electrochemical active surface area of all films (**Figure B1.13**). Cross-section view images also confirm similar particle size across the depth profile (~150 – 170 nm) for different compositions (**Figure B1.14**).

To further confirm the formation of a heterojunction, TEM and high resolution TEM (HRTEM) images of Bi50 sample were taken as shown in **Figure 5.4**. Clear phase contrast can be observed between the bright and dark regions (**Figure 5.4c and d**), where the dark regions are surrounded by the bright regions. Clear lattice fringes can be observed in the bright regions, with d-spacing of 0.85 nm and 0.34 nm corresponding to the (001) and (021) plane of FeVO₄, respectively (**Figure 5.4a and b**). The dark regions, however, do not show any clear fringes. To confirm the composition in the dark regions, Energy Dispersive X-ray analysis (EDAX) was carried out at the sample locations shown in **Figure 5.4c and d**, and the elemental mapping is shown in **Figure B1.15**. The dark regions are verified to be BiVO₄ particles while FeVO₄ particles (bright regions) are more dispersed. From the mapping images, the microscopic structure of BiVO₄ particles intimately surrounded by FeVO₄ particles. This structure also explains why only FeVO₄ phase can be clearly seen in the HRTEM images (bright regions), while the dark regions do not show lattice fringes due to the convolution between the BiVO₄ and FeVO₄ structure. This is further supported by the higher surface Fe/Bi ratio of the Bi50 film (2.2 as revealed from XPS, see **Table B1.1**) as compared to the bulk Fe/Bi ratio of 1 (see **Figure 5.1a**). Such an intricate structure shows a clear evidence for the heterojunction, which enhance the charge carrier separation efficiency in the mixed vanadate films, particularly in the case of Bi50. A core-shell BiVO₄/FeVO₄ structure has indeed been reported to enhance charge separation.^[23]

Figure 5.4 (a) and (b) HRTEM images of Bi50 sample at two different places, showing d-spacing of FeVO₄ (001) and (021) planes to be 0.85 nm and 0.34 nm respectively. (c) and (d) TEM images of the Bi50 sample at two different locations. Note the different scale-bar between the two images.

Figure 5.5 UPS spectra of (a) BiVO₄ and (b) FeVO₄ with a bias of 10 eV. Secondary electron cut-off and valence band maximum positions have been indicated.

For a conclusive confirmation of band alignments, UPS was conducted and the spectra are presented in **Figure 5.5**. The work function can be determined by the secondary electron cut-off. The position of valence band maximum (E_V) with respect to the Fermi level (E_F) can be determined from the low kinetic energy cut-off of the spectrum. As shown in **Figure 5.5**, the work function for BiVO₄ and FeVO₄ can be determined to be 4.5 eV and 4.9 eV, respectively, while the E_V with respect to the E_F is determined to be 2.36 eV and 2.06 eV, respectively. Although the measured work function of BiVO₄ and FeVO₄ is slightly higher than reported values (BiVO₄: 4.56 eV, FeVO₄: 5.1 eV), the difference of the work function position is definitely clear. The band alignments of BiVO₄ and FeVO₄, therefore, are depicted in **Figure 5.6**. The conduction band position is calculated from optical bandgap and valence band position. **Figure 5.6** clearly shows that BiVO₄ and FeVO₄ can form type II heterojunction. Photogenerated holes can thus be more efficiently extracted for water oxidation due to a larger band bending in the heterojunction, which is in agreement with the higher η_{sep} for Bi50 as compared with BiVO₄ and FeVO₄.

Figure 5.6 Schematic diagram of band alignments of BiVO₄ and FeVO₄, confirming the heterojunction alignment. Note that the band bending at the interfaces are not depicted for simplicity.

It is also noted that the optimal charge carrier separation efficiency in the Bi50 film can be caused by the improved charge carrier transport property (i.e., carrier mobility). This is, however, unlikely to be the case. While there is no direct evidence of the carrier mobility in these electrospun films—time-resolved microwave conductivity (TRMC) measurements of the films are not possible since electrospinning the films on quartz (which is required

for TRMC) results in mechanically unstable films—the previous study on sprayed mixed Bi-Fe-vanadates have shown that the carrier mobility continuously decreases with decreasing Bi content.^[20]

5.2.3 Influence of the vanadate mixture on visible light photoactivity

Finally, the photoactivity of the films under different illumination wavelengths was investigated. The incident photon-to-current conversion efficiency (IPCE) curves of all films are shown in **Figure B1.16**. Although the absorption edge of FeVO₄ is ~600 nm, which is considerably longer than that of BiVO₄ (520 nm), the IPCE of FeVO₄ at wavelength above 525 nm is negligibly small (~0) (**Figure 5.7a**). The mismatch of the optical absorption onset and photoelectrochemical onset wavelength of FeVO₄ can be attributed to the low carrier mobility and indirect absorption energy loss at long wavelength range.^[20, 36] Similar to the observation in UV-vis spectra, the IPCE at all wavelengths was enhanced for the mixed vanadates as compared with both FeVO₄ and BiVO₄. (**Figure B1.16**), with Bi50 showing the highest IPCE (**Figure 5.7a**) Further IPCE measurements in H₂O₂ were carried out to better illustrate the onset wavelength for photoactivity by eliminating the effects of surface recombination (**Figure 5.7b**). Bi50 film clearly exhibits extended PEC response to its absorption edge 565 nm (correspond to its indirect bandgap of 2.2 eV in **Figure 5.2c**), while the FeVO₄ and BiVO₄ displayed a low onset wavelength (~520 nm) same as in KPi (**Figure 5.7b**). More direct evidence of the photo response of Bi50 at 550 nm is shown in **Figure B1.17**. It is clear that Bi50 generated measurable photocurrent under monochromatic illumination at 550 nm.

Since FeVO₄ and BiVO₄ shows zero IPCE signal at wavelengths higher than 525 nm, the extended IPCE response for Bi50 can be attributed to the absorption in the FeVO₄ phase assisted by the presence of the BiVO₄/FeVO₄ heterojunction to improve charge separation as mentioned above. The equivalence of the optical onset and PEC onset wavelength for the Bi50 film therefore serves as an evidence for a successful extension of the photoactivity in the mixed BiVO₄/FeVO₄ films.

Figure 5.7 IPCE of FeVO₄, Bi50 and BiVO₄ measured in (a) 0.1 M KPi and (b) 0.1 M KPi + 0.5 M H₂O₂ at 1.5 V vs. RHE. Both insets are the partially zoomed graphs to visualize onset wavelength.

This CoPi deposited Bi50 film was later used for oxygen evolution measurement due to its improved stability. The amount of oxygen generated was quantitatively recorded by gas chromatography. The Faradaic efficiency for oxygen evolution was calculated to be ~88% (Figure 5.8).

Figure 5.8 O₂ evolved from CoPi treated Bi50 film under AM1.5 illumination at 1.5 V vs. RHE. The red dash line indicates the theoretical amount of O₂ based on the charge from the current-time curve. Faradaic efficiency is then calculated to be ~88% by dividing the measured O₂ amount by the theoretical one.

5.3 Conclusions

A series of Bi_xFe_{1-x}VO₄ mixture thin films was successfully fabricated by electrospinning. Instead of forming a solid solution, a mixed phase of BiVO₄ and FeVO₄ was detected from the x-ray diffraction patterns, and the indirect bandgap decreases with decreasing Bi/Fe atomic ratio. The mixed phase with atomic ratio of Bi/Fe = 1, i.e., Bi50, was found to have the optimum charge carrier transfer and separation efficiencies as compared with BiVO₄ or FeVO₄. Improved charge transfer efficiency was achieved due to a higher catalytic activity of Fe/Bi cation mixture, while the enhanced charge separation was attributed to the homogenous BiVO₄/FeVO₄ heterojunction as observed from TEM. In addition, IPCE measurements revealed that the Bi50 composition demonstrates photoactivity up to ~560 nm, which is larger than that of a pure BiVO₄ and consistent with the indirect bandgap of ~2.2 eV. This work illustrates a simple yet successful strategy of forming a mixed phase to expand light utilization as well as charge carrier transfer and separation efficiencies. Further improvement of the mixed phase films may be obtained through strategies well-reported in the literature, such as doping and nanostructuring.

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Chapter 6*

Elucidation of Opto-electronic and Photoelectrochemical Properties of FeVO₄ Photoanodes

In this chapter, triclinic iron vanadate (n-type FeVO₄) thin films were fabricated for the first time by spray pyrolysis and elucidated as a potential photoanode material for solar water oxidation. FeVO₄ has an ideal band gap for a photoanode of ~2.0 eV, which corresponds to a potential solar-to-hydrogen (STH) efficiency of 16%. However, the findings show that the photoelectrochemical performance of FeVO₄ is limited by very poor charge carrier separation efficiency in the bulk. Time-resolved microwave conductivity measurements revealed that the low mobility ($\sim 5 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and short diffusion length ($\sim 2 \text{ nm}$) of undoped FeVO₄ are the main reason for its fast bulk recombination. To overcome the poor charge separation efficiency in the bulk, molybdenum doping was used to enhance its mobility, lifetime, and carrier concentration. This chapter greatly enriches the understanding of FeVO₄ properties.

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6.1 Introduction

Chapter 5 explored the mixture of BiVO₄ and FeVO₄, while the knowledge of FeVO₄ is still limited, due to the fact there are few reports investigating the intrinsic properties of FeVO₄. This chapter will take a close look into FeVO₄ and evaluate it as a photoanode candidate material.

This n-type semiconductor has a triclinic crystal structure consisting of [FeO₆] octahedrons and [FeO₅] distorted trigonal bipyramids, with [VO₄] tetrahedrons connecting the two structures.^[1] It was first identified by a high-throughput screening method as a potential photoelectrode material with good absorption in the visible part of the solar spectrum.^[2] The band gap of FeVO₄ is reported to be ~2.0-2.1 eV;^[3-5] while it is slightly larger than the ideal 1.7-1.9 eV, the theoretical achievable STH efficiency is still a respectable 16%. The photocurrent density of the undoped material is, however, less than 0.1 mA cm⁻² at 1.23 V vs. RHE (potential relative to reversible hydrogen electrode).^[3] Efforts have been reported to improve the performance (e.g., doping with W, partial reduction of Fe³⁺/Fe²⁺),^[4, 6] but the photocurrent enhancement has been marginal. The cause of such a small photocurrent is not clear, because many intrinsic properties, such as the exact band positions, carrier mobility, and carrier lifetime are still unknown. Elucidation of these properties will help to identify the performance limiting factors and apply appropriate improvement strategies.

In this chapter, spray pyrolysis was employed to fabricate crystalline thin film FeVO₄ photoanodes. After heat treatment at 650 °C to obtain the desired phase, the film was subjected to a combination of photoelectrochemical and time-resolved microwave conductivity (TRMC) measurements. The photocurrent of FeVO₄ was found to be limited by poor charge separation efficiency, caused by a very low carrier mobility. Based on this insight, molybdenum (Mo) was introduced as dopant and it successfully improved the carrier transport properties as well as photoelectrochemical performance.

6.2 Results and discussion

6.2.1 Spray-deposited FeVO₄ photoanodes

Figure 6.1a shows the X-ray diffraction (XRD) pattern of both the as-deposited and annealed films. Although the triclinic crystal structure of FeVO₄ already emerges in as-deposited films, annealing at 650 °C for 2 minutes results in higher crystallinity. All peaks match the standard reported pattern for FeVO₄, except for one peak of Fe₂V₄O₁₃ ($2\theta = 12.56^\circ$), which only appears after the high temperature annealing. The molar ratio of secondary phase Fe₂V₄O₁₃ is calculated to be 4.4 % from the Rietveld refinement of the XRD pattern. No hematite (α -Fe₂O₃) peaks are present. This is also found to be the case for various thicknesses of the film (from 25 to 800 nm), as shown in **Figure C1.1**. It is noted that the presence of the secondary phase was only found in films deposited on FTO; no secondary phase was detected for films deposited on quartz (**Figure C1.2**).

Figure 6.1 (a) XRD pattern of as-deposited (black) and annealed (red) films. The reference pattern for FeVO₄ is shown in blue. FTO and Fe₂V₄O₁₃ peaks are also labeled. (b) SEM image of FeVO₄ film annealed at 650 °C for 2 minutes in air. Inset shows the same morphology in smaller magnification.

Scanning electron micrographs show that the as-deposited films have the morphology of stacked rough particles (**Figure C1.3**). Upon annealing, they become interconnected grains with a size of 100-400 nm (**Figure 6.1b**). The smooth grain surface is in good agreement with the higher crystallinity shown by the XRD data. Cross-section SEM images (**Figure**

C1.4) show films with a homogeneous thickness, similar to other materials prepared by spray pyrolysis in the same spray setup.^[7-8] Based on the cross-section of samples sprayed with 50 mL and 100 mL of precursor, thickness values of ~200 nm and ~400 nm were obtained respectively (**Figure C1.4a, b**), indicating a linear relationship between the precursor volume and film thickness.

Figure 6.2 (a) Absorption spectrum, (b) calculated absorption coefficient (α), plotted as a function of photon energy and wavelength, and (c) Tauc plot of 200 nm FeVO₄ film annealed at 650 °C.

The absorption spectrum of a 200 nm FeVO₄ film is shown in **Figure 6.2a**, as obtained from UV-vis spectroscopy using an integrating sphere configuration (spectra for other thicknesses are shown in **Figure C1.5**). The presence of the secondary phase does not affect the overall absorption spectrum, since spectra for films deposited on FTO (4.4 mol% of Fe₂V₄O₁₃ secondary phase is present) and films deposited on quartz (no secondary phase) do not show any significant difference (**Figure C1.6**). The absorption edge is ~600 nm, and the films appear yellow/orange in color (**Figure C1.7**). The absorption coefficient (α) can be calculated by the following equation:

$$\alpha = \frac{-\ln(1 - A)}{d} \quad (6.1)$$

where A is the absorption at a single wavelength and d the film thickness. **Figure 6.2b** shows α as a function of photon energy (wavelength), as obtained from the 200 nm film. For photons with energy above 2.6 eV (wavelength 480 nm), the absorption coefficient

calculated is between 4×10^4 and 10^5 cm^{-1} , corresponding to a penetration depth (α^{-1}) of ~100-250 nm. Overall, a thickness of 400 nm is needed to absorb ~60% of all AM1.5 photons with wavelengths above the bandgap of FeVO₄. The calculated Tauc plots (**Figure 6.2c**) demonstrate that FeVO₄ has a direct band gap of ~2.6 eV and an indirect band gap of ~2.07 eV, enabling a wide range of visible light absorption. The indirect band gap of 2.07 eV agrees with reported values in the literature.^[3-4]

The photocurrents of samples with various thicknesses are shown in **Figure 6.3a**. The current-voltage (J-V) curve of FeVO₄ films under chopped simulated solar light shows moderate photocurrent but a relatively high onset potential of ~0.68 V vs. RHE (**Figure C1.8**). This is in excellent agreement with the flatband potential of the film, which is $-0.69 \pm 0.06 \text{ V}$ vs. RHE, according to the Mott-Schottky analysis (**Figure C1.9**). UPS measurements (**Figure C1.10**) reveal a work function value of $5.1 \pm 0.15 \text{ eV}$ (i.e., the Fermi level is ~0.6 V vs. RHE), which corresponds well with the onset potential and the flatband potential. The optimum thickness is found to be 400 nm, as shown in **Figure 6.3b**; this is presumably caused by the competition between absorption depth and diffusion length of the photogenerated carriers in FeVO₄.

Figure 6.3 (a) Current-voltage curves of samples from 25 nm to 800 nm measured in 0.1 M KPi (pH = 7) under chopped AM1.5 illumination. (b) The photocurrent at 1.2 V vs. RHE as a function of the film thickness. Dashed blue line is a guide to the eye. (c) Charge separation and injection efficiency of the 400 nm FeVO₄ sample.

The photocurrent obtained (0.15 mA cm⁻²) is comparable to previously reported values,^[4] but it is still lower than the theoretical photocurrent based on the band gap (13 mA cm⁻²). In order to understand the cause for such a low photocurrent, further photoelectrochemical measurements were carried out in electrolyte containing Na₂SO₃ as hole scavenger to distinguish the bulk charge separation from surface charge injection efficiencies (see **Appendix C2** on calculation steps). The calculated η_{sep} and η_{inj} of the 400 nm-thick sample are shown in **Figure 6.3c**. η_{inj} increases with applied potential and reaches a value of 60-80% at potentials above 1.2 V vs. RHE. On the other hand, η_{sep} remains lower than 2% over the potential range. It is considered that this may be partially contributed to the presence of the secondary phase, which affects the photocurrent negatively. Nevertheless, this analysis suggests that the surface charge injection in FeVO₄ is not the main problem, but the bulk carrier separation is.

6.2.2 Mo doping of FeVO₄

One common method to address the problem of poor charge separation in the bulk is to improve the conductivity by doping.^[9-12] Here, Mo was introduced to the 200 nm-thick FeVO₄ films (200 nm was chosen as the thickness here since there is only minute differences of photocurrent with the 400 nm, but with much faster deposition time), by simply adding a Mo precursor into the spray deposition solution as mentioned in the experimental section. Mo⁶⁺ is expected to replace V⁵⁺ according to the following defect-chemical equation (in Kröger-Vink notation):

If no trapping at defects sites occurs, the additional electrons will reside in the conduction band and improve the bulk conductivity of the film. This is confirmed by the 5-fold improvement in carrier concentration upon 2% Mo-doping, based on the Mott-Schottky analysis (**Figure C1.9**). Upon addition of Mo, no additional peaks are observed in XRD patterns (**Figure C1.11**). Although this does not exclude the possibility that small amounts of X-ray amorphous or nanocrystalline Mo-oxide have segregated out, the systematic shift

of the FeVO₄ XRD peaks is clear evidence of the successful incorporation of Mo into FeVO₄ lattice (**Figure C1.12**).^[13] No significant changes in morphology or optical absorption are observed for the Mo-doped films when compared to the undoped ones (**Figure C1.13-14**).

Figure 6.4 Core level XPS spectra of (a) Fe, (b) O and V, and (c) Mo of undoped and 2% Mo doped samples.

The chemical composition of the films was investigated by XPS. No other elements or contaminants (except adventitious carbon) are detected in the survey spectrum (**Figure C1.15**). The core level spectra are displayed in **Figure 6.4** to show the oxidation states of elements. **Figure 6.4a** shows the Fe 2p_{3/2} peaks located at 709-716 eV, which can be fitted to the Fe³⁺ multiplets, indicating that Fe exhibits a valence state of 3+ in FeVO₄.^[5, 14] The binding energy of V is 516.85 eV (**Figure 6.4b**), which represents a V⁵⁺ oxidation state.^[10, 15] The O 1s peak is located at 529.9 eV, close to the position expected for a surface lattice oxygen peak.^[10] No significant change is observed in the Fe, V, and O peaks upon Mo introduction. The signal of Mo 3d core level (**Figure 6.4c**) confirms the successful incorporation of Mo in the 2% Mo doped sample. The binding energy of Mo 3d_{5/2} at ~232.3 eV confirms that Mo exists in the 6+ oxidation state.^[10, 16] The Mo/(Mo+V) atomic ratio is calculated to be $1.9 \pm 0.1\%$ from XPS results, which is in well agreement with the concentration of Mo in the precursor.

The photocurrents under chopped AM1.5 illumination for FeVO_4 with varying Mo concentration are shown in **Figure 6.5a**. The photocurrent increases with increasing Mo concentration and reaches a maximum for 2% Mo concentration (see inset of **Figure 6.5a**); beyond this the photocurrent decreases. For the 2% Mo doped film, a photocurrent improvement of $\sim 40\%$ at potentials higher than 1.6 V vs. RHE was obtained, as compared to the undoped film. Again, it should be carefully noted that the photocurrent may be affected (either positively or negatively) by the presence of the $\text{Fe}_2\text{V}_4\text{O}_{13}$ secondary phase. Overall, the photocurrent is comparable with other reports on FeVO_4 in the literature, as summarized in **Table C1.1**.

Figure 6.5 J-V curves of undoped and doped samples measured in 0.1 M KPi (pH = 7). Inset shows the current density changes with Mo doping ratio. (b) IPCE of 2% Mo doped and undoped sample measured at 1.6 V vs. RHE.

The IPCE of the undoped and 2% Mo films are shown in **Figure 6.5b**. Consistent with the AM1.5 photocurrent results, the 2% Mo doped sample shows a strongly enhanced efficiency between 380–480 nm. At longer wavelengths, the IPCE is also improved, but remains lower than 1%. The 480 nm wavelength corresponds to a photon energy of 2.6 eV, which is exactly the direct band gap of FeVO_4 (**Figure 6.2**). Thus, it appears that the direct optical transition contributes much more to the total photocurrent than the indirect one. The charge separation and injection efficiencies of the 2% Mo doped sample were also measured to investigate the influence of doping (**Figure C1.16**). Interestingly, η_{inj}

improves with doping, with values over 90% at potentials larger than 1.35 V vs. RHE. η_{sep} also improves upon Mo doping, but the values remain very low (< 3%).

In order to understand the reason for the very low carrier separation efficiency—even after Mo doping—it is suitable to perform time-resolved microwave conductivity (TRMC) to investigate the carrier transport properties (i.e., mobility, lifetime, diffusion length) of FeVO₄. Only a moderate amplitude of TRMC signals is detected from the undoped FeVO₄ film (**Figure 6.6a**). The TRMC signal ($\phi\Sigma\mu$) of the undoped sample decays rapidly within the first 100 ns, after which it becomes very noisy. The decay curve of the undoped sample can be fitted with power law ($\phi\Sigma\mu = 0.0012 \times t^{-1.06}$, $t < 100$ ns) and the mobility is estimated to be $\sim 4.6 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Upon Mo doping, the microwave signal significantly increases and a clear prolonged decay is observed (**Figure 6.6a**). The decay curve fits well with power law ($\phi\Sigma\mu = 2.66 \times t^{-0.48}$) over a time window ranging from ns to 10 μs (see **Figure 6.6a**). Mobility values of $1.3 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $1.6 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ are extrapolated for AM 1.5 conditions ($\sim 10^9$ photons pulse⁻¹ cm⁻²) for 2% and 4% Mo doped samples, respectively (**Figure 6.6b**). These values are ~ 3 times larger than that of the undoped sample.

Figure 6.6 (a) Time-resolved microwave conductivity (TRMC) signal of 200 nm-thick 2% Mo doped and undoped FeVO₄ films excited by 355 nm laser with an intensity of 3.35×10^{14} photons pulse⁻¹ cm⁻². The blue solid lines are the power law fits of the curves. k , k_1 and k_2 are the decay exponents. (b) Calculated mobility for 2%, 4% Mo doped samples and undoped samples from different light intensities.

The power law decay implies a trap-limited bimolecular recombination mechanism instead of regular band-band recombination.^[17] Such behavior is consistent with the relatively constant mobility and similar decay kinetics at various light intensities (**Figure C1.17**). The decay curves for 2% and 4% Mo-doped samples have the same decay exponent of -0.5. This suggests an identical decay mechanism, most probably due to the interaction (i.e. trapping and detrapping) of charge carriers with a wide distribution of states in the band gap (multiple trapping).^[18] The undoped sample, however, decays much faster than the doped ones in the first ~100 ns, where the decay exponent is close to -1.

The power law decay has been empirically ascribed to trapping-detrapping or carrier tunneling models.^[17, 19-21] For the trapping-detrapping model, a distribution of trap states that leads to a distribution of trapping-detrapping times results in a broad range of recombination time constants and a decay exponent between 0 and -1.^[20] Alternatively, in the carrier tunneling model, the trapped carriers can tunnel to adjacent recombination sites; the broad range of tunneling time constants is then a result of a distribution of short distances between the trap states and the recombination centers. The possibility of tunneling for the undoped samples is inferred from the power law exponent (~-1), which indicates zero-order kinetics, and recombination centers that are close to each other (within a few nm). The addition of Mo leads to a slower decay with a power law exponent of -0.5, which suggests that Mo could prevent fast tunneling, possibly by the interaction of Mo excess electrons with trap states (i.e., pre-filling). The exact mechanism for obtained data is unknown and beyond the scope of this work; further experiments are needed to discriminate this.

The lifetime of the charge carriers, τ , is defined as the time that it takes for the signal to decrease to 50% of its starting value. Values of 29 and 136 ns are found for undoped and 2% Mo doped samples, respectively. Based on these lifetimes and mobilities, the diffusion lengths were calculated to be ~2 nm for undoped and ~7 nm for 2% Mo doped FeVO₄. The improvement in the carrier transport properties for Mo-doped FeVO₄ is consistent with the photocurrent improvement obtained upon Mo-doping. Nevertheless, the values are

relatively low, even with Mo-doping, which explains the very low carrier separation efficiency.

6.3 Conclusions

Spray-deposited n-type triclinic FeVO₄ films have been systematically assessed as a candidate photoanode material. The band gap is 2.07 eV as obtained from optical measurements, which is close to the ideal band gap range for a light absorber (1.7–1.9 eV). Time-resolved microwave conductivity measurements reveal that the low carrier mobility of FeVO₄ is the main factor that limits its PEC performance (see **Table C1.2** for comparison with other metal oxides). The low mobility results in poor conductivity and very limited carrier diffusion lengths. As a result, the photogenerated charge carriers are primarily lost through bulk recombination, resulting in a very low separation efficiency of ~1%. Doping is partially effective in improving the photocurrent, as also shown in other reports.^[4, 6] In this case, Mo-doping leads to significant enhancement in carrier mobility ($\times 3$) and lifetime ($\times 4.5$), which results in 45% increase of the photocurrent density at 1.6 V vs. RHE and major enhancement of the IPCE (7% at 400 nm, vs. 1% for the undoped film). Nevertheless, the carrier diffusion lengths for the doped films are still less than 10 nm; further efforts in improving the carrier separation efficiency (e.g., nanostructuring, heterojunction formation) need to be pursued. In addition, the high donor densities even in the undoped films may also suggest the presence of high number of intrinsic defects generated during the synthesis process, which can act as recombination centers. Higher quality films deposited with greater control over defects (e.g., pulsed laser deposition) need to be developed to further improve the PEC performance of FeVO₄. The materials parameters and insights from this study are expected to help the further development of FeVO₄ and related photoelectrodes.

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Chapter 7

Nanostructured FeVO₄ with Enhanced Visible Absorption and Improved Charge Separation

Nanostructuring has been an effective method to improve the charge separation of semiconductors with poor charge transport properties. In this chapter, nanostructured FeVO₄ was demonstrated to achieve higher PEC performance and lower bandgap than planar film. The improvement was attributed to the higher charge separation efficiency and enlarged absorption range. Initial studies on the annealing duration imply that amorphicity plays a role in changing the bandgap.

7.1 Introduction

Iron vanadate (FeVO₄) has been considered as a promising photoanode material due to its near-optimal bandgap of ~ 2.07 eV.^[1-2] Early stage reported current density at 1.23 V vs, RHE, however, is only within the range of ~ 10 -100 $\mu\text{A cm}^{-2}$.^[3-5] The main reason for its poor photoelectrochemical behavior has been elucidated clearly and can be attributed to the low carrier properties by time-resolved conductivity measurements.^[6] Elemental doping of FeVO₄ film can increase the mobility, but resulted photocurrent increase is marginal.^[4, 6] Another factor that may undermine its performance is the weak absorption in visible range, which leads to a considerable part of efficiency loss.^[7] The moderate absorption coefficient of FeVO₄ requires a film thickness of 400 nm to absorb a 60% of the solar spectrum below the bandgap.^[6] The mismatch of optical absorption requirement (a few hundred nanometers) and short diffusion length (< 10 nm) cannot be simply solved by one modification technique like doping, or catalyst loading.

Modification of the morphology, therefore, is needed for further improvements of FeVO₄ photoanodes.^[1, 6] Nanostructuring has been an effective method to tackle the limitation of poor carrier transport, especially for those photoelectrodes with short diffusion length and lifetime, which is best represented by hematite.^[8-13] Reported photoanodes with a high performance all adopted nanostructure.^[14-17] Constructing nanostructure can allow shorter travelling distance for carriers to reach the surface and offer larger surface area for water oxidation reaction.^[8, 18-19] Adverse effects sometimes occur with increase in surface area, due to more defects or surface states generated; but usually they can be solved with depositing a surface passivation layer.^[18] Recently, nanoporous FeVO₄ photoanodes were investigated to shorten the average carrier transport length.^[20] Nanoporous FeVO₄ showed higher photocurrent than undoped planar film, suggesting it a feasible way to improve the performance of FeVO₄. In contrast, all film shaped FeVO₄ photoanodes failed to obtain higher photocurrent than the nanoporous one.

Herein we introduced a two-step FeVO₄ nanorod growth enlightened by previous reports.^[21-23] By annealing FeOOH nanorod substrates coated with NH₄VO₃ solution at

600 °C for different durations, either nanostructured FeVO₄ (5 min annealing) or film FeVO₄ (20 min annealing) can be obtained. The nanostructured FeVO₄ was constructed into rod-like structure, which demonstrated higher performance in hole scavenger than planar film. Combination of nanostructure and Mo doping results in up to 3 times higher separation efficiency. Visible absorption of nanostructured FeVO₄ surprisingly extends to 640 nm, which allows better utilization of solar spectrum.

7.2 Results and Discussion

7.2.1 Physical characterizations

The morphology of FeVO₄ (**Figure 7.1a**) shows nanorod shape with a diameter varying from 20 - 100 nm and an average length of ~400 nm. Compared with FeOOH nanorod (**Figure D1**), the FeVO₄ nanorods (denoted as FeVO₄ NR) retained similar diameter but are made of small particles aligned in the nanorod form (**Figure D2**).

Figure 7.1b shows the XRD patterns of FeVO₄ photoanodes fabricated on FTO substrates. Both nanostructured and film samples exhibit a triclinic FeVO₄ phase, which is consistent with our reported crystal structure by spray pyrolysis.^[6] Only traces of hematite peak (35.68°) can be observed, indicating there remains very little hematite phase. No other impurity phase was detected except hematite and FTO signal. Nanostructured FeVO₄ sample has a poorer crystallinity than film sample, largely due to the shorter annealing duration. As a comparison, FeOOH grown on FTO substrate without coating vanadium precursor was annealed at 600 °C for 5 min and the X-ray diffractogram is displayed in **Figure 7.1b**. The sample showed characteristic hematite peak at 35.68°, representing the [110] direction of hematite nanorod.^[13] It indicates that 5 min annealing time at 600 °C is sufficient to convert FeOOH into crystalline Fe₂O₃. Therefore, the amount of crystalline hematite in nanostructured FeVO₄ is considered small.

Figure 7.1 (a) Microscopic images of FeVO₄ nanostructure, inset shows the cross-section view. (b) XRD patterns of nanostructured FeVO₄, film FeVO₄, and nanorod hematite grown on FTO. (c) Absorption spectra of both nanostructured and film FeVO₄. (d) Tauc plots calculated from absorption curves.

Distinct absorption spectra were shown for film and nanostructured FeVO₄ (**Figure 7.1c**). The absorption edge of film FeVO₄ was ~600 nm, in accordance with former reported results for thin film FeVO₄.^[3-4, 6] Substantial visible absorption increase was observed for FeVO₄ NR for wavelength higher than 450 nm and the absorption edge shifted to ~650 nm. Tauc plots (**Figure 7.1d**) calculated from absorption curves demonstrated that the bandgap of NR sample was reduced, from 2.08 eV (indirect, film) and 2.5 eV (direct, film) to 1.93 eV (indirect, NR) and 2.15 eV (direct, NR) respectively. The reduced bandgap of NR is close to that of nanoporous FeVO₄ (reported with indirect bandgap 1.92 eV and direct 2.01 eV), which suggests the change of optical properties may be related to the nanostructure.^[20]

Fast-Fourier transform (FFT) pattern and high-resolution transmission electron

microscopy (HRTEM) image was taken to further confirm the crystal structure of FeVO₄ NR (**Figure 7.2a and b**). All the d-spacing can be indexed to triclinic FeVO₄ phase and no other crystalline phase was detected. The rings in FFT pattern reveals the nanorod is made up of polycrystalline nanoparticles, which can be further illustrated in low resolution TEM images (**Figure 7.2c and d**) and is consistent with X-ray diffraction pattern. Small nanoparticles with a diameter of 10 - 40 nm assemble to form the longer rod shape without a preferred orientation.

Figure 7.2 (a) Fast-Fourier transform pattern (b) HRTEM image (c) and (d) low resolution TEM images of FeVO₄ NR.

7.2.2 PEC and IPCE measurements

Besides pristine FeVO₄ NR, Molybdenum (Mo) doping of various concentration was realized by adding different amount of MoO₂(acac)₂ into NH₄VO₃ aqueous precursor to fabricate Mo doped FeVO₄ NR samples. No difference was observed in the morphology, crystal structure and optical absorption between pristine and Mo doped FeVO₄ NR (**Figure D3**). Photoelectrochemical performance of FeVO₄ NR in KPi buffer electrolyte, however, showed no improvement compared with FeVO₄ film (**Figure 7.3a**) even with Mo doping. All the samples were measured in electrolyte containing 0.5 M Na₂SO₃ as hole scavenger to eliminate surface efficiency loss (**Figure 7.3b**). It turned out that pristine FeVO₄ NR obtained more than two times photocurrent as the planar film one and 3% Mo doped NR achieved the highest photocurrent of 0.58 mA cm⁻² at 1.5 V vs. RHE (FeVO₄ film 0.13 mA cm⁻²).

Deconvolution of charge efficiencies demonstrated that charge transfer efficiency (η_{trans}) at the surface of both pristine and Mo doped NR samples is worse than the film sample. η_{trans} for FeVO₄ film was >50% above 1.3 V vs. RHE while for either pristine or doped NR samples only below 20% at 1.5 V vs. RHE. The contrast of η_{trans} may be partially due to the poor crystallinity of NR samples; another important factor could be large numbers of defects generated at the surface of nanostructure with enlarged surface area.^[18]

Charge separation of all NR samples has improved over the whole potential range. In comparison with film FeVO₄, separation efficiency (η_{sep}) of FeVO₄ NR almost doubled at potentials higher than 1.2 V vs. RHE. Such an increase can be assigned to shortened carrier travelling path to electrode-electrolyte interface because of nanostructuring.^[20, 24] Also, large surface area allows higher volume of depletion layer to reduce bulk charge recombination.^[18] In **Chapter 6**, the effect of Mo doping has been shown to increase bulk conductivity due to higher carrier concentration and carrier mobility. These beneficial effects can explain the higher charge separation efficiency of Mo doped NR samples compared with pristine FeVO₄ NR. Here it can be inferred that similar to previous findings,

Mo dopants in FeVO₄ NR lead to higher carrier mobility and longer carrier lifetime; consequently, η_{sep} of Mo doped NR is enhanced.^[6]

Figure 7.3 Current density curve measured in (a) 0.1 M KPi (pH = 7) and (b) 0.1 M KPi + 0.5 M Na₂SO₃. Calculated (c) charge transfer efficiency and (d) charge separation efficiency from (a) and (b).

To investigate the photoresponse under different wavelength illumination, incident photon-to-current conversion efficiency (IPCE) was measured in KPi buffer solution added with hole scavenger Na₂SO₃ (**Figure 7.4a**). IPCE of film FeVO₄ is quite low (<1%) at wavelength higher than 450 nm. While for FeVO₄ NR sample, there is a considerable increase in IPCE from 420 nm to 600 nm. Mo doping also shifts the onset potential from ~550 nm to ~640 nm (**Figure 7.4b**), which means that FeVO₄ NR can still have measurable photoactivity around the absorption edge. To confirm the extended photoactivity at long wavelength, film and nanostructured FeVO₄ samples were subject to chopped monochromatic illumination at 550 nm, 600 nm, 620 nm and 640 nm respectively (**Figure D4 – D8**). Only tiny photocurrent was detected for FeVO₄ film at 550 nm and no further

photoactivity was observed at 600 nm and 620 nm. For FeVO₄ NR, especially Mo doped samples, obvious photocurrent was observed till 640 nm, consistent with the optical onset and photoelectrochemical onset wavelength. It is interesting to note that the incorporation of Mo into NR results in a new absorption feature at ~480 nm, but the underlying reason needs further investigations.

Figure 7.4 (a) IPCE measured in 0.1 M KPi + 0.5 M Na₂SO₃. (2) Zoomed in IPCE to illustrate the onset wavelength.

7.2.3 Effect of annealing duration

As the only difference between pristine FeVO₄ NR and film is the annealing duration (detailed fabrication conditions are stated in **Chapter 3**), the effect of annealing duration is investigated to check if this is the reason for bandgap change. FeOOH sample coated with NH₄VO₃ precursor was investigated by varying the annealing time (2 min, 5 min, 10 min and 20 min) at the same temperature 600 °C. It is found that 2 min and 5 min annealing resulted in nanostructured FeVO₄ while a planar film was obtained above 10 min annealing (**Figure D9**). Increasing annealing time from 2 min to 20 min brought forth a reduction of absorption but an increase in crystallinity as shown in **Figure 7.5a and b** (similar absorption spectra of 2 min and 5 min sample may be due to the sample to sample variation). The bandgap shift can be visualized in the photograph of these samples (**Figure D10**) where the color changes from brownish red to bright yellow as annealing time increases. The amorphous structure here is inferred to play a role in the bandgap change considering

there exists no other crystalline phases or impurities. Further characterizations have to be carried out to elucidate the reason behind.

Figure 7.5 (a) Absorption spectra, (b) X-ray diffractogram, (c) Current density at different potentials of films annealed at 600 °C for 2 min, 5 min, 10 min and 20 min respectively. (d) Comparison of electrochemical active surface area, normalized based on the film sample (20 min annealing).

Current density as a function of annealing time was plotted in **Figure 7.5c**, showing 5 min annealed sample (i.e., pristine FeVO₄ NR sample mentioned in former sections) demonstrates the highest photocurrent. Although the surface area of 2 min annealed sample is more than one order higher than the film one, photocurrent of these two are quite comparable. The PEC performance of 2 min sample is undermined by insufficient crystallinity. It can be proposed that the amorphous part is crucial to enlarge the absorption,^[25] but it does not translate to higher photocurrent due to reduced charge

transport properties. There may exist a balance between crystallinity and nanostructure, which is shown by the best performed 5 min NR sample. Further optimizations on the annealing conditions could improve the PEC performance of nanostructured samples.

7.3 Conclusions

Nanostructured FeVO₄ samples were successfully prepared by transforming FeOOH nanorod with V precursor. As compared with planar film FeVO₄, NR sample obtained a lowered bandgap of ~1.9 eV. The PEC onset wavelength also matches with the optical absorption edge, showing photoactivity till ~640 nm by IPCE measurements. Nanostructuring was responsible for the poor charge transfer efficiency of NR sample while it improved charge separation. Mo doping was incorporated into NR samples and 3% Mo concentration presented the highest photocurrent of 0.58 mA cm⁻² at 1.5 V vs. RHE, which is more than 4 times higher than that of the film. Initial studies on the effect of annealing time have revealed that the amorphous structure may cause the bandgap shift but further investigations is still needed.

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Chapter 8

Discussion and Future Work

This chapter serves as a concluding chapter for the whole thesis. A general discussion on the main results on bismuth vanadate and cation-substituted metal vanadates are presented. It summarizes the performance of bismuth vanadate, iron vanadate and bismuth/iron vanadate mixture photoanodes and highlights the achievements and findings from the results. On the basis of finished work in the thesis, reflections on the limitations of iron vanadate and discussions on the possibility of further improvements of iron vanadate photoanodes are listed in the section of future work. Some initial unpublished results are also discussed here. In conclusion, iron vanadate can be a promising photoanode material if the limitations can be tackled properly.

8.1 General discussion

This thesis mainly addresses the problem of developing a novel metal vanadate photoanode. As has been well stated in Chapter 1, the objective of the thesis is to find a new metal vanadate photoanode with near-optimal bandgap which can extend light absorption beyond BiVO_4 and has comparable or superior charge transport properties as BiVO_4 . Based on literature survey and experimental analysis, Fe substituted bismuth vanadate FeVO_4 has been identified as a promising photoanode candidate with a lower bandgap than BiVO_4 . Detailed discussion on the hypothesis and selection criteria are well stated in Chapter 1.

Prior to looking at FeVO_4 , a study was carried out on BiVO_4 photoanodes to have a better understanding on its characteristics and performance limiting factors. Chapter 4 investigated the photoelectrochemical behavior of graded Mo doped BiVO_4 before and after NiO_x catalyst loading. For the first time the role of NiO_x on BiVO_4 photoanodes was investigated in detail. In addition to improving the surface catalytic efficiency, the p-type catalyst can form heterojunction with n-type BiVO_4 , causing increased separation efficiency. It shows NiO_x acts as a multifunctional catalyst which can not only assist surface charge transfer but also facilitate charge separation and collect holes efficiently. This study helps clarify some ambiguous explanations on the function of NiO_x catalyst.

Chapter 4 plays an important role in understanding the photoelectrochemical performance of BiVO_4 and involves the modification techniques of doping and catalyst doping. Following studies on mixed-cation metal vanadates in Chapter 5 serves as an extension project to Chapter 4. A series of Fe substituted and pristine BiVO_4 mixture were fabricated by electrospinning. Incorporation of Fe into BiVO_4 substantially reduced the bandgap of mixed vanadates from 2.4 eV to 2.1 eV. The lowered bandgap validates the hypothesis of introducing other metal cation to reduce the bandgap of BiVO_4 . In addition to bandgap reduction, mixed metal vanadates photoanodes were superior in charge transfer efficiency and separation efficiency. The optimal Fe/Bi ratio in the mixed metal vanadates photoanodes was tested to be 1 to obtain highest PEC performance. Proper band alignment of BiVO_4 and FeVO_4 formed heterojunction, which improved the charge separation than

the two extreme compositions BiVO_4 or FeVO_4 . Microscopic observations offered direct evidence to the presence of heterojunction. This study opens a new possibility to construct lower bandgap metal vanadate photoanodes simply by mixing. The formation of heterojunction also introduces a way to improve charge separation of metal vanadate photoanodes.

Preliminary results on FeVO_4 in Chapter 5 has reflected that even though it has a near-optimal bandgap of ~ 2.1 eV, the photocurrent obtained is far from its theoretical limit. The reasons for such a huge discrepancy was not clear due to lack of reported intrinsic properties of FeVO_4 . Chapter 6 includes the first report on optical, electrical, electrochemical and photoelectrochemical properties of sprayed FeVO_4 thin film. Charge separation efficiency was found to be the limiting factor of its PEC performance. With the help of time-resolved microwave conductivity measurements, the carrier mobility as well as diffusion length and carrier lifetime can be determined to be much smaller than BiVO_4 . Mo doping was helpful to increase the carrier mobility a few times higher than the pristine one, but the increase in PEC performance of Mo doped FeVO_4 film was still marginal. It is clear that doping alone is insufficient to close the gap between theoretical and experimental photocurrent. Therefore, nanostructuring may be a way to further improve its performance.

Chapter 7 presented the fabrication and photoelectrochemical properties of FeVO_4 nanorod (NR). FeVO_4 NR on FTO was fabricated successfully by introducing vanadium into FeOOH nanorod. Different with FeVO_4 film, the bandgap of FeVO_4 NR was reduced to ~ 1.9 eV. When measured with hole scavenger Na_2SO_3 , FeVO_4 NR showed higher photocurrent. From surface area measurements, FeVO_4 NR sample was shown to have a surface area around an order higher than the film. It implies that nanostructure may bring forth adverse effects like poor surface charge transfer, but it can also improve charge separation due to higher volume of depletion layer, which was verified by calculated charge separation efficiency. Incident photon-to-current conversion efficiency measurements proved the enlarged absorption of FeVO_4 NR.

This thesis demonstrates an explicit way of investigating metal cation substituted vanadate and applying modification techniques to enhance its PEC performance. In the thesis, BiVO₄/FeVO₄ mixture and nanostructured FeVO₄ have successfully been prepared and found to reduce the bandgap than BiVO₄. Some problems, however, remain to be solved and are listed in the following sections.

8.2 Future work

8.2.1 Optimization of nanostructured FeVO₄

One remaining problem in Chapter 7 is the poor crystallinity of nanostructured FeVO₄ annealed for only 5 min. Higher crystallinity can bring forth higher photocurrent, as illustrated in **Figure 7.5c**. Increasing the crystallinity of nanostructured FeVO₄ would be beneficial to its PEC performance. Postannealing for nanostructured FeVO₄ is the most direct way to improve its crystallinity, but the control of ramp rate, annealing temperature, duration, and atmosphere needs to be investigated carefully so as not to damage the nanostructure or undermine carrier mobility.

Another concern is the size of the nanostructure. As shown in **Figure 7.1a**, the diameter of FeVO₄ nanorod 20 - 100 nm is still larger than its diffusion length (~2–7 nm). Ideally, the size of the nanostructure should be similar to the carrier diffusion length to minimize carrier recombination in the bulk. Current diameter of FeVO₄ nanorod is one to two orders higher than its diffusion length, which is reflected by the charge separation efficiency below 10 %. Reducing the size of FeOOH would possibly reduce the diameter of FeVO₄ nanorod.

In addition to reducing the diameter of nanorod, introducing porosity into the nanostructure is also a feasible way. Changing the composition of NH₄VO₃ precursor for drop casting on FeOOH may change the morphology of FeVO₄. Initial results show that a porous structure can be achieved using another vanadium-source solution (**Figure 8.1**) The diameter of nanoparticles is around 10 – 50 nm, which is smaller than FeVO₄ nanorod and the porosity may provide higher surface area for water oxidation reaction. It has been reported that Fe³⁺

doped nanoporous FeVO_4 generate current density up to 1 mA cm^{-2} at 1.6 V vs. RHE , which is the record of FeVO_4 based photoanodes till now.^[1] Combination of nanoporosity and the rod structure could possibly further improve the PEC performance of FeVO_4 photoanodes.

Figure 8.1 Nanoporous FeVO_4 fabricated by VCl_3 solution + FeOOH annealing at 500°C .

8.2.2 Hydrogen treatment

Hydrogen treatment of photoelectrodes by annealing in hydrogen atmosphere has attracted attention since 2011. Hydrogenated TiO_2 was found to increase solar absorption as well as greatly improve the PEC performance.^[2] Except TiO_2 , Yat Li and co-workers applied hydrogen treatment on other metal oxides like WO_3 , and BiVO_4 .^[3-5] Recent reports show that hydrogen annealing can lower the onset potential and improve photoactivity.^[6-7] The improved performance is usually attributed to increased carrier concentration originated from oxygen vacancy of hydrogen doping (in the form of hydrogen insertion). Direct evidence of enhanced carrier lifetime after hydrogen treatment on BiVO_4 is also reported most recently.^[8] Similar results (unpublished) are obtained by collaborators in National University of Singapore that hydrogenated hematite photoanodes have prolonged carrier lifetime and higher separation efficiency.

Considering the charge separation efficiency is still low for Mo doped nanostructured FeVO₄, it can be proposed that hydrogen treatment may further improve its charge separation. Experimental conditions of hydrogen annealing are analogous to that have been carried out on hematite photoanodes and similar characterizations can be executed. Hence hydrogen treatment on FeVO₄ may extend the carrier mobility and lifetime to achieve better photoelectrochemical performances.

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APPENDIX A

A.1 Definitions and calculations of charge carrier efficiency

Here defines the following efficiency terms: (i) η_{abs} , the light absorption efficiency, is the number of electron-hole pairs generated per incident photon, (ii) η_{sep} , the charge separation efficiency, is the number of electron-hole pairs separated out of per absorbed photon, and (iii) η_{trans} , the transfer efficiency (also catalytic efficiency or surface efficiency), is the portion of the photogenerated holes that successfully takes part in the water oxidation process after reaching the material surface.

J_{abs} is the total absorbed photons expressed as the photocurrent density which can be calculated by

$$J_{\text{abs}} = J_{\text{max}} \times \eta_{\text{abs}} \quad (\text{A1.1})$$

where J_{max} for BiVO_4 is 7.5 mA cm^{-2} . The calculated J_{abs} values for our samples are shown in **Figure A2.7**.

Assuming that no surface recombination and facile charge transfer occur in the presence of hole scavenger (Na_2SO_3 in this case), both η_{sep} and η_{trans} can be calculated as follows:^[1-2]

$$\eta_{\text{sep}} = J_{\text{Na}_2\text{SO}_3} / (J_{\text{max}} \times \eta_{\text{abs}}) = J_{\text{Na}_2\text{SO}_3} / J_{\text{abs}} \quad (\text{A1.2})$$

$$\eta_{\text{trans}} = J_{\text{H}_2\text{O}} / J_{\text{Na}_2\text{SO}_3} \quad (\text{A1.3})$$

A2 Appendix figures for Chapter 4

Figure A2.1 Infrared spectra of Ni(II) 2-ethylhexanoate loaded BiVO₄ sample under UV irradiation for a continuous 24 h. The decline of absorption indicated time-dependent ligand decomposition upon UV irradiation. The absorption at ~1600 cm⁻¹ and 2800 cm⁻¹-2900 cm⁻¹, which respectively correspond to C=O and C-H vibrational stretching frequencies of organic ligands, are weakened to almost 0 after 16 h UV illumination.

Figure A2.2 (a) UV-Vis absorption spectra of the uncatalyzed and catalyst loaded BiVO₄ films. Calculated Tauc plot for all samples are shown respectively: (b) uncatalyzed film, (c) NiO_x-200 °C film, and (d) NiO_x-400 °C. Indirect and direct band gaps are labeled in blue and black curves respectively.

Figure A2.3 X-ray diffractograms of NiO_x films on FTO and bare FTO substrate. No additional peaks were observed for the NiO_x films, indicating the PMOD deposited NiO_x layer to be XRD-amorphous.

Figure A2.4 Survey XPS spectra of uncatalyzed, NiO_x-200 °C and NiO_x-400 °C samples.

Figure A2.5 Long term stability measurement of uncatalyzed and NiO_x -400 °C sample for 9000 s under AM 1.5G 100 mW cm^{-2} in 0.5 M Na_2SO_4 electrolyte (pH = 6.8). The photocurrent drop after the initial 1000 s is caused by the accumulation of generated oxygen bubbles from water oxidation as the sample was left unattended during the measurement.

Figure A2.6 Measured photocurrent density as a function of applied potentials in 0.5 M Na_2SO_4 solution with 0.5 M Na_2SO_3 as hole scavenger.

Figure A2.7 Absorbed electron flux with calculated J_{abs} for uncatalysed, NiO_x-200 °C and NiO_x-400 °C BiVO₄ photoanodes.

Figure A2.8 Rapid scan voltammetry (RSV) performed with and without conditioning on uncatalyzed and $\text{NiO}_x-400^\circ\text{C}$ samples. The scan rate is 1 V s^{-1} , and the scan direction is cathodic. The conditioning treatment was done by applying a positive potential of 2.1 V vs. RHE for 2 mins. The capacitance curves shown in Figure 8a were constructed by subtracting the RSV curve without conditioning (dashed lines) from the one with conditioning (solid lines) and dividing it with the scan rate.

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APPENDIX B

B1 Appendix figures and tables for Chapter 5

Figure B1.1 EDX elemental mapping of Bi50 film.

Figure B1.2 XRD peak position of two strong BiVO_4 peaks for Bi0 to Bi100, showing no obvious peak shift.

Figure B1.3 V/(Bi+Fe) ratio determined from EDX for films with varying Bi ratio. Atomic ratio V/(Fe+Bi) in the precursor equals to 100% in all films.

Figure B1.4 Fe 2p and Sn 3p (a), Bi 4f (b), V 2p and O 1s (c) XPS spectra for FeVO₄, Bi50 and BiVO₄ films.

Figure B1.5 Photograph of films with various compositions, from FeVO₄ (upper left) to BiVO₄ (lower left).

Figure B1.6 Calculated absorbed photocurrent density (J_{abs}) for the different films with varying Bi ratio.

Figure B1.7 AM1.5 photocurrent density measured in 0.1 M KPi (pH = 7) under front and back illumination for films with different Bi ratio. The photocurrent values are taken at 1.8 V vs. RHE.

Figure B1.8 AM1.5 photocurrent-voltage curves of films with varying Bi ratio, deposited with different electrospinning time. The photocurrents were measured at 1.8 V vs. RHE in 0.1 M KPi under backside AM1.5 illumination.

Figure B1.9 Charge transfer efficiency (η_{trans}) of all compositions as a function of applied potentials.

Figure B1.10 (a) Comparison of dark water oxidation activity of BiVO₄, FeVO₄ and Bi50 mixture film. FTO is also presented for reference. (b) The obtained Tafel plots from the dark J-V curves in (a).

Figure B1.11 Charge carrier separation efficiency (η_{sep}) of all compositions as a function of applied potentials.

Figure B1.12 SEM images showing the surface morphology of the mixed vanadate films with different compositions. The scale bar indicated in each image represents 100 nm.

Figure B1.13 (a) Capacitive current as a function of scan rate for different compositions. (b) Calculated relative surface area normalized by Bi50 film, as obtained from the relative slope of the capacitive current.

Figure B1.14 Cross-section view images for the 30 min electrospun FeVO_4 , Bi50 and BiVO_4 films.

Figure B1.15 EDAX elemental mapping of Bi50 at two different locations (**Figure 4c and d**). Blue color represents V, green for Bi, red for O, and yellow for Fe.

Table B1.1 Atomic percent calculated from XPS peaks.

	Atomic percent (%)				
Sample	Bi	Fe	V	O	Fe/Bi
FeVO ₄	0	13.2	10.3	76.5	-
Bi50	4.9	10.8	12.0	72.2	2.2
BiVO ₄	18.98	0	10.4	70.6	0

Figure B1.16 IPCE of all films measured in 0.1 M KPi at 1.23 V vs. RHE (a, b) and 1.5 V vs. RHE (c, d) respectively.

Figure B1.17 Current density of Bi50 under single wavelength illumination with applied potential 1.5 V vs. RHE in 0.1 M KPi + 0.5 M Na₂SO₃. The photo response under chopped illumination can be reflected in the current density change.

B2 Electrochemical active surface area (ECSA) measurements.

Electrochemical active surface area measurement was performed in 0.1 M KPi (pH = 7) by cyclic voltammetry at different scan rate, i.e., 20, 50, 100, 150, 200, and 300 mV/s. For each scan rate, the capacitive current from double layer charging can be taken from cyclic voltammograms in a potential range where no Faradaic processes are observed. Plot the capacitive current as a function of scan rate, and the slope of the fitting curve represents the surface area (**Figure B1.13a**). Detailed explanation can be seen in other reports.^[1-2]

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APPENDIX C

C1 Appendix figures and tables for Chapter 6

Figure C1.1 X-ray diffractograms of (a) as-deposited and (b) annealed (650°C in air for 2 mins) FeVO_4 films with various thicknesses.

Figure C1.2 XRD patterns for FeVO_4 films deposited on quartz substrates. Both the unannealed and annealed films show pure phase of triclinic FeVO_4 . The broad hump at 2θ value of around 20° is the signature of the underlying quartz substrate.

Figure C1.3 SEM image of the as-deposited FeVO₄ film.

Figure C1.4 Cross-section SEM images of annealed samples sprayed with (a) 50 mL and (b) 100 mL precursor.

Figure C1.5 Absorption spectra of annealed FeVO_4 with various thicknesses.

Figure C1.6 UV-Vis absorption spectra of FeVO_4 films deposited on quartz and FTO substrates.

Figure C1.7 Photograph of annealed FeVO₄ films with various thicknesses.

Figure C1.8 Enlarged partial J-V curve of the 400 nm-thick annealed FeVO₄ showing the onset potential at ~0.68 V vs. RHE.

Figure C1.9 Mott-Schottky plot of undoped and 2% Mo doped FeVO_4 films (200 nm-thick) measured at 1200 Hz in 0.1 M KPi.

Figure C1.10 Ultraviolet photoelectron spectroscopy (UPS) spectra of undoped FeVO_4 using He I source. The work function (ϕ) of FeVO_4 is calculated by $\phi = h\nu - W$, where W is the width of emitted electrons subtracted from the spectrum (16.1 eV) and $h\nu$ is the energy of He I source (21.2 eV).

Figure C1.11 X-ray diffractograms of undoped and Mo doped FeVO_4 films.

Figure C1.12 XRD peak positions as a function of Mo dopant indicating the peak shift after Mo doping. The selected three peaks, $(0\ 1\ 2)$, $(-2\ 0\ 1)$, and $(-2\ 1\ 1)$, are characteristic peaks in the FeVO_4 XRD pattern.

Figure C1.13 SEM image of 2% Mo doped FeVO₄ film.

Figure C1.14 Absorption spectra of undoped and Mo doped FeVO₄ films. All samples are 200 nm thick.

Figure C1.15 XPS survey spectra of undoped and 2% Mo doped films. The adventitious carbon on the surface is estimated to be ~18% from the C1s peak.

Figure C1.16 Charge injection and separation efficiency of undoped and 2% Mo doped 200 nm sample.

Figure C1.17 TRMC signals recorded for 2% and 4% Mo doped samples under different photon intensities. The curves are overlapped to better show that there is no dependence on the decay profile.

Table C1.1 Comparison of photocurrent on FeVO₄-based photoanodes.

No.	System	Fabrication method	Photocurrent at 1.23 V vs. RHE (mA cm ⁻²)	Electrolyte	Reference
1	FeVO ₄	Drop casting	<0.08	0.5 M NaOH, pH unknown	[1]
2	FeVO ₄	Layer-by-layer coating	0.05	0.1 M KPi, pH=7	[2]
	W:FeVO ₄		0.1		
3	FeVO ₄	Drop casting	~0.025	0.1 M SO ₄ ²⁻ , pH=7	[3]
4	FeVO ₄	Drop casting	≤0.1	0.2 M Na ₂ SO ₄ + 0.1 M Pi buffer, pH=7	[4]
	Fe ³⁺ :FeVO ₄		0.25		
5	FeVO ₄	Spray pyrolysis	0.04	0.1 M KPi, pH=7	This work
	Mo:FeVO ₄		0.05		

Table C1.2 Comparison of carrier properties of other metal oxides.

Material	Mobility (cm ² V ⁻¹ s ⁻¹)	Carrier lifetime	Diffusion length (nm)	Reference
Fe ₂ O ₃	~0.01	3 ps	2-4	[5]
BiVO ₄	~0.04	40 ns	70-100	[6-7]
FeVO ₄	~4.6×10 ⁻⁵	~29 ns	~2	This work
2%Mo:FeVO ₄	~1.5×10 ⁻⁴	~136 ns	~7	This work

C2 Calculation of charge separation/injection efficiency

The charge separation efficiency (η_{sep}) and charge injection efficiency (η_{inj}) can be calculated with the following equations as reported before and similar to **Appendix A1**.^[8-9] η_{inj} here is denoted as charge transfer efficiency (η_{trans}) in Appendix A1.

$$\eta_{\text{sep}} = J_{\text{Na}_2\text{SO}_3}/J_{\text{abs}} \quad (\text{S1})$$

$$\eta_{\text{inj}} = J_{\text{H}_2\text{O}}/J_{\text{Na}_2\text{SO}_3} \quad (\text{S2})$$

J_{abs} is the photocurrent converted from photon absorption rate (**Table C2.1**), $J_{\text{H}_2\text{O}}$ is the photocurrent for water oxidation and $J_{\text{Na}_2\text{SO}_3}$ is the photocurrent measured in electrolyte with hole scavenger Na₂SO₃. Upon the addition of Na₂SO₃, η_{inj} is assumed to be unity (without surface efficiency loss).

Table C2.1 Calculated absorbed photocurrent density (J_{abs}) for samples with different thicknesses. The calculation was done by integrating the product of the absorption curves (**Figure C1.5**), AM1.5 spectrum and elementary charge.

Film thickness (nm)	25	50	100	200	400	600	800
J_{abs} (mA cm ⁻²)	2.29	3.87	5.17	5.78	7.72	8.71	9.27

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APPENDIX D

D1 Appendix figures and tables for Chapter 7

Figure D1 Top-view morphology of as prepared FeOOH nanorod grown on FTO substrate.

Figure D2 High magnification SEM image of cross-section view of nanostructured FeVO₄.

Figure D3 SEM images of (a) top view and (b) cross-section view of 2% Mo doped FeVO_4 NR. (c) Absorption spectra and (d) XRD patterns of pristine and Mo doped NR samples.

Figure D4 (a) IPCE of FeVO₄ film and current density as a function of time (J-t curve) under chopped (b) 550 nm, (c) 600 nm and (d) 620 nm illumination.

Figure D5 J-t curve of pristine FeVO_4 NR under chopped (a) 550 nm, (b) 600 nm, (c) 620 nm and (d) 640 nm illumination.

Figure D6 J-t curve of 1% Mo doped FeVO₄ NR under chopped (a) 550 nm, (b) 600 nm, (c) 620 nm and (d) 640 nm illumination.

Figure D7 J-t curve of 2% Mo doped FeVO_4 NR under chopped (a) 550 nm, (b) 600 nm, (c) 620 nm and (d) 640 nm illumination.

Figure D8 J-t curve of 2% Mo doped FeVO₄ NR under chopped (a) 550 nm, (b) 600 nm, (c) 620 nm and (d) 640 nm illumination.

Figure D9 Side view SEM images of samples annealed at various durations.

Figure D10 Photograph of samples annealed at different durations.