Visible-light driven photo-activity study : m-BiVO₄ based nano-particles and thin film

Luo,Qiong

2020

Luo, Q. (2020). Visible-light driven photo-activity study : m-BiVO₄ based nano-particles and thin film. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/139669>

<https://doi.org/10.32657/10356/139669>

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**Visible-Light Driven Photo-activity Study:
m-BiVO₄ based Nano-particles and Thin Film**

LUO QIONG

School of Electrical & Electronic Engineering

2020

Visible-Light Driven Photo-activity Study: m-BiVO₄ based Nano-particles and Thin Film

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School of Electrical & Electronic Engineering

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

2020

Statement of Originality

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

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A handwritten signature in black ink, appearing to read 'Tan Ooi Kiang', with a stylized flourish at the end.

Tan Ooi Kiang

Authorship Attribution Statement

*(B) This thesis contains material from 2 papers published in the following peer-reviewed journals / and 4 from papers presented at conferences in which I am listed as an author.

Chapter 4 is published as **Q. Luo**, L. Zhang, X. F. Chen, O. K. Tan, K. C. Leong, “Mechanochemically synthesized m-BiVO₄ nano-particles for visible light photocatalysis”, *RSC Adv*, vol. 6 (19), pp. 15796-15802, 2016.

The contributions of the co-authors are as follows:

- Prof Tan provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Dr Zhang Li.
- I performed all the laboratory work at the School of Electrical & Electronic Engineering, I also analyzed the data. X-ray photoelectron spectroscopy and TEM were taken with assistance of lab specialist.
- Dr. Chen Xiao Feng guided the use of ball-milling platform.
- Dr. Zhang Li assisted in the interpretation of the X-ray photoelectron spectroscopy.
- Mr Leong was the project manager of the joint-industry PhD program from Globalfoundries who provided the scholarship.

Chapter 4 is also presented as **Q. Luo**, X. F. Chen, M. D. Han, O. K. Tan, M. S. Tse, “Photocatalytic degradation of RhB by high energy ball-milled BiVO₄ nano-particles”, 5th *MRS-S Conference on Advanced Materials*, Singapore 2012.

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- Prof Tan provided the initial project direction and edited the manuscript drafts.
- I performed all the laboratory work at the School of Electrical & Electronic Engineering, I also analyzed the data.
- Dr. Chen Xiao Feng guided the use of ball-milling platform.
- Dr. Han Mandi shared her expertise in the material characterization of BiVO₄ nano-particles from her own thesis work
- Assoc Prof Tse helped to vet the experiment design.

Chapter 5 is published as L. Zhang, **Q. Luo**, X. F. Chen, M. S. Tse, O. K. Tan, K. H. H. Li, Y. Y. Tay, C. K. Lim, X. Guo and K. C. Leong, “Mechanochemically synthesized CuO/m-BiVO₄ composite with enhanced photoelectrochemical and photocatalytic properties”, RSC Adv, vol. 6 (69), pp. 65038-6504, 2016.

The contributions of the co-authors are as follows:

- Prof Tan provided the initial project direction.
- Dr. Zhang Li and I contributed equally in this paper.
- I performed all the materials synthesis and characterization except X-ray photoelectron spectroscopy and TEM, which were carried out with assistance of lab specialist, I also analyzed the data.
- Dr. Zhang Li helped draft the manuscript with the data I provided and analyzed.
- Dr. Chen Xiao Feng guided and assisted the setup of Kelvin Probe system.
- Assoc Prof Tse helped to vet the experiment design.
- Dr. Li, Dr. Tay, Dr .Lim and Mr Guo offered their expertise in further analyzing X-ray photoelectron spectroscopy and TEM data.
- Mr Leong was the project manager of the joint-industry PhD program from Gloabalfoundries who provided the scholarship.

Chapter 5 is also presented as **Q. Luo**, X. F. Chen, M. D. Han, O. K. Tan, M. S. Tse, “Influence of doping and surface loading CuO on photocatalytic properties of high energy ball-milled BiVO₄ nano-particles”, *International Conference of Young Researchers on Advanced Materials*, Singapore 2012.

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- Prof Tan provided the initial project direction.

- I performed all the materials synthesis and characterization except X-ray photoelectron spectroscopy and TEM, which were carried out with assistance of lab specialist, I also analyzed the data.
- Dr. Chen Xiao Feng guided and assisted the setup of Kelvin Probe.
- Dr. Han Mandi offered her expertise in the material characterization of BiVO₄ nanoparticles from her own thesis work
- Assoc Prof Tse helped to vet the experiment design.

Chapter 6 is presented at Q. Luo, X. F. Chen, M. D. Han, O. K. Tan, M. S. Tse, “RhB degradation and Photo-response performances of sol-gel BiVO₄ thin films”, *International Conference on Materials for Advanced Technologies (ICMAT)*, Singapore 2013 and Q. Luo, X. F. Chen, M. D. Han, O. K. Tan, M. S. Tse, “Preparations and Photo Response Studies of Photocatalytic BiVO₄ Thin Films”, *4th International Conference on Semiconductor Photochemistry (SP4)*, Prague 2013.

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- Assoc Prof Tse helped to vet the experiment design.

03-May-20

Date

Luo Qiong

Summary

Over the past few decades, semiconductor photocatalysts have received increasing amount of research interests for their environmental applications in various fields, such as water-splitting, water decontamination and air treatment. Titanium dioxide (TiO_2) is reported to be the most efficient photocatalyst driven by UV-light irradiation. However, its applications are restricted to the UV-light range, which makes up of less than 5% of the solar spectrum, as a result of its wide bandgap of 3.2 eV. Alternative metal oxides with smaller bandgap are studied to develop a visible-light driven photocatalyst. Among them, bismuth vanadate (BiVO_4) has become a promising candidate, as a result of its intrinsic narrow bandgap of 2.4 eV, which is suitable for visible light absorbance and proper band-edge position for water splitting. It can be synthesized by hydrothermal process, sonochemical method, co-precipitation and high temperature solid state reaction.

In this work, monoclinic scheelite BiVO_4 nano-particles were synthesized and modified for the purpose of improving photocatalytic efficiency. Furthermore BiVO_4 thin films with photocatalytic property were developed and studied for their photo-response activity. Besides using photoelectrochemical (PEC) stations to investigate the photo-activity of BiVO_4 nano-particles and thin film, a customized Kelvin probe coupled with multiple LED sources was developed to study the surface photovoltage (SPV) as a non-contact tool to understand the charge generation and separation that occurred at the semiconductor surfaces.

BiVO_4 nano-particles were synthesized by high energy ball mill process, which yielded a good throughput compared with wet-chemical approaches and produced fine nano-particles with relatively large surface areas. To improve the crystallinity, post annealing at 300°C to 600°C were followed. Nano-particles annealed at 400°C were found to exhibit the highest efficiency in photocatalytic performance. This can be explained by the trade-off between

crystallinity, which increased with annealing temperature and favored the photocatalytic reactions by reducing the defects and recombination sites, and surface area distribution reduction, which generated less number of active sites for photocatalytic reactions to occur.

In an attempt to further enhance the photocatalytic efficiency, p-type CuO was deposited onto BiVO₄ nano-particle surface to form p-n heterojunctions. This helped to bring down the recombination rate and was reflected in terms of the suppression of photoluminescence (PL) signal, the enhancement of photo-currents upon light illumination, as well as large and fast SPV response.

In terms of application on surface cleaning, thin film is more easily managed. Hence m-BiVO₄ thin films were fabricated using spin coating method. The deposited films were further annealed at 350° to 500°C to form monoclinic scheelite BiVO₄ following pyrolysis. The annealed thin film exhibited reasonable photo-degradation capability. The photocatalytic efficiency corresponded well with the SPV response. The best photo-efficiency came from BiVO₄ thin film annealed at 450°C. This was the result of the increase in good crystallinity, and the most efficient charge transportation arising from the enhancement in hole movement due to lone-pair distortion in local crystal structure, benefiting the photocatalytic reactions by reducing recombination sites and increasing charge separation, respectively.

Acknowledgement

First and foremost, I would like to express my deepest gratitude to my supervisor, Prof. Tan Ooi Kiang, for his valuable insight and continuous guidance for my thesis project.

Next I would like to express my special thanks to Dr Chen Xiaofeng, Dr Zhang Li and Dr Han Mandi for their detailed guidance and valuable assistance towards the completion of my thesis work.

Thanks to my teammates from sensors & actuators lab, Dr. Tan Pei Yun, Dr. Fang Xiaoqin, Dr. Chow Chee Lap, Dr. Leiw Ming Yian, Dr. Lim Chiew Keat and Dr. Chua Chin Sheng for their kind and useful support.

I would also like to thank lab manager Mr. Chua Tong Sun and Mr. Ng Yong Chiang at sensors & actuators lab for equipment training and safety housekeeping, as well as all technicians in microelectronics division for allowing the usage of lab apparatus after giving proper training.

Last but not the least; I'd like to thank my parents and my younger brother for always believing in me and encouraging me in every aspect of life.

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CHAPTER 1 Introduction

1.1 Motivations

In the past few decades, visible-light driven photocatalyst have drawn increasing attention in the field of environmental remedies for applications in water-splitting [1, 2], in-door air cleaning and organic pollutant degradation [3, 4].

After the first discovery of its water-splitting property by Fujishima and Honda [5], titanium dioxide (TiO_2) has emerged and occupied the major research interest in the field of photocatalyst because of the low cost, high thermal stability as well as its chemical and biological inactiveness. It is proven to be the most efficient photocatalyst under UV-light [3, 6-9]. However with a wide bandgap of 3.2 eV, it renders itself inefficient under visible light irradiation which makes up for more than 43% of the whole solar spectrum. Hence, a lot of research interests are devoted to extend its photo-response towards visible range by narrowing TiO_2 bandgap by doping transition metals such as chromium, iron and nickel [10-13] and non-metals such as nitrogen, sulfur and carbon[14-16], whereby the substitutional/interstitial doping introduces local energy bands to achieve a red shift in the light absorption spectrum. However, these modified TiO_2 systems suffer from poor thermal stability originated from the dopants introduced. They, on the other hand, also serve as recombination sites, thus lowering the charge separation efficiency. Alternative way of developing visible-light driven photocatalyst is to employ other metal oxides with inherently smaller bandgap that absorbs light in the visible range. Bismuth-based oxides emerge and stand out to be one of the promising candidature materials [6, 17-19].

In particular, monoclinic Bismuth Vanadium Oxide (m-BiVO_4), which has a bandgap value of 2.4 eV with n-type semiconductor behavior, has caught a lot of research attention. The

synthesis options are flexible: solid state reaction [20], wet chemical approaches via co-precipitation process [21], hydrothermal route [22, 23], chemical bath deposition [24], and sonochemical route [25, 26], flame spray pyrolysis [27], and metal organic decomposition [28]. Among all, the most popular synthesis method is “bottom up” hydrothermal method. It is able to produce m-BiVO₄ particles with nearly perfect crystalline structures and modify their surface morphologies in a controlled environment [29]. However the low throughput makes large scale-up applications not feasible.

BiVO₄ material itself also faces a big challenge in photocatalytic application due to its relatively low absorptive ability and difficulty in effectively separating electron-hole pairs. To mitigate the risk and boost photocatalytic efficiency, co-catalysts as in the case of TiO₂ are utilized to extend the visible light absorbance, and more importantly to prompt effective charge separation. Using noble metal is one of them. Attempts have been made on Au/BiVO₄ [30], Co/BiVO₄ [31], and Ag/BiVO₄ [32] to take advantage of low Fermi levels of these noble metals as compared to BiVO₄. In thermal equilibrium when Fermi levels of above-mentioned noble metals and BiVO₄ are aligned, electrons generated upon light excitation can migrate from the conduction band (CB) of BiVO₄ to the surface-loaded metal particles, leaving holes behind in the valance band (VB) at the semiconductor surfaces, hence achieving effectiveness in charge separation. Another type of co-catalyst is semiconductor oxides with suitable bandgap energy and structure, for example Co₃O₄/BiVO₄ [33], Bi₂O₃/BiVO₄ [34] and RGO(reduced grapheme oxide)/BiVO₄ [35, 36]. The formation of heterojunction and composite structure with n-type BiVO₄ is the major contributor to facilitate and accelerate charge separation that results in improved photocatalytic efficiency [33].

In the present work, the synthesis and characterization of m-BiVO₄ and its composites were studied and evaluated for the development of an efficient visible-light driven photocatalyst

system that can be easily scaled up with good absorptive properties as well as efficient charge separation. For practicality, thin film structure is a better choice than powder system in terms of the recyclability and surface applications, which was also be investigated in the present work.

1.2 Objectives and Scope

The objective of this thesis work was to develop a visible-light driven photocatalyst system based on BiVO_4 that can be easily scaled-up and with good absorptive properties as well as efficient charge separation. The synthesis approach of interest was mechanochemical high-energy ball milling process to generate BiVO_4 nano-particles with large yield and surface modifications with co-catalyst loading onto the BiVO_4 surfaces. Study was carried out to understand the photo responses of the BiVO_4 systems upon irradiations. Specifically,

- systematic work on the mechanochemical high-energy ball milling parameters, including milling speed and duration, was firstly carried out to synthesize m- BiVO_4 nano-particles, followed by continued wet milling in ethanol to reduce particle size. Lastly, post annealing in dry air was conducted to reduce and eliminate the distortions and defects introduced during the milling processes. The optimized milling parameters and annealing temperatures were derived.
- next, different amounts of copper oxides (CuO) were loaded onto BiVO_4 surfaces by wet milling the mixture of BiVO_4 powders and copper nitrate ($\text{Cu}(\text{NO}_3)_2$) solutions followed by the drying and annealing to decompose $\text{Cu}(\text{NO}_3)_2$ to CuO . The goal was to improve charge separation. The incorporation of CuO into BiVO_4 achieved this through the formation of p-n heterojunction to promote photocatalytic reactions; on the other hand, CuO powder particles loaded onto BiVO_4 surfaces could occupy

otherwise active sites and bring down total number of reaction sites. To achieve best result, an optimal amount of CuO loading needs to be found.

- In addition to BiVO₄ photocatalyst in powder form, thin film BiVO₄ was also synthesized by sol-gel spin coating process.
- BiVO₄-based photocatalysts in powder form and thin film were then further characterized using various tools to investigate their physical, chemical, optical and photocatalytic properties. The photo-responses were monitored by a customized Kelvin Probe-based surface photovoltage (SPV) measurement system. As SPV monitored the surface potential change upon irradiation as the result of charge transportation and separation, it complemented the result from the photoluminescence (PL) spectroscopy, which was primary due to band to band recombination. The distinctive difference was observed between pure BiVO₄ powders and CuO/BiVO₄ composites as explained by the electron-hole interactions between surface-loaded CuO and BiVO₄ at the interface. Furthermore, cyclic voltammograms and photocurrent studies of BiVO₄-based photocatalysts were included to complete the investigation of photo-activities in multiple BiVO₄-based systems.
- Finally, in close examination of the photocatalytic performance, correlations between the degree of photo-activities and photocatalytic efficiency was established for in-depth understanding of the photocatalytic activities in visible-light driven photocatalyst system, especially the enhancement made to improve the overall efficiency.

1.3 Major Contributions of the Thesis

The contribution of this thesis focuses on a new attempt for the synthesis and characterizations of BiVO₄-based photocatalytic nano-particles and thin films, which is summarized as follows:

1. BiVO₄ nano-particles were successfully obtained by high energy ball milling method in combination with post annealing process. The throughput of 30 grams per batch with a yield of ca. 90% is much higher than the output of the popular hydrothermal approach in the range of several grams. The particle size was less than 100 nm in average when annealing temperature did not exceed 400 °C, exhibiting much higher surface area (9.52-16.31 m²/g) than most reported work in literature (<3 m²/g) [37] . Despite the difficulty in controlling the surface morphology and crystal growth in ball milling process, BiVO₄ powders annealed at 400 °C showed excellent photocatalytic performance with reaction constant k of 0.107 h⁻¹, which was comparable to some of the reaction constants of m-BiVO₄ single crystals [38]. The post annealing treatment was found effective in improving the crystallinity of the powders as well as reducing and repairing crystal distortions and defects introduced during both ball mill and follow-up wet mill processes, which would otherwise serve as recombination centers, harm the electron-hole pair separation and are detrimental for photocatalytic reactions to occur. However, the thermal anneal also caused grain size to grow, reducing the surface area distribution which would hinder the photocatalytic reactions. As a result of the trade-off, pure BiVO₄ powders annealed at 400 °C showed the best photocatalytic performance.
2. The systematic study of the loading effect of p-type CuO onto BiVO₄ surface was conducted to enhance and optimize the photocatalytic efficiency of CuO/BiVO₄ composite system. CuO has a bandgap of 1.7 eV narrower than that of BiVO₄, facilitating the wide absorbance in the visible light range. Besides that, the formation of p-n heterojunction at the interface prompted charge separation with good suppression of carrier recombination. At thermal equilibrium, photo-generated electrons on the conduction band (CB) of CuO were prohibited and prevented to transfer to CB of BiVO₄ due to the existence of the energy barrier resulting from the discrepancy of energy

bandgap. Holes excited from BiVO₄ were prompted to migrate to the valence band (VB) of CuO. As a result, the transportation of photo-generated electron-hole pairs at the interface led to the effective charge separation on BiVO₄ semiconductor. Taking these two factors into consideration, the reaction constant of CuO/BiVO₄ composite structure almost tripled compared with pure BiVO₄.

3. BiVO₄-based photocatalysts were characterized and investigated using various tools, including X-ray diffraction (XRD) for crystallographic properties and Raman spectra for local structure studies; transmission electron microscopy (TEM) for advanced study of microstructure, crystal phase and elemental composition; field emission scanning electron microscopy (FESEM) for surface morphology, UV-Vis diffused reflectance spectrophotometer (DRS) for optical property and bandgap estimation; three-electrode photoelectrochemical measurement (PEC) for photocurrent studies. The values of specific surface area (SSA) of powder samples were analyzed using BET method. More importantly, X-ray photoelectron spectroscopy (XPS) was used for the chemical analysis. The binding energies of each element were found to originate from the typical BiVO₄ scheelite structure. For CuO/BiVO₄ composites, the existence of the doublet for Cu 2p orbits and the presence of satellite states confirmed that copper has been successfully incorporated and existed in the form of CuO.
4. A Kelvin probe-based SPV system was custom-built to study the surface potential change due to the irradiation. The KP probe was based on patented off-null detection technique by mounting a vibrating tip above the surface of the specimen, serving as the reference surface in capacitive mode with the sample surface. It incorporated a commercial UHV Kelvin probe unit (from KP Technology Ltd) with an optical monochromatic illumination system having the wavelength range between 340 nm and 700 nm through a quartz window. Alternative switchable high-power LED sources ranging from UV (365 nm) to

near infrared (850 nm) were added to study the enhanced SPV effect of the test samples. In principle, SPV arises from the transportation and separation of photo-generated electron hole pairs, which is crucial for photocatalytic reactions. It complements the Photoluminescence (PL) signals as PL is originated from band-to-band- recombination. Generally, a fast and large SPV response is desirable as it implies a good charge separation is achieved. A good correlation between SPV response and photocatalytic efficiency was established in this work and it agreed well with the photocurrent observation.

5. A bandgap model of BiVO_4 was proposed based on bandgap extraction from diffused reflectance. With reported bandgap information on CuO , the energy band diagram of p- $\text{CuO}/\text{n-BiVO}_4$ heterojunction was constructed to illustrate the electron-hole pair transportation and separation upon illumination to enhance the separation efficiency. The mechanism for enhanced photocatalytic performance in CuO/BiVO_4 composite structure was also proposed.
6. For more practical surface cleaning applications, photo-catalyst in thin film form is a better choice than particle form. Highly transparent and smooth (over 70% transmittance in UV-VIS range and surface roughness below 50 nm) BiVO_4 thin films were fabricated by a simple spin coat process. Their photo-activities were then systematically studied including SPV response by KP and photocurrent measurements using PEC study and eventually photo-degradation of Rhodamine B (RhB). With these combined characterizations, m- BiVO_4 thin film with 450°C post anneal treatment was found to possess the best photocatalytic efficiency with the most rapid SPV and the largest photocurrent upon irradiation. Nearly 75% of the initial dyes were removed within 12 hours, and being one of the only few reported work on direct photocatalytic reactions over BiVO_4 thin films.

1.4 Organization of the Thesis

The thesis contains 7 chapters, including Chapter 1 for introduction and major contributions.

Chapter 2 presents the literature review of topics pertaining to this research work. Firstly, it explains the origin of BiVO_4 as an effective visible-light driven photo-catalyst and techniques to optimize photo-catalytic performance. Next, it introduces what SPV phenomenon is and its significance in electron hole pair mediated chemical reaction followed by the illustration of Kelvin Probe system used to measure SPV.

Chapter 3 describes the experimental set-up used including the synthesis procedures for powder and thin film BiVO_4 , detail material characterization tools, in particular the customized Kelvin probe system. The photocatalytic test setup is also presented.

Chapter 4 explores the BiVO_4 powder system by studying the effect of annealing temperature on BiVO_4 . The thermal treatment helps to reduce and repair crystal damages caused by ball milling processes, which is beneficial for photocatalytic reactions. On the other hand, it introduces crystal growth, which causes the surface area to reduce. The balance of these two factors determines the optimal annealing temperature.

Chapter 5 investigates the introduction of CuO onto BiVO_4 surface in CuO/BiVO_4 composite. With the successful formation of p-n heterojunction, the improvement on charge separation and photocatalytic performance are discussed in details with proposed mechanisms.

Chapter 6 describes the synthesis of m- BiVO_4 thin film by spin coating method followed by detailed characterizations and photo-activity investigations.

Chapter 7 concludes the thesis work and provides recommendations for future work.

CHAPTER 2 Literature Review

2.1 Fundamental Principles of Semiconductor Photocatalysis

In semiconductor photochemistry, photocatalysis is a process to initiate or accelerate associated reduction and oxidation (redox) reactions in presence of semiconductors under light irradiation. It generally involves three steps as illustrated in Figure 2-1, including:

- (i) Electron – hole pair (EHP) generation excited upon absorbed photons with energy larger than semiconductor bandgap;
- (ii) Transportation and separation of carriers at semiconductor surface
- (iii) Participation of these active carriers in chemical reaction involving various pollutants through a series of intermediate species at semiconductor surface

Figure 2-1: Photocatalytic mechanism.

Unlike the conventional catalysis, both spontaneous and non-spontaneous reactions can be facilitated in the presence of photocatalyst. In spontaneous reaction, photo energy stored inside semiconductor from the incident photons would go through a series of electronic transfer and participate in surface reactions to convert into chemical energy in the end. The chemical energy alone will be sufficient to activate the redox reactions to promote photocatalytic reaction. In non-spontaneous reaction, although it is not able to overcome the

activation barrier by the same chemical energy alone, it can participate in reactions which produce intermediates and byproducts chemically active to initiate photocatalytic reaction. As shown in Figure 2-2, for many semiconductors, electrons from conduction-band (CB) are able to serve as reductants with a chemical potential of +0.5 to -1.5 V versus the normal hydrogen electrode (NHE) whereas holes from valence-band (VB) are strong oxidant with a chemical potential of +1.0 to +3.5 V versus NHE.

Figure 2-2: Band-edge positions of semiconductor photocatalysts relative to the energy levels of various redox couples in water [39].

The photocatalytic reactions were summarized by Legrini et al. in 1996 [40]. In the event of redox reaction, photo-generated electrons will migrate to semiconductor surface and react with electron acceptors such as adsorbed oxygen molecules (O_2) to reduce them and render them to be chemically active as in reactions (2-1) to (2-5) ; on the other hand, photo-generated holes will react with electron donors such as adsorbed substrate, water molecules (H_2O) and hydroxide (OH^-) dissociated from water molecules to oxidize them and make them oxidative as in reactions (2-6) to (2-7). The full mineralization of organic pollutants to

carbon dioxide and water are made possible with the existence of oxidative species. The mineralization of organic pollutants includes the process to degrade and oxidize the organic compounds to CO₂ and H₂O, accompanied by various intermediate species. A complete mineralization happens when all organic compounds are removed in the form of CO₂ and H₂O.

In the reduction path, electrons scavenged by O₂ give rise to the formation of super-oxide anions ($\bullet\text{O}_2^-$) as in reaction (2-1). Instead of direct participation in water reduction, the generated super-oxide anions ($\bullet\text{O}_2^-$) serve as intermediates to trigger second round of reactions, ending up in producing hydrogen peroxide radical ($\bullet\text{OOH}$) and hydrogen peroxide (H₂O₂) as in reaction (2-2) to (2-4), respectively.

In oxidation path, hole scavengers or various types of electron donors will be oxidized to form hydroxyl radical ($\bullet\text{OH}$) or directly oxidize the adsorbed semiconductor substrate. Compared to the latter, due to the large concentration of hydroxide (OH⁻) in aqueous solution, the formation of $\bullet\text{OH}$ radicals are more likely as in reaction (2-5) to (2-6).

The radicals ($\bullet\text{OH}$, $\bullet\text{OOH}$, H_2O_2) produced from above redox reactions at semiconductor surface, are capable for water splitting and full mineralization of organic pollutants. The pollutant source contains but is not limited to volatile organic compound (VOC) [41] and bacteria [42]. This has brought up immense research interest into semiconductor photocatalyst in exploring its potential in water splitting and water treatment application, air purification and quality control, antibacterial applications and self-cleaning surfaces.

2.2 Semiconductor Photocatalyst

2.2.1 Titanium-based Photocatalyst

Titanium dioxide (TiO_2) electrodes were first discovered by Fujishima and Honda in 1970s for their water splitting phenomenon [43]. Since then TiO_2 has been the major research subject in the field of semiconductor photocatalyst due to its potentials in solar energy conversion. In nature, TiO_2 exists in three forms: anatase, rutile and brookite [44]. Among them, anatase and rutile TiO_2 are commonly employed in photocatalytic applications. The transformation temperature between anatase and rutile phase are found to be dependent on starting phase and particle size as well as doping concentration and reaction environment. [44]. In reality, anatase shows greater potential in photo-oxidation and is more frequently applied in photocatalytic activity, while rutile is primarily used in pigment sector making use of its light scattering properties. Even though anatase TiO_2 is with a larger bandgap of 3.2 eV compared to 3.0 eV of rutile phase, it exhibits superior photocatalytic reactivity, largely contributed to the lower occurrence of charge recombination [45]. The band edge position difference between rutile and anatase makes the mixture of 2 phases potentially to be more photo-active than anatase alone. The lower conduction band of rutile phase promotes photo-excited electron migration from anatase to rutile, leaving holes behind to prevent charge

recombination occurrence. Degussa P25 is a benchmark photocatalyst consisted of 80% anatase and 20% rutile and BET surface area around 50 m²/g [46].

One apparent limitation of TiO₂ is its relatively large bandgap, which constrains their effectiveness in EHP generations for photocatalysis in UV light regime. However, UV light regime takes up less than 5% of solar spectrum, and hence limits TiO₂ for both outdoor and visible-light driven photocatalytic applications.

Figure 2-3: The solar spectrum[47].

There have been various bandgap engineering techniques applied to expand the photo-absorption of TiO₂ into visible light regime to improve the overall efficiency of photocatalytic reaction, including doping with transition metals, doping with non-metals, and oxygen vacancy creation inside TiO₂ bandgap.

Doping with transition metals

The doping with transition metals is one effective solution to introduce additional energy band within semiconductor bandgap [44, 48]. In theory, electrons from these local energy

bands can lead to the formation of free radicals that are responsible for redox reaction to take place at a longer wavelength excitation. On the other hand, these electrons excited at longer wavelength $>$ semiconductor bandgap threshold can easily recombine with charges at metal ion energy band positioned nearer to semiconductor conduction band edge. This is the main drawback for doping with transition metals.

Doping with non- metals

Besides transition metals, another doping option would be non-metals including Nitrogen [49-55], Carbon [56], Sulphur [57, 58], Phosphorus [59], or Fluorine [60] to narrow the bandgap to enable visible-light driven photo-activities.

Among them, yellow N-doped TiO_2 has been studied most extensively for its light absorption capability of up to 500 nm and photo-degradation ability of organic dye pollutant solution under visible light illumination. The existence of N doping is supported by two distinctive N1s peaks from X-ray Photoelectron Spectroscopy (XPS) at about 396 eV and 400 eV, assigned to substitution and interstitial nitrogen doping, respectively. Both doping behaviors are responsible for the visible-light driven photo-activity in conflicting ways [61]:

- 1) Substitution nitrogen species are responsible for bandgap narrowing of TiO_2 . They create states right above VB maxima to be able to hybrid with O 2p valence states to effectively bring down the bandgap to improve visible light absorption.
- 2) Interstitial nitrogen species are the potential culprit for charge recombination. They create deep energy states within the bandgap to serve as recombination centers and hinder the photo-activities, in the form of NO unit as molecular antibonding states when coupled with lattice oxygen atom.

Oxygen vacancies inside TiO₂ bandgap

Oxygen vacancies and Ti³⁺ present in the lattice are desirable as they serve as electron scavengers as a means to reduce recombination [62, 63]. As early as 1959, oxygen vacancies inside TiO₂ were studied and found they lied between 0.75-1.18 eV below CB of reduced anatase TiO₂[63] [66]. This effectively brought down TiO₂ bandgap to as low as 2.0 eV, corresponding to light absorption under 615 nm to allow visible light absorption of up to 615 nm, as demonstrated in the TiO₂ band diagram in Figure 2-4 below.

Other than in its reduced form, TiO₂ prepared by magnetron sputtering [64] and with surface modifications including plasma treatment [65, 66], hydrogenation [67] and vacuum activation [68] were able to create oxygen vacancies and Ti³⁺ states within bandgap.

Figure 2-4: Proposed band diagram of anatase TiO₂ with oxygen vacancy states below CB [66].

2.2.2 BiVO₄ as visible –light driven photocatalyst

With both pros and cons of TiO₂ – based materials discussed in section 2.2.1, the research interest has been shifted to explore the potential of other narrow bandgap semiconductors as

visible-light driven photocatalyst, for example cadmium sulfide (CdS) and cadmium selenide (CdSe). Table 2-1 summarizes the bandgap of various semiconductor photocatalyst. The greatest challenge of this type of material is photo-corrosion when the chemical stability of the catalysts themselves becomes a problem during practical application [69]. Among them, one of the promising semiconductor photocatalyst candidate is bismuth vanadate (BiVO_4 , bandgap of 2.4 eV) [1]. It has received growing research interest due to its stability and pH neutral in water, which is essential for environmental applications.

Table 2-1: Bandgaps of semiconductor photocatalyst candidates [70]

Semiconductor	Bandgap (eV)	Absorption wavelength maximum (nm)
TiO_2 (anatase)	3.2	388
ZnO	3.2	388
TiO_2 (rutile)	3.0	413
WO_3	2.8	443
CdS	2.4	516
BiVO_4 (monoclinic scheelite)	2.4	516
Fe_2O_3	2.3	539

In nature, BiVO_4 exists in three crystal forms: monoclinic scheelite structure (m- BiVO_4), tetragonal scheelite structure (st- BiVO_4) and tetragonal zircon structure (zt- BiVO_4). The phase transformation temperature is illustrated in Figure 2-5 [71]. What is even more important is that, m- BiVO_4 is discovered to show best potential as visible light-driven

photocatalyst candidates, as a result of its unique lone-pair electrons from asymmetric crystal structure.

Figure 2-5 BiVO_4 in (a) monoclinic scheelite, (b) tetragonal scheelite, (c) tetragonal zircon and (d) phase transition among them according to different heat treatment [71].

In terms of lattice constant a, b and c, st- BiVO_4 is quite similar with m- BiVO_4 as shown in Table 2-2, however it does not show potential in photocatalysis. The key difference lies in the degree of symmetry in crystal structure.

Table 2-2: BiVO₄ lattice comparison

Crystal structure	Lattice constant a (Å)	Lattice constant b (Å)	Lattice constant c(Å)	$\beta(^{\circ})$
m-BiVO ₄	5.1966	11.7044	5.0935	90.383
st- BiVO ₄	5.1509	11.730	5.1509	90

Unlike m-BiVO₄, both st-BiVO₄ and zt-BiVO₄ have highly balanced symmetry. In st-BiVO₄, eight identical VO₄³⁻ tetrahedrons surround bismuth cation (Bi³⁺) in well balanced symmetry ($a=c$, $\beta=90^{\circ}$). Within each VO₄³⁻ tetrahedrons, there is only one type of V–O bond (V–O = 1.72 Å). Under this symmetric lattice configuration, no lone-pair electron distortion around Bi³⁺ can be found.

In m- BiVO₄ however, there are two types of V–O bond with different bond length: 1.69 Å in V–O^I bond and 1.77 Å in 2nd type V–O^{II} bond. It will show up as two distinctive Raman peak at different wave number in Raman spectrum, which makes Raman spectrum a very useful instrument to study the lone-pair distortion in local structure. Bi³⁺ surrounded by two types of VO₄³⁻ tetrahedrons are no longer in balanced symmetry and lone-pair distortion starts to build up around Bi³⁺. This leads to a distinct electronic structure for m-BiVO₄. As a result , the valence band of m-BiVO₄ is made up of hybridized Bi 6s and O 2p orbital, while the conduction band formed by typical V 3d orbital as in other d⁰ oxide as shown in Figure 2-6 [72].

Figure 2-6: Proposed band diagram of tetragonal and monoclinic scheelite BiVO_4 by Kudo et al [72].

Like other oxide catalyst, BiVO_4 itself is not capable of H_2 evolution due to its low conduction band vs. NHE. But it is noteworthy that the hybrid valence band is of great potential for water oxidation accompanied by 4-electron oxidation. The overlapping of Bi 6s and O 2p orbital facilitate hole migration upon photo-excitation, which is crucial for charge separation and for photo-reaction to occur, mainly the photo-oxidation process. The accelerated hole mobility is due to the reduction of effective hole mass, originated from the hybrid valence band. By the means of Drude model, carrier mobility (μ) can be defined to be inversely proportional to their effective mass by $\mu = q\tau / m^*$, whereby m^* = effective carrier mass and τ = relaxation time between elastic collisions by carrier scattering [73]. A lighter hole in effective mass leads to a higher mobility.

Ding et.al compared the relative effective mass in BMVO_4 ($M=\text{V, Nb and Ta}$) based on density functional theory (DFT) calculation to conclude superior carrier mobility of BiVO_4 in [010] direction [74] and the discovery was consistent with Zhao's [75] and Walsh's group [76]. Though there are discrepancy in the absolute value of effective hole mass m_h^* with respective to the mass of free electron m_e in BiVO_4 ($m_h^* = 0.7 m_e$ [75] and $m_h^* = 0.3 m_e$

[76]), it is common agreement that it is much smaller than that of other metal oxide, $m_h^* = 16 m_e$ in In_2O_3 [73]

Next comes the preparation methods of BiVO_4 . Studies via wet-chemical approach have demonstrated that the photocatalytic performance of BiVO_4 nano-crystals is largely dominated by particle size, surface morphology and facets. Pros and Cons of listed process methods are summarized in Table 2-3.

Due to low charge separation efficiency in BiVO_4 , different groups of researchers have been working on methods to improve the charge separation efficiency in BiVO_4 based semiconductor system. Details are discussed in the following section 2.2.3.

Table 2-3: Comparisons of BiVO_4 synthesis method

Methods	Advantages	Disadvantages
Wet chemical approach including: aqueous approach [71] hydrothermal treatment [77] sonochemical route [78]	Good control in crystal size, facet and morphology;	Low throughput
High temperature solid-state reaction [79]	High throughput	Large particle size in μm range; Lower surface area

2.2.3 Methods to Enhance Photo-conversion Efficiency on BiVO_4 -based Semiconductor

Two main hurdles contributed to the relative low efficiency in solar energy conversion by pure m- BiVO_4 are: fast charge recombination [80] and bandgap limitation of absorption edge at 516 nm [81].

Methods to promote charge separation of photo-generated electrons and holes in BiVO_4 in reported works contain morphology control or reduction in physical size of pure m- BiVO_4 to increase surface area [82-84] and the construction of heterojunction with metal or non-metal to form BiVO_4 composites [30, 85-88].

Nano-sized m- BiVO_4 particles have been reportedly obtained via hydrothermal treatment [77], sonochemical route [78], microwave-assisted synthesis [84] and high energy ball milling process [89]. The last mechanochemical synthesis method has yielded good throughput to produce fine BiVO_4 nano-particles with large surface area. It is a relatively simple preparation procedure, and is being employed and optimized in this work. Size reduction is also achieved by morphology control during synthesis. m- BiVO_4 with distinctive morphologies are obtained in 1-Dimensional fibers [90], 2-Dimensional sheets [91] and plates [92], 3-Dimensional microspheres [93] and tubes [94]. These nano-structures are useful in increasing the specific surface area, and enhancing charge separation by extending the optical path [95].

Up to now, different groups of views exist regarding the charge separation mechanisms in photo-generated electron-hole pairs on semiconductor photocatalyst formed by heterojunction, as summarized below:

- (i) In thermal equilibrium and flat band condition, the bandgap difference between n-type and p-type semiconductor results in the generation of built-in electric field pointed towards p-type semiconductor. Under the force of electric field, electrons are drawn to n-type semiconductor surface and holes moving in opposite direction. As a result, charge separation is achieved through the built-in electric field [96, 97].

- (ii) Another research group proposed the dominating drive-in force in charge separation is the band edge position difference in semiconductor interface, which allows electrons to move to a lower conduction band and holes to move to a higher valence band to reach thermal equilibrium state [98-100].
- (iii) A combination of built-in electric field and band edge position was proposed by Long's group. Three types of p-n heterojunction are discussed as shown in Figure 2-7 [100].
 - (a) The band edge position is aligned such that there is no energy barrier present at semiconductor interface. Under the force of built-in electric field at interface, charge separation is achieved with photo-generated electrons from p-type semiconductor drawn to the conduction band of n-type semiconductor, and vice versa for photo-generated holes.
 - (b) The band edge position is aligned such that there is energy barrier built-up in conduction band of semiconductor interface. It prevents photo-generated electrons in conduction band of n-type semiconductor from migrating to that of p-type semiconductor, but does not hinder holes generated in n-type semiconductor to move out to a higher valence band in p-type semiconductor. That is to say, the minority carriers, which determine the rate of charge recombination in n-type semiconductor, are moved out. This way, charge separation in n-type semiconductor is achieved.
 - (c) The band edge position is aligned such that there is energy barrier in both conduction and valence band. This kind of alignment does not promote any type of charge transportation and should be avoided.

Figure 2-7: Three Possible charge separation scenarios for semiconductor heterojunction upon light excitation [100].

Although it is hard to get everyone align on the same charge separation mechanisms, several guidelines and criteria are well recognized and referenced in the development of semiconductor composite system.

- (i) Both semiconductors are chemically stable and free from photo-corrosion for environmental reasons.
- (ii) At least one of the semiconductor's bandgap is small enough to be able to absorb visible light.
- (iii) The band edge position should be able to align in either type (a) or (b) configuration to promote at least one way charge transportation, if not two ways.
- (iv) Charge generation should be fast and efficient.

After examining all the above criteria, CuO with bandgap of 1.7 eV is a promising p-type co-catalyst to form heterojunction with BiVO₄. With the incorporation of CuO, there is a red-shift in light absorption edge and it follows type (b) mechanism for charge transportation and

separation, as shown in Figure 2-8 [101]. When p-type CuO and n-type BiVO₄ are in contact with each other, the energy band would bend at the interface to reach Fermi level equilibrium. The holes from BiVO₄ are able to migrate to the valence band of CuO. In light of the existence of up-hill energy barrier at the heterojunction, electrons from CuO are forbidden to migrate to the conduction band of BiVO₄. Hence charge separation is achieved at BiVO₄ surface to further prevent charge recombination. Although there have been few reported work on CuO/m-BiVO₄ composite synthesis in literature [102-105], the particles size obtained is usually large (> 100 nm) and lack of direct experimental verification on charge separation enhancement. This provides relevant insight to CuO/BiVO₄ composite powder in this thesis work.

Figure 2-8: Proposed band diagram of CuO/BiVO₄ heterojunction [101].

Another way to fabricate heterojunction structure is by noble metal coupling on BiVO₄ surface. M-BiVO₄ (M=Au, Pt, Ag) composite enhances the photocatalytic efficiency in the following two aspects, take gold for example: [30, 86, 106]

- (i) Due to its lower Fermi level (Au: 0.5 V and BiVO₄: 0 V vs. NHE) as shown in Figure 2-9, Au nano-particles can serve as electron sinks to attract photo-generated electrons from conduction band of BiVO₄ upon light excitation. As a result, these electrons are able to migrate and accumulate on Au surface, which is

at lower energy state until new interfacial charge equilibrium is obtained. This in the end leads to charge separation on BiVO_4 surface. Such charge transfer process is similar to type (b) mechanism discussed in charge separation of BiVO_4 –based semiconductor heterojunction.

- (ii) There is additional surface plasmon resonance (SPR) excitation at Au nanoparticles to promote charge separation.

Figure 2-9: Enhanced charge separation in Au- BiVO_4 composite: (i) the transpiration photo-generated electrons from BiVO_4 CB to Au particles under visible light irradiation and (ii) surface plasmon resonance (SPR) absorption in the presence of sacrificial agent $\text{S}_2\text{O}_8^{2-}$ [30].

2.3 Kelvin Probe Based Surface Photovoltage Technology

In both heterojunction structure (p-type semiconductor or noble metal – BiVO_4), charge separation is key to enhance photo-activity. In light of this, surface photovoltage (SPV) is an important indicator of charge separation efficiency and can be directly used to explain any enhancement in photocatalytic performance.

2.3.1 Surface Photovoltage (SPV) Phenomenon

The SPV is defined as the change in surface potential of a semiconductor sample induced under light excitation. At the surface of semiconductor samples, the periodic structure termination can lead to the formation surface of localized electronic states within the semiconductor bandgap and/or the accumulation of a double layer of charges. The appearance of surface-localized states induces charge transfer between bulk and semiconductor surface, which results in a non-neutral region in the semiconductor bulk, commonly known as surface space charge region. Upon illumination, incident photons provide energy to generate EHP via band-to-band transitions and free trapped carriers by trap-band transitions. Thus a significant amount of charges can be transferred and/or redistributed within the surface or the bulk. The charge redistribution of generated carriers would lead to SPV formation, and the detailed analysis of the SPV depends strongly on the dominant carrier excitation mechanism, i.e. super-bandgap (incident photon energy > semiconductor bandgap) or sub-bandgap (incident photon energy < semiconductor bandgap).

Figure 2-10 shows an example of the change in band bending before and after light illumination in a p-type semiconductor in super –bandgap [107]. In dark condition, holes are trapped in the surface states, leaving behind negative charges in the vicinity of the surface within the semiconductor to form a space charge region (SCR) causing energy band to bend downwards under the force of built-in electric field. The degree of band bending at thermal equilibrium in the dark is noted as V_{bb}^{eq} .

Under light illumination, when the photon energy is sufficient for electron hole pair excitation, the positive charge built up in surface states previously under dark condition will screen further hole movement towards the surface and attract electrons towards it. The net result of this will cause SCR to be less electrically non-neutral, and decrease the band

bending at the surface to V_{bb} . Change in band bending before and after light illumination ($V_{bb}^{eq} - V_{bb}$) is defined as surface photovoltage as illustrated in Figure 2-10.

Figure 2-10: Super band-gap SPV.

Another dominant SPV mechanism is for sub band-gap illumination, which means the incident photon energy is below bandgap value.

Figure 2-11 (a) and (b) shows super band-gap SPV due to carrier separation under electrical field and preferential trapping of electrons (i) or holes (ii) within semiconductor bandgap.

Figure 2-11 (c) and (d) shows sub band-gap SPV due to the excitation of trapped electrons (i) or holes (ii) and Franz- Keldysh absorption as a result of overlap of electron wave (ψ_e) and whole wave (ψ_h).

As stated above, the charge movement is crucial for SPV. The significance of SPV is mostly due to the charges trapped at surface states and the induced electric field at SCR, which have a major influence on the local chemical reactivity on semiconductor surfaces. Variations in work function as a result of the local band bending can affect charge transfer between the surface and absorbents [108], which determines the reaction rate.

Figure 2-11: Illustration of sub-bandgap SPV, band bending after photo excitation is dotted [99].

2.3.2 The Evolution of SPV Characterization

SPV method is a known contactless technique for semiconductor characterization [107]. The studies of surface photovoltage started in the late 1940s as pioneered by Brattain [109] to measure the change in contact potential of silicon upon illumination. Besides the Kelvin probe based system to measure contact potential difference directly by a null-method, there was another approach with “artificial” MIS structure proposed by Morrison [110]. Metal insulator structure was obtained by leaving air/vacuum gap in between a static platinum grid and sample as insulator. Due to their different physical principles, Kelvin probe via vibration capacitor is more suitable for phenomena with large time constants whereas MIS technique via light modulation is for fast relaxation phenomena. Thus Kelvin probe based SPV measurement system is the choice of technique for this thesis work.

Using SPV method, Johnson [111] and Goodman [112] demonstrated the measurement of minority carrier lifetimes and the mathematical modeling of the minority carrier diffusion length, respectively. In the early 1970s, surface photovoltage spectroscopy (SPS) as the next major breakthrough [113] was applied to practically all important semiconductor materials like Group IV, III-V, and II-VI semiconductors [107]. It could be used to extract important information about semiconductor properties such as bandgap energy and its defect states. With the emerging of atomic force microscopes (AFM) and scanning tunneling microscopy (STM) technologies, the SPV mapping technology was developed in the early 1990s to provide the great improved lateral resolution [114, 115]. In the last ten years, the recent SPV research work is starting to move from the traditional semiconductors to nanostructured metal oxide semiconductors for solar cells [116, 117] and photocatalytic oxidization [118] applications. Figure 2-12 provides SPV spectra comparison for different TiO_2 nanostructures: TiO_2 –CNT heterojunction and TiO_2 nanotubes using Kelvin Probe [119] as the direct experimental evidence to demonstrate higher photo-response capability of TiO_2 –

CNT heterojunction. Furthermore, the Kelvin probe is reported to be developed as an inline, contactless tool to monitor the doped layer quality in a roll-to-roll PECVD production line for thin film silicon solar cells [120].

The challenge is that the behavior of these nanostructured metal oxide semiconductors is difficult to predict like the traditional semiconductors and more related to their fabrication process, stoichiometric composition and microstructure. Simultaneously, it has considerably driven the development of data analysis and the upgrade of experimental tools.

Figure 2-12: (1) SPV spectra comparisons of TiO₂–CNT heterojunction and TiO₂ nanotube; (2) Electron transportation paths in TiO₂ nanotube (a) and TiO₂–CNT heterojunction (b) [95].

2.3.3 Kelvin Probe Operation Principle

For the photocatalytic reactions to occur, electron-hole pairs must be effectively generated and separated to participate in the reduction and oxidation processes, respectively [121]. The surface potential will change under light illumination as a result of electron and hole movements. This potential change is defined as surface photo-voltage (SPV). Kelvin probe (KP) based SPV technique is developed to show insight into the charge generation, transportation and separation process. It provides a non-contact and non-destructive way of

measuring the surface work function of semiconductors and surface potential change upon irradiation due to charge transportation. In general, a large and fast SPV signal indicates that a good charge separation has been achieved.

The Kelvin probe method was first postulated by the renowned Scottish scientist Lord Kelvin in 1898. The principle behind was based on Fermi-level equilibrium model shown in Figure 2-13.

Figure 2-13: Energy band diagram of two materials before contact, after contact, and with external bias voltage applied V_b . ϵ_1 , ϵ_2 , and, ϕ_1 , ϕ_2 refer to the Fermi levels and work functions of 1 and 2, respectively [122].

If an external electric connection is made between these two electrodes, the inequality in work function will cause a potential gradient (termed as contact potential difference V_{CPD}) between the two electrodes to reach electrostatic equilibrium. The two electrodes will become oppositely charged. The external voltage (V_b), which is used to offset V_{CPD} , is supplied to the system with tip electrode vibrating above sample electrode. If $V_b = -V_{CPD}$, the potential gradient will disappear and a null current is detected in external circuit. As a result, the work-function difference or the surface potential difference with reference to the vibrating tip can be determined. Since the work function of the vibrating tip is kept constant, any change in contact potential difference is due to change of surface conditions in the sample of interest. Surface treatment, surface roughness, surface charge and contamination as well chemical

composition all play their parts in inducing measurable changes in work functions. Therefore, Kelvin probe based experiment could be developed into a highly sensitive tool for analyzing the surface properties such as areas of adsorption, surface contamination and chemistry, surface photovoltage (SPV) and so on.

2.4 Concluding Remarks

Recently nanostructured monoclinic BiVO_4 has shown promising potential as alternative visible-light driven photocatalyst to TiO_2 for its excellent photocatalytic activities for water splitting applications and removal of pollutants for environmental applications. Photocatalytic reaction is a surface chemical reaction that requires large and sufficient surface area to provide active sites for the separated electrons and holes to participate in the associated redox reactions. This is accomplished largely through the control of facet and crystal morphology in wet chemical synthesis method. Alternatively, powders with high surface area can be produced by high energy ball milling approach. To improve photocatalytic efficiency, holes have to be effectively separated from photo-generated electrons so that they can participate in the oxidation reaction individually instead of being lost in recombination. To further enhance charge separation, BiVO_4 composite structure with either p-type semiconductor or noble metal is designed and fabricated. To quantitatively compare charge separation efficiency, surface photovoltage is measured in Kelvin probe system to provide direct evidence of charge separation effectiveness.

CHAPTER 3 Experimental Setup

3.1 Sample Preparation

BiVO_4 powders were produced via mechanochemical ball milling process starting from commercially available Bi_2O_3 (99.9%, Sinopharm) and V_2O_5 (99.8%, Alfa Aesar), as shown in flow chart Figure 3-1.

The ball milling process first took place inside a tungsten carbide jar (250-ml) with the assistance of 10 tungsten carbide balls (20-mm in diameter) on a Retsch PM100 planetary high energy ball milling platform. It lasted up to 8 hours at room temperature with milling speed of 200 rpm. For every 25-minute intervals, it would pause for 5 minutes before resuming the milling process to prevent over-heat of the platform. A 2nd round of wet milling was conducted after collecting the powders from 1st round of milling and mixing them with YSZ (Yttria-Stabilized Zirconia) balls (1-mm in diameter) and ethanol inside an YSZ bowl. The ratio among powder: YSZ balls: ethanol = 1:20:0.5 in weight. The 2nd round of milling lasted for 8 hours with milling speed of 550 rpm and intermittent pause for every 10 minutes. The final products as-milled were collected by sieving through a 325# sieve.

The post-milling heat treatment was conducted in dry air in Lindberg quartz furnace for 1 hour in a temperature range of 300 to 600 °C to repair and reduce the defects inherited from the milling process.

Before finalizing this route, additional anneal at 400°C was inserted prior to wet milling in attempt to further enhance crystallinity. It was dropped due to less efficient photo-degradation as compared to the existing route. It showcased the Rhodamine-B dye degradation in a more completed picture as discussed in section 4.3.

Figure 3-2 showed the preparation route for CuO/BiVO₄ composite powders. BiVO₄ powders as obtained from Figure 3-1 were first mixed in 1M Cu (NO₃)₂ solutions. The mixture was then exposed to 3 hours milling in ethanol under a speed of 100 rpm. CuO was loaded onto BiVO₄ surface by 1-hour heat treatment of the dried-up mixture to decompose Cu (NO₃)₂ to CuO at 300°C. Composites with 2%, 5% and 10% CuO in atomic weight were prepared.

Figure 3-3 shows the fabrication of BiVO₄ thin film by spin coating and calcination of Bismuth and Vanadium containing sol-gel. Bismuth source came from Bi(NO₃)₃ dissolved in HNO₃ solution (0.4M Bi(NO₃)₃), while Vanadium came from NH₄VO₃ dissolved in HNO₃ solution (0.2M NH₄VO₃). Citric acid was added with a molar ratio of 1:2 to metal source to avoid the particle agglomeration due to its chelating characteristic. pH of citric solution was neutralized with the addition of NH₃·4H₂O before mixing. 5 mL of mixed solution was extracted and added with 0.1 g of Polyvinylpyrrolidone (PVP) to form sol-gel spin coating. The mixed solution was coated to clean FTO at a speed of 2000 rpm for 30 seconds. The coated samples were kept at 150°C for 10 minutes in ambient to evaporate the remaining solvent and 300°C for 10 minutes for pyrolysis. After that, the samples were annealed in Lindberg quartz furnace from 350 to 500°C for 1 hour to form m-BiVO₄ thin film.

Figure 3-1: Powder synthesis of BiVO_4 and treatment on dry-milled BiVO_4 .

Figure 3-2: Powder synthesis of CuO/BiVO_4 composite.

Figure 3-3: Sol-gel preparation and decomposition of Citric acid and chelating compounds.

3.2 Material Characterization

3.2.1 X-ray diffraction for Crystallography Study

The X-ray diffraction (XRD) patterns of BiVO_4 powders and thin films were collected on Shimadzu 6000 X-ray diffractometer with a step scan of $2^\circ/\text{min}$ under $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) over of $5^\circ \sim 75^\circ$ range.

Bragg's law was applied by XRD technique to determine the diffraction angle where a peak signal is detected. The basic principle behind Bragg's law is demonstrated in Figure 3-4.

Figure 3-4: Bragg's law: X-ray diffraction from a crystal plane.

For crystalline material, the incident X-ray beams penetrating the crystal structure will interfere with each other, constructively or destructively. For constructive superposition to occur, the path difference between beam 1 & 2 must satisfy the following condition:

$$2d \times \sin \theta = m\lambda, \text{ where } m = 1, 2, 3 \dots \quad (3-1)$$

Based on equation (3-1), it's obvious that for a certain wavelength λ and plane spacing d strong diffraction will only be detected at specific angles, which characterize the underlying crystal orientation.

The grain size is further calculated by Scherrer formula:

$$\text{Size} = K\lambda / \beta \cos \theta, \quad (3-2)$$

where K is Scherrer constant, usually 0.9, β the full width at half maximum (FWHM) located at θ peaks.

Each diffraction peak is recorded and referenced against JCPDS card (Joint Committee on Powder Diffraction Standards) to find out the underlying crystal orientation. The crystallographic structure of the material is deduced from the peak positions and their

intensities from the diffraction profile. In addition, the area beneath the peaks is an important indicator of the grain size inside the material.

3.2.2 Raman Spectrum for Localized Crystal Structure Investigation

The local crystal structures were investigated by Raman spectrometer (Witec Alpha 300R Plus Confocal Raman Microscope) using green laser ($\lambda=532$ nm) for excitation.

Raman spectrum is based on the light interaction with the chemical bond vibration within the crystal material. A small amount of the incident laser beam with wavelength (λ_0) are scattered away with a larger wavelength (λ). Raman shift in cm^{-1} $\Delta = (1/\lambda_0 - 1/\lambda)$ is then recorded at different peak position with different intensities. Specific chemical bond vibration manifests in Raman spectrum as a distinctive Raman peak. Thus Raman spectroscopy is able to provide insight into the localized crystal structure.

Figure 3-5: A confocal Raman microscopy using laser beam excitation and an air cooling charge coupled device (CCD) detector [123].

3.2.3 Electron Microscope for Surface Morphology Study

The surface morphologies of samples were examined by field emission scanning electron microscopy (FE-SEM, Jeol JSM-6340F). The secondary and backscattered electrons used for imaging originate from sub-surface depth of a few Å; hence facts about surface morphologies can be deducted.

High-resolution transmission electron microscopy (HRTEM) was further used to study morphologies at the atomic level. Samples were prepared by dispersing BiVO₄ powders into carbon/nickel grids after 15 minutes sonication in ethanol and drying them up. Images were captured on HRTEM (JEM-2100F, JEOL) at 200 kV.

3.2.4 Specific Surface Area by Brunauer–Emmett–Teller (BET) Theory

The specific surface areas (SSA) of BiVO₄ powders were measured on adsorption analyzer (ASAP 2020, Micromeritics) by common BET method. For each sample, there was 12 hours degas at 180 °C.

BET method estimates SSA by calculating the physical adsorption and desorption of gas molecules (Nitrogen). The volume of gas adsorbed on the powder surface is measured and entered in to BET plot to determine volume of gas adsorbed (V_m) at standard temperature of 273.15 K and pressure of 1.013×10^5 Pa to create a monolayer on surface to deduce the specific surface area.

$$\text{The total surface } S_{total} = Ns(V_m/V) \quad (3-3)$$

$$\text{BET specific surface area (m}^2\text{/g) } S_{BET} = S_{total}/a \quad (3-4)$$

where N = Avogadro's number, s = the adsorbate gas's adsorption cross section, V_m = volume of gas adsorbed at standard temperature and pressure (STP) to create monolayer on surface, V = molar volume of adsorbed gas, a = mass of the powder sample [124] .

3.2.5 UV-Vis Diffuse Reflectance for Optical Study

The absorbance spectrum of BiVO_4 powders and thin films in the range of 350 to 800 nm were obtained after Kubelka–Munk transformation of the measured reflectance from UV-Vis spectrometer (Shimadzu UV-2450) with referenced to BaSO_4 .

The absorption edge is useful for bandgap estimation. The bandgap of BiVO_4 (E_g) can be directly extrapolated from $(\alpha h\nu)^2$ versus photon energy plot (Tauc plot) based on the equation:

$$\alpha h\nu \propto (h\nu - E_g)^{1/2} \quad (3-5)$$

where α , h and ν are the absorption coefficient, Planck's constant and the incident light frequency, respectively.

3.2.6 X-ray Photoelectron Spectroscopy (XPS) for Surface Chemical Study

The XPS spectra was recorded with Thermo fisher Scientific XPS, using Al $K\alpha$ monochromatic X-ray source (1486.6 eV). The binding energies were corrected by the C1s line at 285.0 eV from adventitious carbon. The survey spectrum up to 2 KeV in 1 eV step was recorded for each sample, followed by high resolution spectra to zoom in for each binding energy peak in 1 eV step. To prepare powder sample for XPS scan, compact powder pellet of 1mm thick and 6 mm in diameter was pressed and vacuumed in XPS chamber.

XPS is a very powerful characterization instrument to study the surface chemistry by determining the binding energy (BE) of each element present on sample surface based on

photoelectron ejection from surface by X-Ray bombardment. It is surface sensitive in the range of 1 to 10 nm. By measuring the kinetic energy of emitted photoelectron (E_k), BE of electrons can be obtained. BE energy peaks scanned over a range of energy in eV can be identified and indexed against standard BE of known element to deduce the elements present, their atomic ratio and oxidation states as well as depth profile for composition. This becomes very helpful on understanding how CuO is incorporated into BiVO₄ by identifying the oxidation states of Cu and its atomic concentration at surface as detailed in Chapter 5.

3.2.7 Photoluminescence (PL) Spectroscopy for Charge Recombination Study

PL spectra were collected on Shimadzu RF-5301 spectroscopy with excitation wavelength at 340 nm. PL spectroscopy has been established as a useful instrument to study the charge separation efficiency in semiconductors. In the case of BiVO₄, it is more often used when BiVO₄ is modified to couple with metals [125, 126] or semiconductors [87, 127, 128] to form a composite structure in order to study the effect of surface modification on electron-hole pair separation. The same methodology applies in this thesis work.

The underlying principles were summarized by Baer et.al [129] in their book. Upon photon absorption, electrons are excited from semiconductor valence band to conduction band, leaving holes behind. The excited electrons would quickly relax radiatively by photon emission when recombined with holes from valence band or non- radioactively by loss of the extra energy to traps and defect states within bandgap or to another electron. PL spectroscopy thus picks up the signal from the emitted photon due to radiative recombination. Its intensity increases as recombination increases, which help quantify the electron-hole recombination. In nonradiative recombination, the excess energy instead of being emitted as luminescence, is dissipated in other forms: (i) heat (ii) creation of lattice defects and (iii) photochemical modification of the excited semiconductor [130].

3.2.8 Thermal Analysis

In this work, both differential thermal analysis (DTA) / thermogravimetric analysis TGA analysis were conducted on B-V sol-gel mixture using Shimadzu DTG-60H under air ambient from 30°C to 600°C. The ramp up and ramp down rate was the same at 10°C/min. To prepare the sample, 5 ml of B-V sol-gel was dried at 80°C and placed in an alumina crucible for testing.

Thermogravimetric analysis (TG) is known to detect the mass change in studied material upon heating in a controlled environment, due to composition change as a result of dehydration, decomposition, desorption, and oxidation processes.

A more widely used method for thermal analysis is differential thermal analysis (DTA). It compares the sample temperature with an inert reference material (Al_2O_3) in a programmed temperature change environment. Whenever there is thermal event, for example, melting and decomposition, a temperature delta would occur between the studied sample and reference material. A minimum will emerge in the DTA graph when an endothermic event occurs to slow down the sample temperature ramp up rate as compared to the reference. Similarly, a maximum will appear in the presence of exothermal reactions within the sample.

3.3 Custom-built Kelvin Probe-Based Surface Photovoltage System

Surface photovoltage (SPV) response is reflected from the change in contact potential difference (ΔCPD) of the sample with and without light irradiation. CPD is caused by work function difference between sample electrode and reference electrode.

$$e \cdot \text{CPD} = \varphi_{\text{TIP}} - \varphi_{\text{S}} \quad (3-6)$$

where φ_{S} = work function of sample electrode, and φ_{TIP} = work function of Kelvin probe calibrated against Au electrode and remains constant with and without light irradiation.

SPV response due to irradiation can be extracted as

$$e \cdot SPV = e \cdot \Delta\phi_s = e \cdot \Delta CPD \quad (3-7)$$

The key would be identifying the CPD change in each test. It was measured by a custom-built KP system illustrated in Figure 3-6 consisting of a commercial UHV Kelvin probe unit (from KP Technology Ltd) with vacuum pump and external light sources. The options for external light source include high-power LED (Mightex LED) with multiple wavelength selections from UV (365 nm) to near infrared (850 nm) and xenon light with full light spectrum. The incident light enters the Kelvin probe chamber where the test samples are placed through a quartz window. In this work, LED source was chosen to achieve monochromatic light with high output power. Its maximum output power = 350 mW at 455 nm wavelength. The equivalent schematic is shown in Figure 3-6.

To prepare particulate films for KP measurements, powder samples were first dispersed in propylene carbonate binder solution (QPAC@40). The binder solution was obtained after overnight stirring of 1.5 g of QPAC@40 dissolved in 10 g acetone. 0.1 g powder was added in 0.5 ml binder solution and mixed to get a well-dispersed paste. The paste was then coated onto FTO glass by doctor blade method and dried up to get the final sample ready for KP measurement.

Figure 3-6: Schematic of KP configuration.

3.3.1 Kelvin Probe Detection System

In our system, off-null detection was used to improve signal-to-noise ratio (SNR) to detect CPD and its equivalent circuit is shown in Figure 3-7.

Figure 3-7: Equivalent detection circuit of Kelvin probe.

By real time vibration, the time varying Kelvin capacitance between reference electrode and sample electrode is given by

$$C_K(t) = \frac{\epsilon_0 \epsilon_r A}{d(t)}; \quad (3-8)$$

where ϵ_0 is the permittivity of free space; ϵ_r is the relative permittivity, A is capacitor area, $d(t)$ is time varying distance between two electrodes.

Furthermore, time varying distance can be described in a periodic sinusoidal form.

$$d(t) = d_0 + d_1(1 + \epsilon \sin(\omega t)); \quad (3-9)$$

where d_0 is mean spacing, d_1 is the amplitude of tip vibration. With Equation (3-8) and (3-9),

$$C_K(t) = C_0/(1 + \epsilon \sin(\omega t)) \quad (3-10)$$

In which C_0 is mean Kelvin capacitance, ϵ is the modulation index given by $\epsilon = d_1/d_0$

$$\text{Charges stored by Kelvin capacitor is } Q_s = (V_c + V_b)C_k(t) \quad (3-11)$$

In which V_c is contact potential difference (CPD), V_b is the applied bias voltage. Therefore the output current is

$$I(t) = \frac{\delta Q_s}{\delta t} = (V_c + V_b) \frac{\delta C_k(t)}{\delta t}, \quad (3-12)$$

At the instant when CPD is offset by applied bias voltage V_b , a null current is obtained. The peak to peak voltage observed at the output site after amplifier varies along the time as shown in Figure 3-8.

$$V_{ptp} = (V_c + V_b)R_f G C_0 \sin(\omega t + \varphi) \quad (3-13)$$

R_f = I/V converter feedback resistance, G = the gain of the preamplifier (R_2/R_1), C_0 = the average Kelvin Probe capacitance, ω = the angular frequency of vibration and φ is a phase angle. The amplitude of V_{ptp} is then proportional V_b as shown in Figure 3-9. From Equation

(3-13), contact potential difference ($CPD = V_c$) with respect to tip probe can be extrapolated as the intercept with x-axis when plotting V_{ptp} vs. V_b , the gradient is approximately 300.

Figure 3-8: V_{ptp} varying with time.

Figure 3-9: V_{ptp} vs. V_b .

With inclusion of light source into the system, contact potential difference before and after light illumination can be measured to obtain SPV value

$$SPV = CPD \text{ (dark)} - CPD \text{ (light)} \quad (3-14)$$

In general, n type semiconductor exhibits a positive SPV, and p-type semiconductor exhibits a negative SPV.

3.3.2 SPV System Setup

The operating conditions were:

The detail of the Kelvin probe is not specified in the manual provided by KP Technology Ltd. However, the work function of Kelvin probe tip is calibrated against gold, and does not vary upon light illumination. The vibration amplitude of the tip (2 mm in diameter) was set at $AMP = 32 \text{ steps} \times 0.254 \mu\text{m}/\text{step} = 8.13 \mu\text{m}$; the vibration frequency was set at 84 Hz, slightly off the resonance frequency of the vibration tip as calibrated in Figure 3-10. The vacuum pump was used when measuring the SPV response under vacuum. It was also used to clean the chamber as well.

Before KP measurements, the as-prepared samples were put inside KP chamber overnight to reach dark equilibrium after being vacuumed using turbo pump down to 10^{-6} torr to remove the surface adsorbed particles. The measurements were then conducted under low vacuum, approximately 0.1 torr.

Figure 3-10: Resonance frequency detected at 86 Hz for the vibration tip.

3.4 Photoelectrochemical (PEC) Station Setup

Three-electrode electrochemistry potentiostat (Solartron 1287) was built for photo-current and C-V measurements of working electrode (the same BiVO_4 and CuO/BiVO_4 powders coated onto FTO glass by doctor blade method for SPV measurement and BiVO_4 thin films, 1 cm in diameter) in 0.5M Na_2SO_4 electrolyte using platinum plate as the counter (CE) electrode and Ag/AgCl (0.210 V vs. NHE) as reference electrodes (RE), as shown in Figure 3-11. The incident light of choice was 455 nm LED (Mightex LED) illuminated from working electrode back side with output power density at 20 mW/cm^2 . 5 minutes of nitrogen purge was carried out prior to each measurement.

With light on and off for every 10 seconds interval, PEC behavior for BiVO_4 or CuO/BiVO_4 electrodes were monitored. The current- potential curves for potential sweep were obtained at a rate of 5 mV / s .

Figure 3-11: PEC Cell with 3-electrode setup.

3.5 Photocatalytic Test

Photocatalytic efficiency was extracted from the photo-degradation rates of Rhodamine B (RhB) dye under visible light illumination in the presence of synthesized BiVO₄ powder and thin film. The photocatalytic test system consisted of light source, work station for photocatalytic reaction to occur, centrifuge kit to separate BiVO₄ powder from RhB solution at each sampling point and UV-Vis spectrometer (Shimadzu UV-2450) to measure the intensity changes and peak shifts for absorbance maximum of RhB solution (λ_{max} = 554 nm for pristine RhB solution) over time.

In this work, a white LED (Prizmatix optical devices, cut-off wavelength of 420 nm) with an output power density of 50 mW / cm² was used for visible light illumination. The distance between work station and light source was calibrated and adjusted so that the power intensity received by BiVO₄ samples was reduced to 1.5 mW / cm², which was about the same level of indoor light condition measured by broadband energy/power meter (Melles Griot).

The photocatalytic reaction took place in 50 mL RhB solution of 15 μ M inside a closed box in a controlled environment. In case of powder samples, 0.1 g of BiVO₄ was added into RhB solution and was left in dark stirring for 3 hours to reach dark absorption equilibrium under constant stirring. In case of thin film, BiVO₄ coated on to 2cm x 2cm FTO glass were placed at the bottom of a Pyrex vessel.

UV-Vis spectrometer measured the change in absorbance of RhB solution, specifically the reduction of intensity at absorption peak corresponding to the destruction of conjugated structure [131]. The change in absorption intensity was directly related to change of RhB concentration over time.

The ratio of RhB concentrations at dark absorption equilibrium (C_0) and their changes over certain reaction time t (C_t) were used to extrapolate photo-degradation rate. The reaction constants k , were then determined by first-order kinetics as in $\ln (C_t/C_o) \propto kt$.

CHAPTER 4 Ball-Milled BiVO₄ Nano-particles

4.1 Background

Since Fujishima and Honda discovered the water-splitting capability of TiO₂ electrode with light excitation in 1970s [43], titanium – based semiconductor photocatalyst has been the center piece of semiconductor photocatalyst development for decades. Limited by its intrinsic wide bandgap of 3.0 eV to 3.2 eV, TiO₂ is unable to utilize the visible light range in the solar spectrum. To improve visible light utilization, one research interest remains on titanium – based semiconductor to modify the pristine TiO₂ by doping [61] or surface treatment to create extra acceptor or donor states within bandgap to effectively narrow down the bandgap. Another option is to sort out alternative semiconductor materials with narrow bandgap as photocatalyst candidates. Among them, BiVO₄ with a 2.4 eV bandgap makes a promising candidate for its chemical stability and visible light absorption ability. In this work, BiVO₄ nano-particles and BiVO₄ composites were studied for the gain of enhanced photocatalytic efficiency, specifically BiVO₄ in monoclinic scheelite form (m-BiVO₄). Compared to its counterparts in tetragonal crystal structure, m-BiVO₄ is a better photocatalyst candidate as a result of its narrow bandgap of 2.4 eV and hybrid valence band to facilitate hole movement as explained by Kudo, et al. [1].

As summarized in section 2.1, three key factors control how photocatalytic reactions take place, namely charge generation upon irradiation, electron hole pair separation to form essential redox species and large surface area with sufficient active sites to allow redox species to participate in chemical reactions. Under these criteria, it is essential to develop a simple synthesis method to be able to produce nano-particles with large surface area and good throughput. The low yielding of final product in wet chemical methods along with its complexity in preparing precursors are known shortcomings with wet chemical method,

despite the good control of surface morphology [132-137]. Solid state reaction, on the other hand is able to produce in large quantities, but the particle size is uncontrollable and can be as large as several microns [79].

To control crystal growth and eventually the particle size, several research groups have reported preparing BiVO₄ nano-particles by making use of polymer surfactants during wet chemical approach [83, 134, 135, 138, 139]. Our group was one of them and has previously reported the successful synthesis of m-BiVO₄ octahedral nano-crystals using hydrothermal method and making use of sodium dodecyl benzene sulfonate (SDBS) to constrain the crystal growth [134]. The final size of m-BiVO₄ nano-crystals can be adjusted to less than 200 nm; however, the gain in specific surface area was undesirable which was only less than 4 m²/g. In a different hydrothermal approach, ethylene diamine tetra acetic acid (EDTA) was added before precipitation to guide the crystal growth rather than during the precipitation process as a chelating agent to achieve surface area up to 10 m²/g [135].

Other non-aqueous methods including reverse-microemulsion process to produce nano-sized m-BiVO₄ down to 35 nm at 400 °C [83] and microwave-heating approach based on in-situ twin polymerization to reach surface area of 7–16 m²/g were reported [139].

Last but not the least, conventional high energy ball milling process parameters, such as milling time and ball to powder ratio were also closely examined in order to produce spherical-like BiVO₄ nano-particles with an average size of 20 nm [138]. Inherited crystal defects and deformation in the as ball- milled powders can be repaired or reduced by heat treatment [89, 140]; the recombination sites were then significantly reduced and were beneficiary to photo-activity of interest.

This has brought our attention into mechanochemical synthesis method due to its manufacturability and high throughput, which add up to its capability to produce fine nanoparticles with large surface area.

Bismuth-containing ferroelectrics have been reported to be directly synthesized from oxide precursors via the high-energy milling. As summarized by L.B. Kong et al, it comprises two stages. At stage one, the grain size / particle size of the starting oxide are milled down due to fragmentation. This brings more close contact of precursors. It also leads to the formation of clean interfaces and high defect densities with shorter diffusion distances, which are responsible to increase the reactivity of the precursors. At stage two, the nucleation and crystal growth start to occur after a sufficient activation [141].

Ferroelastic phase transition of BiVO_4 single crystals are studied by A. R. Lim and S-Y. Jeong. The stress-strain hysteresis loops measured at different temperatures in Figure 4-1 reveals that the strain in ferroelastic phase (m- BiVO_4) does not recover to the initial position; the hysteresis loops at 50 °C, 100 °C, and 200 °C belong to the characteristic shape of a ferroelastic phase. When temperature approaches T_c , where $T_c = 255$ °C, the transformation temperature between m- BiVO_4 (ferroelastic phase) and st- BiVO_4 (paraeleastic phase), the strain decreases. No stress-strain hysteresis is observed for the paraelastic phase[142]. Inherited from the ferroelastic characteristic of m- BiVO_4 , the ball-milling process would inevitably induce strain in BiVO_4 lattice to the extent of lattice deformation, due to the stress originated from ball milling process. This is the opposite of what we want, as it greatly increases the chance of charge recombination. Thus post ball-mill heat treatment is of great interest and necessity for this work.

Figure 4-1: The stress-strain hysteresis loops at 50 °C , 100 °C, 200 °C, and 280 °C [142]

The ball-milling process itself comprises of 2 parts, dry milling to synthesize the powder followed by wet milling in ethanol to mill down the particle size.

The physicochemical characteristics of annealed m-BiVO₄ nano-particles synthesized mechanochemically were closely examined to provide insight into their photocatalytic performance in degrading Rhodamine B (RhB) under visible light irradiation. On top of that, surface photovoltage (SPV) response was recorded to provide indications for charge separation which was the key factors affecting photocatalytic efficiency.

4.2 Material Characterizations on Ball Milled-BiVO₄ Nano-particles

4.2.1 Crystallography and Morphology of BiVO₄ Nano-particles

XRD spectrum of as-milled BiVO₄ and annealed ones were collected. Their diffraction peaks aligned well with the corresponding peaks of pure m-BiVO₄ (JCPDS No. 04-1688), especially the characteristic peak splitting features at 19° and 35°, which were illustrated in the inset of Figure 4-2. Peak splitting feature evidently differentiated monoclinic scheelite BiVO₄ (m-BiVO₄, JCPDS No. 04-1688) from scheelite tetragonal (st-BiVO₄, JCPDC No. 48-0744) [143], despite the fact that these two forms of BiVO₄ are of similar lattice constant. The degree of peak splitting became more obvious at higher annealing temperature with increasing peak intensity, signifying the importance of thermal anneal on improving crystallinity. On the other hand, thermal anneal promoted crystal growth, manifested as sharpening peak with reducing full width at half maximum (FWHM) in radians in XRD spectrum. The grain size was further calculated by Scherrer formula for peak centered at $2\theta = 28.8^\circ$ (Equation 3-2).

Size = $K\lambda/\beta\cos\theta$, where K = Scherrer constant, usually 0.9, β = the full width at half maximum (FWHM) located at 2θ peaks.

The average grain size of BiVO₄ powders increased together with annealing temperature from 21 to 26 nm, summarized in Table -1. As-milled BiVO₄ powder was calculated to be 20.0 nm in average, comparable to those values (18.0-21.6 nm) reported for mechanochemically synthesized BiVO₄ milled for 6-11 hours [138].

Figure 4-2: XRD spectra of as-milled BiVO₄ powder and with anneal at various temperatures.

At the same time, particle size (d_{BET}) was estimated from BET surface area (S_{BET}), assuming spherical shape for all particles: $d_{\text{BET}} = 6/S_{\text{BET}}\rho$, $\rho_{\text{BiVO}_4} = 6.95 \text{ g/cm}^3$. The spherical shape for all particles has been confirmed by SEM images shown in Figure 4-4.

Particle size calculated from BET method were generally larger than grain size obtained from XRD by taking into consideration of particle agglomeration on surface. BET surface area of our BiVO₄ nano-particles synthesized mechanochemically was still above 10 m²/g with post anneal up to 400°C (10-17 m²/g). Some of the good examples from reported work were 7 m²/g by Ressnig et al. [144], 10 m²/g by Sun et al. [135] and 7-16 m²/g by Hofmann et al. [139]. Compared to these works, it demonstrated that mechanochemical method was effective in producing fine nano-sized particles effectively.

Table 4-1: physicochemical properties of as-milled BiVO₄ powder and with anneal at various temperatures

Annealing T (°C)	Crystallite size (nm)	BET SSA (m ² /g)	Particle size (nm)	Bandgap (eV)	SPV (mV)	Reaction Constant k (h ⁻¹)
As-milled	20	17	51	2.66	-	-
300	21	16	53	2.64	160	0.056
400	26	10	91	2.61	210	0.107
500	32	3	276	2.60	100	0.046
600	36	1	639	2.59	80	0.031

Raman spectrum was collected in conjunction with XRD to further study the local crystal structure and was useful in examining bond stretching mode. All five signature Raman stretching bands of m-BiVO₄ were clearly present in all samples, namely, external mode at 210 cm⁻¹, asymmetric and symmetric bond bending of VO₄³⁻ tetrahedron at 327 and 368 cm⁻¹, respectively and stretching mode of long and shorter V-O bond in VO₄³⁻ tetrahedron at 710 and 827 cm⁻¹, respectively [145]. The band position of 823 cm⁻¹ for as-milled BiVO₄ was lower than other annealed samples as well as values (826-827 cm⁻¹) commonly reported in literature [146] [145]. A few explanations can be provided: Firstly, it was mostly attributed to longer bond length of V-O bond from the known functional correlation between peak position of Raman band and length of metal-oxygen bond [79, 146].

Secondly, it can be linked to the nano-sized crystal grains mimicking the quantum confinement effect. In theory when physical size shrinks to a certain limit, Lorentzian phonon band of bulk solids would turn into an asymmetric Raman band [147]. This was experimentally verified on mesoporous BiVO₄ particles with size of ca. 8 nm [82].

Upon closer look at Raman band at around 823 cm^{-1} , Raman peak shifted towards longer frequency with increasing annealing temperature. This blue-shift in Raman band indicated a reduction in V-O bond length and was believed to cause greater local distortion in VO_4^{3-} tetrahedrons surrounding Bi^{3+} , which was good for facilitating hole movement and beneficiary for photocatalytic reactions. The strengthening of Raman band with increasing anneal temperature was another proof that post anneal treatment was effective in crystallinity improvement.

Figure 4-3: Raman spectra of as-milled BiVO_4 powder and with anneal at various temperatures.

Surface morphology of as-milled BiVO_4 and annealed samples were captured by FESEM in Figure 4-4 (a) - (e). For as-milled BiVO_4 , spherical shape of particles with average size of 50 nm was obtained as shown in Figure 4-4 (a). Comparing BiVO_4 annealed at 300°C in Figure 4-4 (b) with as-milled sample, no visible change was observed in the field of surface morphology or particle size distribution. For BiVO_4 annealed at 400°C , BiVO_4 particle size started to grow due to significant segregation on surface, but still well below 100 nm in average as shown in Figure 4-4 (c) and further confirmed by HRTEM in Figure 4-4 (f). With further increasing annealing temperature to 500°C , apparent increase in particle size was observed in Figure 4-4 (d). At elevated anneal

temperature of up to 600°C, there was a drastic increase in particle size as evidenced in Figure 4-4 (e), due to fast particle sintering. All above observations from FESEM image were well tallied with findings from XRD grain calculation and BET surface area. It was evident there should be a trade-off point between crystallinity, which improved with increasing anneal temperature and particle size distribution, which also grew undesirably bigger as anneal temperature went up, in order to reduce charge separation rate without sacrificing surface area.

The underlying crystal structure of BiVO₄ synthesized mechanochemically was investigated by HRTEM on 400°C annealed samples. In Figure 4-4 (g)-(h), (040) plane of monoclinic BiVO₄ were revealed and identified by the characteristic lattice distances of 0.291 nm and 0.286 nm, which matched well with known reported values [132].

Combining the XRD and Raman study, one can conclude that m-BiVO₄ was successfully synthesized by ball-milling approach and post-milling anneal was necessary to promote crystallinity quality. From FESEM and HRTEM images, it was clear that high temperature post-milling anneal should be prohibited to maintain uniform distribution of nano-sized particles. Hence it was essential to find the optimal anneal temperature to reach a good trade-off between crystallinity and particle size, both factors played important roles in photocatalytic reactions.

Figure 4-4: FE-SEM images of as-milled BiVO_4 (a), 300 °C annealed BiVO_4 (b), 400 °C annealed BiVO_4 (c), 500 °C annealed BiVO_4 (d), 600 °C annealed BiVO_4 (e), TEM images of 400 °C annealed BiVO_4 (f), and their HRTEM images of different sites (g and h).

4.2.2 Chemical State Study of BiVO_4 Nano-particles

Figure 4-5 (a) to (c) shows high-resolution core level XPS spectra of $\text{Bi}4f$, $\text{V}2p$ and $\text{O}1s$ orbit from BiVO_4 annealed at 400 °C. The $\text{Bi}4f$ spectra consisted of well-deconvoluted doublets for $\text{Bi } 4f_{5/2}$ and $\text{Bi } 4f_{7/2}$ orbits of Bi^{3+} cation location at 164.6 eV and 159.3 eV, respectively. The $\text{V}2p$ spectra revealed doublets of $\text{V } 2p_{1/2}$ and $\text{V } 2p_{3/2}$ orbits centering at 524.5 eV and 517.0 eV, respectively originated from V^{5+} cation in BiVO_4 particles [148]. The $\text{O}1s$ spectra consisted of one intense O 1s peak at 530.1 eV and another soft peak at 532 eV. The intense peak was attributed to

lattice oxygen, while the soft peak was normally due to adventitious species at surfaces that was inevitably found in ambient environment, such as adsorbed water bonds (OH_{ads}) and carbonate species (C-O , C=O) [149]. XPS spectra of Bi, V and O double confirmed that BiVO_4 with correct stoichiometry was synthesized mechanochemically by high energy ball-milling and with post anneal treatment.

Figure 4-5 (d) revealed total density of states (DOS) in valence band (VB) of BiVO_4 annealed at 400 °C. From photoemission onset, VB edge was below Fermi level, which was the characteristic of n-type semiconductor, by 2.0 eV derived from the total bandgap of 2.4 eV in BiVO_4 . More importantly, DOS in valence band provided evidence of hybrid VB from Bi 6s and O 2p orbital in m- BiVO_4 , which differentiated monoclinic scheelite BiVO_4 from its tetragonal counterparts. With respect to Fermi level in VB, the isolated photoemission peak started from 12 eV was attributed to partial DOS of Bi 6s states; the wide span of photoemission a range of 2 eV to 9 eV was the result of multiple DOS consisting of [150]:

- (i) unhybridized O $2p_\pi$ and Bi 6s states mixed at approximately 2.65 eV
- (ii) O $2p_\pi$ state at approximately 3.67 eV
- (iii) O sp^2 / V 3d hybrid state at approximately 5.63 eV
- (iv) O sp^2 / Bi 6p hybrid state at approximately 7.45 eV

Figure 4-5: XPS spectra of Bi4f (a), V2p (b), O1s (c) and total DOS of VB (d) from of annealed 400°C BiVO₄.

4.2.3 Optical Properties of BiVO₄ Nano-particles

XRD and Raman spectra, TEM and XPS studies all confirmed monoclinic scheelite BiVO₄ nano-particles with desirable crystal plane and correct chemical stoichiometry was obtained by high energy ball milling followed by anneal. The samples' visible light absorption ability was further examined by UV-Vis diffuse reflectance followed by surface photovoltage response.

UV-Vis diffusion reflectance

Figure 4-6 consolidated UV-Vis absorption spectra of all samples including as-milled BiVO₄ and BiVO₄ annealed at different temperatures. The dominant absorption range for all samples lied in the range of 350 to 550 nm. Compared with as-milled BiVO₄, all annealed samples showed a red-shift towards the longer wavelength in visible light range in absorption edge, which led to bandgap narrowing in annealed samples as summarized in Table 4-1.

The energy bandgap was extrapolated from Tauc plot based on the Equation (3-5) in Figure 4-6 (b). Tauc plot is applicable to direct bandgap semiconductor, which BiVO_4 has been reported to be one of them [151]. Unoccupied V3d orbital forms the conduction band minimum while Bi 6s and O 2p hybridized orbital makes up the valence band maximum [150]. The bandgap of BiVO_4 was extrapolated to be 2.66 eV from Tauc plot resulting in an absorption edge at $\lambda = 466$ nm, similar with the reported value for nano-sized BiVO_4 powder prepared in microwave-assisted approach [139], but larger than values commonly reported for BiVO_4 prepared by hydrothermal approach in the range of 2.4-2.5 eV [145]. One possible explanation was quantum confinement effect rising from small physical size and internal lattice distortion [139]. When as-milled BiVO_4 was treated with thermal anneal, a red-shift were revealed in absorption edge with further extension into visible light range, indicating a continuous narrowing in energy bandgap. In the end, it was down to 2.59 eV for 600 °C annealed sample. The bandgap narrowing effect as a result of increasing anneal temperature was brought up by the increasing overlapping of Bi 6s and O 2p orbits in valence band due to lone-pair distortion in local structure, supported by the blue-shift towards longer vibration frequency in Raman spectrum with increasing anneal temperature in Figure 4-3. The blue-shift corresponded to a shorter V-O bond in VO_4^{3-} tetrahedron exerting more local distortion around Bi^{3+} to allow more hybridization of Bi 6s with O 2p to effectively narrow down the energy bandgap. Hybrid VB not only increased the visible light utilization, but can also facilitate hole transportation as holes excited from VB can transport to Bi 6s states within VB, and was proven helpful in the subsequent photo-activity evaluation.

Figure 4-6: UV-Vis absorption spectra of as-milled BiVO₄ powder and with anneal at various temperatures (a) and Tauc plot for bandgap extrapolation (b).

Surface photovoltage response (SPV)

The Kelvin probe based SPV system records the contact potential difference change (ΔCPD) in reaction to light illumination. Like UV-Vis absorption spectra, the extent of SPV response is quantifiable and is determined by the quantity of photo-generated electron hole pairs upon photon excitation, but it is also affected by carrier transportation rate to surface states [149]. Hence it can be used as direct indicator of charge separation efficiency. The larger the SPV response, the better charge separation is achieved [152].

A typical n-type semiconductor behavior was revealed for BiVO₄ annealed samples at 400°C and above whereby a positive SPV value was obtained after light irradiation. On the other hand as-milled and 300°C annealed BiVO₄ showed negligible photo-response, probably due to no or insufficient recovery of lattice distortion inherited from ball milling process.

The SPV values were recorded in Table 4-1 for comparison. The carrier lifetime of 40 ns together with diffusion length of 70 nm have been reported by Abdi et al [153]. The carrier lifetime is much shorter than our sampling frequency of 11,000 Hz; this can explain the fluctuation in the SPV. A change in Kelvin probe size to allow faster vibration than current 84 Hz and a continuous update in the detection circuit can reduce the noise to SPV spectra. Among all, BiVO₄ annealed at 400°C showed fastest and largest SPV response, indicating best charge separation efficiency. The charge separation was achieved in either or both of the following aspects: (i) The good crystallinity obtained with post-milling thermal anneal repairing or reducing the crystal defects inherited from milling step, hence reducing the chance of charge separation; and (ii) The small physical size would shorten the diffusion and transportation distance, resulting less time for charge recombination to occur.

BiVO₄ annealed at 400 °C exhibited a good compromise between crystallinity and particle size as repeatedly emphasized in XRD analysis; hence it was able to exhibit a large SPV response.

Figure 4-7: SPV spectra of BiVO₄ powders with anneal from 400 °C-600 °C.

4.3 Photocatalytic Performance Evaluation of BiVO₄ Nano-particles

Rhodamine B (RhB) is one of the most commonly used cationic dyes in industry for printing and textile/paper/paints/ leather coloring. However, it can cause potential environmental and health problems, like irritation to skin and eyes. Hence it presents a great challenge for its removal. The positive surface charges from RhB make them attractive to negatively charged surfaces. Zeta potential of BiVO₄ in aqueous solution is analyzed by Malvern Nano ZetaSizer model ZEN3600 with a 633 nm red laser. It is the electrical potential between the powder material (BiVO₄) and dispersion environment (water). Since the ionic composition of water is kept unchanged, zeta potential is representative of the surface charge of BiVO₄. A negative zeta potential of - 42.5 mv signifies a negatively-charged BiVO₄ surface. Rhodamine-B degradation in aqueous solution was thus employed to model photocatalytic activities of synthesized BiVO₄ powders under visible light illumination

Figure 4-8: Zeta potential distribution of BiVO_4 in water.

4.3.1 Photo-degradation of RhB by BiVO_4 Nano-particles

As shown in Figure 4-9, RhB control sample without any presence of BiVO_4 powders showed constant absorbance intensity over time, this ruled out the photolysis. The reduction in intensity would be attributed to the photo-degradation process. What's more, as-milled BiVO_4 due to its ferroelastic characteristic was susceptible to charge recombination attributed to the induced distortion occurred during high energy ball milling, hence showed no photo-degradation activity [154]. The lattice distortion could be later reduced and repaired by re-crystallization during post-milling thermal anneal. This emphasized the necessity and importance of post thermal anneal in preparing photo-active materials by high energy ball mill approach.

The photo-degradation rate of each annealed sample was calculated based on first order kinetics and compared to determine optimal anneal temperature. The degradation rate was in the same order as in SPV response: $k_{400^\circ\text{C}} > k_{300^\circ\text{C}} > k_{500^\circ\text{C}} > k_{600^\circ\text{C}}$. 400°C annealed BiVO_4 showed superior photo-degradation than the others. This can be explained by the optimized crystallinity improvement and particle size growth happening at the same time

during post thermal anneal. Further increase in anneal temperature showed deteriorated photo-degradation efficiency. One possible cause was the apparent particle size growth that reduced surface area of BiVO_4 and provided less active site for photocatalytic reactions to take place.

In short, post-milling thermal anneal was a must and effectively way to prepare photo-active BiVO_4 and the optimal anneal temperature was found at 400 °C.

Figure 4-9: Photo-degradation of RhB in the presence of as-milled BiVO_4 powders and with anneal from 300°C to 400°C upon light illumination ($\lambda > 420 \text{ nm}$ and light intensity of 1.5 mW/cm^2) with the first order reaction kinetics shown in bottom right inset.

4.3.2 Photo-degradation Mechanisms of RhB by BiVO_4 Nano-particles

For photocatalytic reaction to occur, photo-generated electron holes pairs need to be separated.

For BiVO_4 , it follows a typical charge separation behavior of semiconductor photocatalyst, as illustrated in chapter 2.1. Specifically, oxygen adsorbed on BiVO_4 surface is the main electron acceptor to form superoxide radical ($\cdot\text{O}_2^-$), targeting hydroxylated species to

reproduce $\bullet\text{OOH}$ radicals Both pathways are supported by recent electron spin resonance (ESR) analysis [155].

Photo-generated holes in valence band can oxidize hydroxide (OH^-) dissociated from water molecules to produce highly active the hydroxyl radical ($\bullet\text{OH}$) as shown by Equation (2-6). $\bullet\text{OH}$ radicals can further participate in oxidation reaction responsible for the decomposition of organic pollutants. This is the main degradation mechanism.

Pristine RhB is fully covered by 4 methyl groups as shown in Figure 4-10. The decomposition of Rhodamine-B takes place in two competitive ways: *N*-dealkylation and the destruction of conjugated structure [131, 156].

Decomposition of Rhodamine – B by removal of methyl group

N-dealkylation or the removal of methyl group from RhB was accompanied by the blue shift of absorption maximum λ_{max} towards shorter wavelength observed in Figure 4-11 and in accordance with reported work [131, 156].

Figure 4-10: Pristine RhB.

De-ethylation proceeded in a step-wise manner, meaning methyl ($-\text{CH}_3$) was removed one by one with various intermediate Rhodamine species remaining in RhB solution as pointed out in Table 4-2 [157].

Table 4-2: Rhodamine-B and intermediate Rhodamine species

Rhodamine Species	Number of methyl group in conjugated structure	Absorption maximum $\lambda_{\text{max}} / \text{nm}$
Rhodamine-B	4	554
N,N,N'-Triethyl-Rhodamine	3	539
N,,N'-Diethyl-Rhodamine	2	522
N-Ethyl-Rhodamine	1	510
Rhodamine	0	498

Figure 4-11: Absorption spectra of RhB solution with BiVO₄ powders with additional anneal prior to wet milling as compared to the current established route.

Decomposition of Rhodamine – B by destruction of conjugated ring

The cleavage of the conjugated ring structure was accompanied by peak intensity reduction. With no cleavage of the conjugated ring structure, the difference in molar extinction coefficient gave rise to maximum peak intensity reduction at 30% (RhB: $11.5 \times 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$ vs. Rhodamine: $8.4 \times 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$). That is to say, decomposition of RhB by removal of methyl group alone would shift peak position from 554 nm to 498 nm and bring down absorption intensity to 70% of pristine RhB. In reality, the peak intensity at 498 nm was much less than 70% and was a good indicator of the destruction of conjugated ring structure that took place in a later stage with prolonged light exposure, which tallied with the findings in other reported work that de-ethylation dominated the decomposition of RhB in early stage. [157].

In short, decomposition of RhB took place via de-ethylation and destruction to the conjugated ring structure over time. De-ethylation took place causing a blue-shift in absorption maximum and dominated in initial stage of decomposition. The maximum peak intensity

reduction was 30% for de-ethylation alone. Further reduction in peak intensity was due to the cleavage of conjugated ring structure to the extent that complete removal of RhB was possible with prolonged light exposure to reach full mineralization as shown in Figure 4-11.

4.4 Concluding Remarks

Monoclinic scheelite BiVO_4 was successfully synthesized mechanochemically by high energy ball milling process followed by post thermal anneals. When anneal temperature did not exceed $400\text{ }^\circ\text{C}$, BiVO_4 nano-particles with particles size of less than 100 nm in average and good BET surface area of $10\text{ m}^2/\text{g}$ were produced. The effect of post thermal anneal temperature on photo-activity was further investigated by surface photovoltage study, whereby BiVO_4 annealed at $400\text{ }^\circ\text{C}$ showed largest and fastest photo response, providing evidence of its superior charge separation efficiency. The photo-activity was further examined by photo-degradation of RhB. Due to the gain from crystallinity improvement and undesirable growth of particle size rising from post thermal anneal, the $400\text{ }^\circ\text{C}$ annealed BiVO_4 showed the fastest reaction rate in decomposing RhB during which both removal of methyl groups and breakdown of conjugate ring happened. Hence the optimal anneal temperature was found to be $400\text{ }^\circ\text{C}$ and laid ground work for further improvement of charge separation on BiVO_4 – based semiconductor photocatalyst for practical environmental applications.

CHAPTER 5 CuO/BiVO₄ Composite Structures

5.1 Background

Nano-sized m-BiVO₄ particles with uniform particle size distribution and surface area were successfully produced by high energy ball milling process with the assistance of post thermal anneal, as described in CHAPTER 4. The optimum anneal temperature was found to be 400°C to render BiVO₄ nano-particles to be photo-active under visible light [158]. Next step would be to further improve their photo-activity by means of enhancing charge transportation and separation on BiVO₄ surface.

BiVO₄ coupling with metals [159, 160], non-metals [161] and other semiconductors [102, 162-165] with suitable band edge positions to form heterojunction was very useful to enhance the photocatalytic performance of m-BiVO₄. BiVO₄/Co₃O₄ heterojunction with 0.8 wt% cobalt was found to significantly increase and stabilize the photo-current generation w.r.t pure BiVO₄ [162]. BiOCl/BiVO₄ p-n heterojunction structure was another example of BiVO₄ composites for photo-efficiency enhancement on the aspect of photodegradation rate of methyl orange [165]. γ -Bi₂O₃/m-BiVO₄ core-shell p-n heterogeneous nanostructure by a novel alkaline “etching” process was demonstrated by our group previously for improving photocatalytic performance on the aspect of photodegradation rate of Rhodamine B [164]. In these p-n heterojunction structures, charge transportation at semiconductor interface was facilitated and accelerated by the built-in electric field due to difference in band edge positions in p and n-type semiconductors [95].

p-type Cupric oxide (CuO) with a narrow bandgap of 1.70 eV was an excellent choice of co-catalyst to couple with other semiconductor to improve the overall charge separation towards better photocatalytic performance including TiO₂ [166], ZnO [167], and SnO₂ [168], although CuO itself has poor photocatalytic performance due to poor charge transportation.

In this work, CuO/m-BiVO₄ composite was synthesized mechanochemically by high energy ball milling and comprehensively characterized to understand the underlying mechanisms for the visible-light driven enhancement in photoelectrochemical (PEC) and photocatalytic properties. The band structure and associated charge transportation paths were proposed. Specifically, increment on photon absorption was confirmed by diffuse reflectance spectroscopy (DRS), reduction of charge recombination rate was elucidated by photoluminescence (PL) and increase in charge separation efficiency was verified by surface photovoltage (SPV) study.

5.2 Material Characterizations on CuO/BiVO₄ Composites

5.2.1 Morphology and Crystallography of CuO/BiVO₄ Composites

Insights on the morphology and structure of CuO/BiVO₄ composites were investigated by TEM. The TEM samples were prepared by dispersing the composite powders in ethanol via ultra-sonication and subsequently dropping the dispersion on nickel grid to dry. TEM image of 5 at. % CuO/BiVO₄ in Figure 5-1 (a) showed the size distribution of composite nanoparticles from 50-120 nm, re-assuring the effectiveness of producing fine nano-particles by higher energy ball-milling process. The larger particle size compared to pure BiVO₄ can be explained by agglomeration on BiVO₄ surface. HRTEM images in Figure 5-1 (b)-(c) clearly revealed that spherical CuO shell with 5 nm diameter in average covering BiVO₄ surface, instead of doping into BiVO₄ lattice. The lattice distance of BiVO₄ remained the same as 0.291 nm. What's more, element mapping from dark field scanning TEM (STEM) and instant EDS profiles in Figure (d)-(e), respectively reconfirmed the deposition of CuO nanoparticles onto BiVO₄ surface, and more importantly the distribution was uniform. This summarized that the incorporation of CuO onto BiVO₄ surface was achieved by surface

deposition and confirmed the existence of p-n heterojunction with no detection of Cu element inside BiVO_4 lattice to alter its lattice structure.

Figure 5-1: TEM image of 5 at.% CuO-loaded BiVO_4 composite (a) and corresponding HRTEM images (b-c), EDX element mappings of Bi, V, O, and Cu by STEM (d) and EDS profiles (e).

The phase structure and local crystal structure of CuO/BiVO_4 composite with various CuO loading percentages in atomic weight were examined by XRD and Raman, respectively, and compared with that of BiVO_4 with no CuO loading.

As illustrated in XRD spectra for all composite and BiVO_4 powders in Figure 5-2 (a), the diffraction peaks of all samples indexed well with the characteristic peaks of pure m- BiVO_4

(JCPDS No. 04-1688), especially the distinctive peak splitting feature at 35° which differentiated monoclinic scheelite BiVO_4 (m- BiVO_4) from scheelite tetragonal (st- BiVO_4 , JCPDC No. 48-0744) [143]. The lattice spacing of 0.291 nm was well identified and matched with d-spacing of (040) plane of monoclinic BiVO_4 [169] in TEM image for 5 at.% CuO/BiVO_4 in Figure 5-1 (b), reconfirming that the monoclinic structure remained intact with the incorporation of CuO .

It was also noted about the lack of major characteristic diffraction peaks at $2\theta = 38.759^\circ$ for CuO (111) and 35.558° for ($\bar{1}11$) planes (JCPDS No. 89-5899) in the composite powders. This was explained by the minute amount of CuO incorporated into BiVO_4 that cannot be detected by XRD pattern. For CuO peak to appear, it was discovered by Xu et al. that the atomic percentage of CuO need to reach 40% in CuO -loaded BiVO_4 when calcinated at 300°C [170]. An even larger percentage was reported by Zhang et al. on $\text{CuO}-\text{BiVO}_4$ supported fly ash cenospheres [171], whereby a minimum weight percentage of 40% was required before diffraction peaks of CuO started to occur, corresponding to a minimum atomic percentage of 70%. Another possible attribute for the lack of CuO diffraction peak could be the uniform deposition of CuO nano-particles onto BiVO_4 surface instead of incorporation into BiVO_4 lattice. This was supported by the missing of position change for BiVO_4 diffraction peaks in Figure 5-2 (a).

Another observation from XRD pattern was that FWHM for all composite samples remained the same as BiVO_4 . This proved that the decomposition of $\text{Cu}(\text{NO}_3)_2$ into CuO at 300°C did not induce a second time grain growth of BiVO_4 and preserved the integrity of BiVO_4 . The surface area of composite powders was expected to be similar with those of pure BiVO_4 nano-particles. BiVO_4 nano-particles with grain size of 26.0 nm in average based on Scherrer's equation and surface area of $10 \text{ m}^2/\text{g}$ based on BET theory were obtained on our early work by the same high energy ball milling process [158].

As shown in the Raman spectra from Figure 5-2 (b), all five characteristic band position of monoclinic BiVO₄ were identified and no change in band position or addition of new bands was observed. This was in accordance with XRD and HRTEM analysis that the deposition of CuO onto BiVO₄ surface did not exert changes to the local crystal structure of BiVO₄.

Table 5-1: Raman band positions of m-BiVO₄ [142]

Band Position (cm ⁻¹)	Assignments
210	External mode
327	Asymmetric bending of VO ₄ ³⁻ tetrahedron
368	Symmetric bending of VO ₄ ³⁻ tetrahedron
710	Stretching mode of V-O bond
827	Stretching mode of shorter V-O bond

In short summary, CuO/BiVO₄ composite with similar grain size and surface area distribution as pure BiVO₄ nano-particles from our early work was successfully synthesized via high energy ball-milling. The extra heat treatment at 300°C to decompose Cu (NO₃)₂ did not alter the crystal structure of BiVO₄ or induce second time grain growth. The incorporation of CuO onto BiVO₄ was a surface deposition process, no Cu element was found inside BiVO₄ lattice to alter the lattice spacing. The integrity of BiVO₄ remained intact with CuO loading.

Figure 5-2: XRD (a) and Raman spectra (b) of CuO-loaded BiVO₄ composites at different atomic percentages.

5.2.2 Surface Chemical States Study of CuO/BiVO₄ Composites

The stoichiometric concentration and oxidation states of Bi, V, and Cu were determined by XPS for 5 at. % CuO/BiVO₄ composite. Figure 5-3 consolidates the spectra of Cu 2p orbit as well as that from Bi 4f, V 3d and O 2p orbit. In Cu 2p orbit spectrum, Cu 2p_{1/2} and Cu 2p_{3/2} orbits of Cu (II) location at 953.5 eV and 933.7 eV in a manner of well-deconvoluted spin – orbit split was observed, confirming the existence of Cu in the form of Cu²⁺. In addition, another identification marker for Cu (II) were found in the range of 965.0-960.0 eV and

950.0-938.0 eV , a.k.a shake-up peaks reconfirming the incorporation of Cu ion in Cu^{2+} status [172].

In Bi 4f orbit spectra, Bi $4f_{5/2}$ and Bi $4f_{7/2}$ orbits of Bi (III) centered at 164.6 eV and 159.3 eV in doublet form were identified, confirming the existence of Bi in form of Bi^{3+} . In V 2p orbit spectra, V $2p_{1/2}$ and V $2p_{3/2}$ orbit were assigned to V(V) positioned at 524.5 eV and 517.0 eV in form of V^{5+} [148]. In O 2p orbit spectra, two peaks were observed: a primary peak originated from lattice oxygen in BiVO_4 crystal cell located at 530.1 eV and a soft peak located at 532 eV due to ambient contamination [149].

What's more, Figure 5-3 (f) compared total DOS in valence band of BiVO_4 and with 5 at. % CuO. Extra DOS in the range of 2 to 1 eV were found in 5 at. %CuO loaded BiVO_4 , and provided an upward shift in VB edge towards the Fermi level. This could be explained by the energy band bending when p-type CuO was in contact with n-type BiVO_4 . In thermal equilibrium, Fermi levels of both semiconductors were aligned to reach flat band condition. Since Fermi level of p-type CuO was much closer to VB edge, an upward bending in n-type BiVO_4 was expected. Another possible explanation is the effective bandgap narrowing due to the addition of states within BiVO_4 bandgap by introduction of CuO whose bandgap is only 1.7eV [170, 171].

In short summary and based on the overall analysis of XRD, Raman and XPS spectra, it is evident that incorporation of CuO onto BiVO_4 surface was not only successful but it did not compromise the integrity of BiVO_4 crystal cell. The fact the Cu signal was evident in XPS analysis but non-detectable in XRD pattern, reconfirmed the incorporation of CuO onto BiVO_4 was a surface deposition process. The atomic ratio of Cu: Bi: V was calculated to be 0.18:1:1.03 based on relative sensitivity factors (RSF) of Cu 2p (5.321), Bi 4f (9.14), and V

2p (2.116). The atomic ratio was more than three times of the bulk concentration (5%), confirming the surface enrichment of CuO species on BiVO₄.

Figure 5-3: XPS survey scan of 5 at.% CuO/BiVO₄ composite (a), and detailed XPS orbit spectra including Cu2p , Bi4f , V2p and O1s (b-e) and VB scan (f).

5.2.3 Optical Properties of CuO/BiVO₄ Composites

As it is obvious in UV-Vis diffuse reflectance absorption spectra of CuO/BiVO₄ composites in Figure 5-4 (a), UV-Vis light absorption of all composite samples were improved with the heavier CuO loading. In closer examination of light absorption in the long wavelength as shown in the inset, a broad absorption band centered at 730 nm was found and it corresponded to the absorption edge of surface deposited CuO, whose bandgap was only 1.7 eV. This emphasized the role of CuO in light absorption enhancement in visible light range, even though there was no apparent red-shift in absorption edge in all composite samples.

Similar observations were reported on CuO/BiVO₄ composites prepared by solution combustion and impregnation approaches [102]. This can be attributed to the relatively low concentration of CuO, too low to be able to alter the crystal structure of BiVO₄ cell and influence the electronic structure of the bandgap. The bandgap of composite samples were estimated to be 2.61 eV extrapolated from Tauc plot in Figure 5-4 (b) and comparable with pure BiVO₄. Hence the additional DOS found within BiVO₄ bandgap during VB scan in Figure 5-3 (f) was more likely due to Fermi level alignment between p-type CuO and n-type BiVO₄, rather than bandgap narrowing by CuO.

Figure 5-4: UV-Vis absorption spectra of CuO-loaded BiVO₄ composites at different atomic percentages (a) and the extrapolated bandgap (b) .

5.3

Evaluation of Photo-activities of CuO/BiVO₄ Composites

5.3.1 PL Emission Spectra and SPV Responses of CuO/BiVO₄ Composites

Charge recombination and charge separation rate within semiconductor upon light excitation were studied by PL emission spectra and SPV responses, respectively. PL luminescence is the result of photon emission when photo-excited holes excited from O 2p valence band recombine with electrons in V 3d conduction band and emit photon in the process, while SPV measures the change of contact potential difference upon illumination. The magnitude of SPV is determined not only by the number of photo-generated carriers, but also the transportation of these carriers to surface states for stabilization [149]. A stronger SPV response therefore demonstrated more photo-generated charges can diffuse to particle surface [152], which in turn signified a higher charge separation efficiency.

In Figure 5-5 (a), PL peak of pure BiVO₄ nano-particles was found at around 500 nm, which was red-shifted from the absorption edge of 466 nm estimated from Tauc plot. The delta was explained by electrons excited from V 3d orbit recombined with holes from hybrid Bi 6s orbit instead of O 2p orbit. There was also a 40 nm delta in PL peak position as compared to the typical value of 540 nm [173]. The small size of BiVO₄ nano-particles can be the cause of this shift. Since PL emission peak is originated from band to band recombination, a shorter wavelength would come from a larger band gap. This is consistent with the band gap extrapolation from Tauc plot (Figure 4-6). The band gap of BiVO₄ was extrapolated to be 2.66 eV from Tauc plot, similar with the reported value for nano-sized BiVO₄ powder prepared in microwave-assisted approach [139], but larger than values commonly reported by hydrothermal approach in the range of 2.4-2.5 eV[145]. One possible explanation was quantum confinement effect rising from small physical size and internal lattice distortion [139]. D. Ressnig et al. measured band gaps up to 2.58 eV for m-BiVO₄ formed by

hydrothermal approach and partially contributed to quantum confinement effect for particles with dimensions < 50 nm [174]. Max Hofmann et al. also attributed the larger band gap of more than 2.40 eV to quantum confinement effect for BiVO_4 synthesized using microwave heating. Their average crystal size calculated by Scherer equation was between 42 to 72 nm [139]. Based on Scherer equation, crystal size of our BiVO_4 nanoparticles (20-36 nm) were below < 50 nm in diameter to have quantum effect kicking in.

With CuO loading, PL peaks of all composite samples were significantly lowered compared with pure BiVO_4 , signifying the great suppression of charge recombination. With formation of p-n heterojunction between surface-loaded CuO and BiVO_4 , CuO served as an effective hole scavengers, while the photo-generated holes at VB of BiVO_4 can transport to VB of CuO, hence charge recombination in BiVO_4 surface was avoided and suppressed. There was continuous reduction in PL peak intensity with increasing amount of surface-loaded CuO. However, it started to trend up in the case 10 at. % CuO/ BiVO_4 , although it was still significantly lower than that of pure BiVO_4 . This could be explained by the agglomeration of CuO introducing undesirable interstates to serve as recombination centres.

In Figure 5-5 (b), BiVO_4 and CuO/ BiVO_4 composite demonstrated a typical n-type semiconductor behavior with positive SPV value upon light illumination. In n-type BiVO_4 , electrons are trapped in surface states leaving holes behind in thermal equilibrium. This leads to an upward band bending and the formation of built-in electric field in surface charge region (SCR). The intensity of built-in electric field is the driving force behind charge separation. Upon irradiation, photogenerated holes are driven towards surface to bring down the net surface charges and hence reduce the band bending. The degree of change in band bending is quantified by SPV. It saturates when the net surface charges become neutral.

In BiVO_4/CuO composite, holes generated from BiVO_4 VB can have the option to migrate to VB of CuO , while in pure BiVO_4 , it can only rely on the built-in electric field in SCR to drive the holes towards surface. At the same time, the intensity of built-in electric field decays with the net charges reduction, and causes the long response time to reach SPV saturation point for BiVO_4 . This was observed in Figure 5-5 (b).

For CuO/BiVO_4 composite, the SPV response in magnitude was higher and more importantly took place instantaneously upon light illumination, as compared to pure BiVO_4 . This signified the fast charge transportation in composite structure, which led to better charge separation and ultimately better photocatalytic performance in practical applications.

Figure 5-5: PL spectra of CuO -loaded BiVO_4 composites at different atomic percentages (a) and SPV response of 5 at. % CuO/BiVO_4 vs. pure BiVO_4 (b) .

5.3.2 Photoelectrochemical (PEC) Activities of CuO/BiVO₄ Composites

Two types of data collection were done on the in-house 3-electrode station, cyclic voltammograms under constant light illumination of 455 nm and periodic photocurrent with chopped light illumination of 455 nm every 10 seconds at constant 0.6 V vs. Ag/AgCl electrode. From the cyclic voltammograms in Figure 5-6 (a), a hysteresis loop was formed for pure BiVO₄ nano-particles as well as 5 at. % CuO/BiVO₄ composite. The negative sweep showed a main cathodic peak at -0.6 V vs. Ag/AgCl reference electrode for stand-alone FTO electrode, which has been attributed to the electroreduction of hydrous tin oxide [175].

Pure BiVO₄ electrode exhibited a typical anodic photocurrent which originated and increased with positive applied potential as expected for n-type semiconductor. The onset potential for anodic photocurrent was found at about -0.52 V vs. Ag/AgCl electrode, which was similar to the flat band voltages reported for BiVO₄ [162, 176]. Under the force of applied potential, electron can migrate to the FTO substrate while the left-behind holes on semiconductor surface can participate in water oxidization and produce peroxide species, giving rise to the anodic photocurrent [162]. When reversing the potential sweeping direction to the negative side, the diminishing of anodic photocurrent was followed by the appearance of a weak cathodic photocurrent at about +0.1 V, whereby similar behavior pattern was seen in other semiconductor electrodes like Co₃O₄/BiVO₄ [162] and ZnO [177]. The adsorbed oxygen and surface peroxide species produced by water oxidation process can accumulate and serve as electron scavengers to drive holes to transport to FTO substrate instead, giving rise to the cathodic photocurrent [162].

The onset potential of anodic photocurrent did not change in the presence of CuO. However, multiple oxidation and reduction peaks (I) appeared in the range of 0 V and -0.1 V vs. Ag/AgCl electrode, evidence of strong redox occurrence. The small yet distinctive peak-to-

peak separation (II) was also evident of fast charge transfer [173], which proved to be beneficial in photocatalytic reactions.

Periodic photocurrent over time under chopped light illumination was collected and summarized in Figure 5-6(b) for pure BiVO_4 nano-particles and 5 at. % CuO/BiVO_4 composite. The photocurrent generation efficiency was significantly enhanced in the presence of CuO by more than 15 times as compared to pure BiVO_4 due to more efficient charge separation, which agreed well with the SPV response and indicated promising enhancement in photocatalytic activities for CuO/BiVO_4 composite. The anodic photocurrent was the net result of charge separation at the electrode/electrolyte interface: photogenerated holes were transferred to the semiconductor electrode surface and captured by OH^- in the electrolyte to participate in redox reactions generating peroxide by-products, while electrons were transferred to the bulk semiconductor [178]. Similar to the findings on $\text{Co}_3\text{O}_4/\text{BiVO}_4$ [162] and CoBi/BiVO_4 [179], a decay of photocurrent generation was observed over time.

The decay was a signal for recombination, where CB electrons would transfer to the electrolyte and recombine with holes. Since the surface recombination current and the hole current toward the electrolyte were of the opposite directions, the measured PEC current would decay until a new steady states. Surface peroxide by-products produced during water oxidation were responsible for this decay as they could accumulate and become recombination centers to suppress photocurrent generation. The photocurrent generation can be restored once peroxide species are reduced back to water by starting CV with cathodic scan [162] or dark experiment [180]. In the cathodic scan, reduction peak at -0.2V vs. Ag/AgCl indicated the occurrence of reduction reactions to reduce the peroxide species back to water and restore the anodic current. In the dark condition and negatively bias, electrons from bulk semiconductor would diffuse to BiVO_4 surface and reduce peroxide species to

water. Another possible explanation for photocurrent decay was the corrosion of CuO/BiVO₄ electrodes due to holes and protons accumulated on the electrode [179].

Figure 5-6: Cyclic voltammograms of BiVO₄ electrode and 5 at.% CuO/BiVO₄ composite electrode swept at 5 mV/s in 0.5 M Na₂SO₄ under constant light of 455 nm (a); and their photocurrent density under chopped light for every 10 seconds (b).

5.3.3 Evaluation of photocatalytic performance by CuO/BiVO₄ Composites

The photo-degradation of RhB was also used to assess the photocatalytic performance of CuO/BiVO₄ composites. As discussed in section 4.31, photo-degradation of RhB takes place in two comparable ways, removal of four methyl groups one by one indicated by the blue shift of absorption maximum and the destruction of conjugated ring structures indicated by the peak intensity drop to less than 70% of initial RhB aqueous solution [131, 156].

From Figure 5-7 (a), RhB without presence of any photocatalyst was used as control group and showed negligible degradation over time, ruling out the possibility of photolysis. Reaction rate of CuO/BiVO₄ composites with different CuO loading were studied by the first order kinetics shown in the inset of Figure 5-7 (a). Reaction constants k calculated for each sample followed the order of 5 at.% CuO/BiVO₄ (0.29460/hr) > 10 at.% CuO/BiVO₄ (0.22650/hr) > 2 at.% CuO/BiVO₄ and pure BiVO₄ (0.07837 and 0.08363/hr). In comparison of CuO loaded samples vs. pure BiVO₄, 5 at. % CuO/BiVO₄ tripled the photo-degradation rate and its photo-degradation efficiency ($1-(C_t/C_0)$) reached 60% in less than 3 hours. This intense reduction of peak intensity resulted from destruction of conjugated ring structure. The blue-shift of absorption maximum λ_{max} towards shorter wavelength observed in Figure Figure 5-7 (b) was the result of partial removal of methyl groups in RhB.

It was also noted there was a decrease in photodegradation efficiency with further increasing of CuO concentration from 5% to 10%, due to the excess loading of CuO to either agglomerate to occupy otherwise photoactive sites or become recombination centres as expected from the increase in PL signals (Figure 5-5(a)).

Figure 5-7: Photo-degradation rate of RhB by BiVO₄ and CuO-loaded BiVO₄ composites at different atomic percentages under light illumination ($\lambda > 420$ nm, light intensity of 1.5 mW/cm²), with the first order reaction kinetics capture in the inset (a) and RhB absorption spectra for 5 at.% CuO/BiVO₄ composite (b).

5.4 Mechanism for Enhanced Photo-activities of CuO/BiVO₄ Composites

The significant enhancement in photo-activities in presence of CuO/BiVO₄ composites including changes in transient SPV response and photocurrent behavior as well as photocatalytic degradation rate of RhB compared to pure BiVO₄ can be attributed to improvement on visible light absorption by incorporation of CuO and charge separation facilitated by the construction of p-n heterojunction.

The photo energy conversion efficiency is known to rely on the photo-generation of EHP on semiconductor catalyst surface upon light illumination. From light absorption perspective, pure BiVO₄ nano-particles with a bandgap of 2.61 eV showed absorption tail spanning to 550 nm. In the presence of CuO loading onto BiVO₄ surface, another absorption band centered at longer wavelength of 730 nm started to appear arising from CuO with small bandgap. The enhancement in light absorption promoted charge generation upon light excitation.

From the charge separation aspect, a more efficient charge transportation system is desirable to sustain enough charge to participant in photo-activities. Charges generated upon excitation can otherwise easily recombine in volume or on surface, forbidding their participation in photo-activities, rendering them useless in photocatalytic reactions. A more effective charge separation path existed in CuO/BiVO₄ composites as expected from the obvious suppression of PL recombination peak and faster and larger SPV response. This can be modeled by the proposed band diagram of p-n heterojunction between p-type CuO and n-type BiVO₄ in Figure 5-8.

Figure 5-8: Proposed band diagram of p-n heterojunction between p-type CuO and n-type BiVO₄ before contact (a) after contact and visible-light driven photocatalytic reactions associated with the photo-generated EHP (b).

The following equations were used to construct the relative band edge positions of both CB and VB, respectively [170]:

$$E_{CB} = X - E^e - 0.5E_G \quad (5-1)$$

$$E_{VB} = E_{CB} + E_G \quad (5-2)$$

where X = the absolute electronegativity (*ca.* 5.81 eV for CuO and 6.035 eV for BiVO₄) [181, 182]; E^e = free electron energy (*ca.* 4.5 eV), E_G = semiconductor bandgap energy, (1.70 eV for CuO and 2.61 eV for BiVO₄). As a result, the band structures for CuO and BiVO₄ were proposed in Figure 5-8 (a) based on the predicted band edge positions on hydrogen scale. Fermi level in p-type CuO is closer to VB as a result of higher concentration of holes present in VB than electrons in CB and vice versa for n-type BiVO₄ whereby its Fermi level is closer to CB. When in contact, holes in VB of CuO would diffuse across interface and neutralize with the excess of electrons from CB of BiVO₄. As a result, a charge depletion region is formed with a built-in electric field pointed from BiVO₄ to CuO. At thermal equilibrium, Fermi level of both CuO and BiVO₄ are aligned with an energy barrier present in CB of BiVO₄ as depicted in Figure 5-8 (b). Under the force of built-in electric field,

holes generated from VB of BiVO₄ can be accelerated and migrate to VB of CuO, while electrons generated from CB of BiVO₄ are prohibited to migrate to CB of CuO by the existence of energy barrier in CB of BiVO₄. The net result would be charge separation obtained on BiVO₄ surface with the formation of heterojunction. The effective charge separation leads to higher PEC and photocatalytic efficiency. The separated holes and electrons can then engage adsorbed oxygen or dissociated hydroxyl from water to form reactive oxygen species (ROS) including $O_2^- \cdot$ and $OH \cdot$ radicals. These ROS with strong reduction-oxidation (redox) power are responsible for the acceleration of photocatalytic performance to either reduce or oxidize the adsorbed pollutants with suitable redox potential by undergoing a series of charge transportation to accomplish mineralization.

5.5 Concluding Remarks

From works done previously on pure BiVO₄ nano-particles, mechanochemical high energy ball milling approach has proven itself to be an effective way to produce BiVO₄ fine particles to be a promising visible-light driven photocatalyst. However, its photocatalytic efficient was limited by the known poor charge separation in BiVO₄. CuO/BiVO₄ composite with formation of p-n heterojunction was then proposed in this work to further enhance the photocatalytic performance, and synthesized by high energy ball milling and impregnation approach with various CuO concentrations. The objective was to find the optimized composite that can maximize charge separation.

5 at. % loading of CuO demonstrated the best photo energy conversion efficiency among all composites. 15 times larger photocurrent was generated than that of pure BiVO₄. And 3 times faster photocatalytic degradation rate of RhB upon weak outdoor light simulation by both methyl group removal and destruction of ring structure.

The incorporation of CuO onto BiVO₄ did not alter the monoclinic scheelite structure of BiVO₄ as confirmed by XRD and Raman analysis. Surface Cu concentration calculated from XPS analysis showed a much higher ratio than the bulk one, indicating the incorporation of CuO onto BiVO₄ was a surface deposition process. Surface loaded CuO helped to bring up visible light absorption to nearly 800 nm due to its small bandgap and evidenced by UV-Vis absorption and XPS VB spectrum. This was beneficiary to charge generation. The charge separation improvement in the composite was evident in PL recombination suppression and SPV studies. It was achieved by the formation of p-n heterojunction to facilitate charge separation on BiVO₄ surface. The band structure and possible charge transportation path in CuO/BiVO₄ composite was proposed to demonstrate the charge separation in the composite system. In conclusion, the enhancement of photo energy conversion efficiency in CuO/BiVO₄ composite structure was the combined effect of enhanced visible light absorption and formation of p-n heterojunction to promote charge separation.

CHAPTER 6 BiVO_4 Thin Films via Spin-coating

6.1 Background

For practical utilization process, photocatalytic nano-particles in large volume of water solution face great challenge in recycling involving post-usage separation and recovery, which requires extra financial costs and human resources in disposition of water solution. Photocatalyst existing in thin film however does not require such resource allocation. It provides the opportunity to fabricate highly functional thin film coating with photocatalytic capability and can be applied in large surface and easy for recycle with the growing development in thin film deposition techniques. m- BiVO_4 thin film has been reportedly fabricated by dip-coating [183], spin coating [184], combustion synthesis [185] and reactive ballistic deposition (RBD) by bismuth and vanadium co-evaporation in oxygen ambient [186]. In these reported work, a relatively high calcination temperature of 400°C to 500°C was required to obtain the desirable m- BiVO_4 . Visible light absorption was achieved up to 500 nm to 516 nm, corresponding to a bandgap of 2.4 eV to 2.45 eV. The direction to go is to fabricate thin film with similar or better photocatalytic performance which requires lower post anneal temperature and is able to absorb longer wavelength in visible light range.

In this work, m- BiVO_4 thin film was successfully fabricated by spin coating of sol-gel solution and exhibited photo response of up to 520 nm. Thermal analysis by differential thermal analysis (DTA) / Thermogravimetric analysis (TGA) was conducted on the sol-gel sample, phase change reaction started to occur at as low as 250°C. The photocatalytic capability of thin film was discussed and explained, supported by more comprehensive characterization on the thin film samples.

6.2 Material Characterizations of BiVO₄ Thin Films

6.2.1 Differential Thermal Analysis (DTA) / Thermogravimetric Analysis (TG)

In this case, both DTA/TGA were conducted on B-V sol-gel solution. In Figure 6.1, gradual weight loss of approximately 10% was observed at temperature ramp up and centered at 100°C due to the removal of moisture with two distinctive endothermic peaks at less than 120°C. Another 30% weight loss at 180°C accompanied by three exothermic event from 150°C to 180°C followed by a final 50% weight loss at 250°C can be attributed to the citrate decompose and combustion [185]. A series of exothermic event occurred >250°C, related to the change in crystal structure. As a result, 300°C indicated a complete pyrolysis and the higher temperature from 350°C to 500°C was chosen to study the annealing effect on crystallinity and photo-activity.

Figure 6-1: DTA/TGA of the dried gel.

6.2.2 Crystallography and Morphology Studies of BiVO₄ Thin Films

XRD pattern of the prepared BiVO₄ thin films in Figure 6.2 revealed that monoclinic structure was formed as indicated by the peak at 28.8° (star labeled), while other major peaks came from the underlying FTO substrate. m-BiVO₄ phase started to appear when annealed at as low as 350°C. The peak intensity was low, due to X-ray being able to penetrate BiVO₄ thin film and pick up the strong signal from the FTO substrate. The broad peak width compared with BiVO₄ particles implied poorer crystallinity of BiVO₄ thin film, and a much weaker photo-activity would be expected. The peak intensity gradually increased signifying the improvement on crystallinity as shown in Figure 6-2 right section.

Figure 6-2: XRD spectra of BiVO₄ thin film. Inset showed the peak from m-BiVO₄ (040).

The crystal formation was further confirmed by Raman spectrum, whereby all the characteristic bands for monoclinic BiVO₄ were observed. In particular, band positioned at 702 cm⁻¹ corresponding to V-O vibration bond, shifted towards lower frequency with increasing annealing temperature up to 450°C before it was red-shifted at 500°C as shown in Figure 6-3. The blue-shift in band position indicated an increase in V-O bond length exerting

more distortion in local structure from the surrounding VO_4^{3-} tetrahedron to Bi^{3+} cation from lone-pair electrons that resulted in a higher degree of hybridization in VB from Bi 6s and O 2p orbit. This ultimately accelerated hole movement and became beneficiary for charge separation. The degree of distortion was in the order of $450^\circ\text{C} > 400^\circ\text{C} > 350^\circ\text{C} > 500^\circ\text{C}$ annealed thin film. At 450°C , the blue shift reached maximum. As a result, fastest photo-response would be expected for BiVO_4 thin film annealed at 450°C and was re-confirmed in subsequent photo-activity studies, including SPV response, photocurrent generation and RhB dye degradation as shown in Figure 6-6.

Figure 6-3: Raman spectrum of BiVO_4 thin film annealed at different temperatures.

Combining the XRD and Raman spectrum analysis showed m- BiVO_4 thin film was successfully fabricated by spin coating and post anneal at temperature as low as 350°C . Based on the AFM image in Figure 6-4, the fabricated BiVO_4 thin film was continuous and smooth (surface roughness < 50 nm). From Figure 6-5, the fabricated BiVO_4 thin film was able to absorb light with wavelength larger than 500 nm.

Figure 6-4: AFM of 450°C annealed BiVO₄ thin film.

Figure 6-5: Transmittance of BiVO₄ thin films annealed at different temperature.

6.3 Photo-activity Studies of BiVO₄ Thin Films

In Kelvin Probe-based SPV measurement, samples with size of 2 cm by 2 cm were loaded into the KP chamber and kept in dark condition overnight to reach dark equilibrium prior to measurement. LED light wavelength was fixed at 455 nm and was repeatedly switched on and off for an interval of 180 seconds. Contact potential difference varied accordingly with light exposure. In the presence of photo-excitation, photo-generated holes migrated to VB

edge to reduce band bending as illustrated earlier in Figure 2-11 (a) and (b). As a result, CPD (light) was reduced and positive SPV value was produced as determined in the Equation (3-14), $SPV = CPD(\text{dark}) - CPD(\text{light})$. The large amount of carriers generated and transported to surface states defined the magnitude of SPV response. The transient SPV showed that 450 °C annealed thin film exhibited the largest SPV response, 90 mV in value and at least 3 times as large as the rest of annealed thin films, as shown in Figure 6-6 (a). The amount of SPV was in the order of $450^{\circ}\text{C} > 400^{\circ}\text{C} > 350^{\circ}\text{C} > 500^{\circ}\text{C}$ annealed thin films. This followed the degree of lone-pair distortion in the local structures, revealed in Raman band position shift and represented the order of charge separation efficiency. Higher degree of asymmetry enhanced hole mobility that would accelerate hole migration to BiVO_4 electrode to achieve charge separation, which in turn determined the speed and magnitude of SPV response. In the absence of light, the band bending would gradually restore by means of charge recombination, as shown by a decay of SPV value in Figure 6-6 (a). Gradually there was a shift in CPD baseline with more cycling at annealing temperatures except 450 °C, however, ΔCPD (SPV) remained constant. Suspected root cause was photogenerated electrons being trapped at surface states and causing more band bending each time, although the majority of them were transferred to the bulk semiconductor. At 450 °C, we attributed the missing of this phenomenon to the lack of these undesirable surface states which can become recombination centers and were less favorable for photocatalytic activities.

In the three-electrode electrochemical station, the incident light source was the same as in KP set-up. Nitrogen was purged into 0.5 M sodium sulfate solution for 15 minutes prior to measurement. The Pt electrode served as counter electrode, while the reference electrode was made of Ag/AgCl in 3M KCl. The generation of anodic current at 0.6 V vs. Ag/AgCl, as shown in Figure 6-6 (b), revealed the migration of photo-generated electrons towards the FTO substrate and the transfer of photo-generated holes onto BiVO_4 electrode surface to

react with surface absorbents. The amount of photocurrent generated was in order of $450^{\circ}\text{C} > 500^{\circ}\text{C} > 400^{\circ}\text{C} > 350^{\circ}\text{C}$ annealed thin film. This did not exactly follow the degree of local structure distortion as deduced from Raman spectrum or charge separation efficiency as deduced by SPV response. This implied other factors, such as surface chemistry, surface morphology and crystallinity could play a more important part in photocurrent generation besides facilitating charge transportation. The 500°C annealed thin films showed the best crystallinity among all samples, which would help in photocurrent generation by reducing recombination sites due to crystal defects. A similar trend in photocatalytic test would also be expected. Like the photocurrent generation, it is a surface- reaction dominated process as well.

As shown in Figure 6-6 (c), the photo-degradation rate of RhB followed the same order of photocurrent, $450^{\circ}\text{C} > 500^{\circ}\text{C} > 400^{\circ}\text{C} > 350^{\circ}\text{C}$ annealed thin film. The reaction kinetics rate coincided well with photocurrent generation efficiency where 450°C annealed thin films exhibited the best photocatalytic performance. The organic pollutant degradation was a complex reaction system which was affected by multi-factors, among them charge separation was only one of the key factors; this explained the discrepancy between RhB photo-degradation rate and SPV response. This result re-confirmed that SPV response was an effective and direct indicator of charge separation efficiency.

Figure 6-6: SPV response (a), photocurrent (b) and RhB dye degradation (c) of BiVO₄ thin films annealed at different temperatures from 350°C to 500°C.

To further understand the SPV behavior and photocurrent generation with interaction of light spectrum, incident light with chopped wavelength from 365 nm to 625 nm was used to repeat SPV and photocurrent measurements for the 450°C annealed thin film. As shown in SPV spectrum in Figure 6-7, clear cut of SPV response was observed at 525 nm, which corresponded to a bandgap value of 2.38 eV, close to the value in other reported work [117].

Figure 6-7: SPV spectrum of 450°C annealed thin film.

In the 2nd PEC measurement, similar to the observation in SPV spectrum the onset of photocurrent generation also laid around 520 nm as shown in Figure 6-8. Together this demonstrated that the annealed thin film was physicochemical active up to 520 nm and showed great potential to be applied on surfaces for self-cleaning purpose.

Figure 6-8: Photocurrent generated in 450 °C annealed thin film at different wavelength.

6.4 Concluding Remarks

m-BiVO₄ thin film with the desirable crystal plane of (040) was successfully fabricated by the method of spin coating with post anneal. m-BiVO₄ was achieved at anneal temperature as low as 350°C, lower than most reported works. The temperature effect of post anneal was carefully examined to determine 450 °C as the optimum calcination temperature. It exhibited the fastest SPV response and most efficient photocurrent generation as well as RhB dye degradation. This can be largely attributed to the efficient charge separation within the thin film due to lone-pair distortion in local crystal structure as indicated by the blue-shift in Raman spectrum giving rise to hole mobility enhancement. With further examination of wavelength effect to SPV response and photocurrent generation of the 450 °C annealed thin film, it turned out that the as-fabricated thin film started to be photo-active at 520 nm, which was close or better than some of the reported works[178,179].

CHAPTER 7 Conclusion and Future works

7.1 Conclusions

This thesis work has demonstrated both m-BiVO₄ nano-particles and thin films as promising visible-light driven semiconductor photocatalyst for environmental remediation.

In particular, BiVO₄ nano-particles were synthesized mechanochemically by high energy ball milling. The throughput was more than 90%, much higher than the popular hydrothermal approaches and made mass-production feasible. The micro-stress exerted to the BiVO₄ crystal cells from ball milling process made post anneal treatment a must to have. The complete synthesis of BiVO₄ nano-particles was developed to include the ball milling process itself from Bi₂O₃ and V₂O₅ powders followed by 1-hour heat treatment in dry air from 300°C to 400°C to reduce and repair crystal damages by recrystallization. The obtained particle size of as-milled BiVO₄ in the absence of heat treatment was around 20 nm with associated surface area of 17 m²/g, which was superior to most BiVO₄ synthesized using various approaches. XRD and Raman confirmed the successful formation of monoclinic scheelite BiVO₄ (m-BiVO₄) with and without post anneal. With post anneal, the grain first started to grow slowly from 20 nm to 26 nm up to 400 °C with associated surface area down to 10 m²/g, which was still better than most of reported works. The grain growth became accelerated at elevated anneal temperature and almost doubled the size at 600 °C, with associated surface area down to 1 m²/g, as compared to as-milled powders. This defined the ceiling anneal temperature in order to produce nano-sized particles. As-milled BiVO₄ nano-particles showed no photo – activity explainable by the recombination centers originated from lattice distortion from ball milling process. Anneal temperature at as low as 350°C was sufficient to render them photo-active by improving the crystallinity to reduce recombination. A higher degree of crystallinity was achieved by further increasing the anneal temperature. Direct evidence on

charge separation efficiency was provided by a custom-built KP system to measure SPV response over time upon light irradiation. The photocatalytic performance of BiVO₄ nano-particles was evaluated by RhB dye degradation. A full mineralization was achieved by prolong exposure to light. The optimum BiVO₄ nano-particles were obtained with 400°C anneal for 1 hour with at least 2 times faster reaction rate compared to other annealed samples, largely attribute to the good trade-off between surface area and crystallinity.

After obtaining the optimum annealing temperature, m-BiVO₄ nano-particles were surface coated with CuO nano-particles by high energy ball milling and impregnation approach. The purpose was to further extend visible light absorption at longer wavelength (>700 nm) and promote charge separation efficiency by the formation of p-n heterojunction. A possible charge transportation and separation path was provided based on the proposed band diagram to explain the enhanced photo-efficiency compared to stand-alone BiVO₄ nano-particles. The enhancement showed 15 times large photocurrent and triple photocatalytic oxidation rate. The incorporation of CuO was confirmed by XPS surface chemistry study showing its atomic concentration tripled at surface as against the bulk, signifying CuO enrichment on surface. The HRTEM revealed the uniform dispersion of spherical shaped CuO with an average diameter of 5 nm on BiVO₄ surface. The enhancement in charge separation and suppression of charge recombination were confirmed by the fast and large SPV response as well as the reduction in PL intensity. CuO of 5% atomic concentration showed the best photocatalytic rate among all, mainly due to the efficient charge separation without the over load of CuO that will block the surface reaction sites.

Comparing our BiVO₄ and CuO/BiVO₄ with the most recent development on BiVO₄ heterojunction as listed in Table 7-1, high energy ball milling turned out to be an effective way to produce highly active BiVO₄ nanoparticles. The choice of the 2nd semiconductor material to form p-n heterojunction with BiVO₄ greatly affected the turnover rate of BiVO₄ –

based composite. Our CuO/BiVO₄ composites had a turnover rate of 3, which was comparable with BiVO₄/Ag/rGO by hydrothermal growth [187], but lower than CdS/BiVO₄ heterojunction which exhibited much higher turnover rate of more than 10 times [188]. It is part of the future work recommendations to explore other sources of semiconductor to form heterojunction with BiVO₄ by high energy ball milling to enhance the overall efficiency.

Table 7-1: Comparison of our BiVO₄ and CuO/BiVO₄ with the most recent development on BiVO₄ heterojunction

Materials	Synthesis method	Reaction constant (normalized to the same incident power intensity of 50 mW/cm ² , h ⁻¹)
BiVO ₄ and CuO/BiVO ₄	High energy ball milling	BiVO ₄ : 0.08363 BiVO ₄ : 0.2946
BiVO ₄ and	One-Pot in Situ	BiVO ₄ : 0.059
BiVO ₄ /Ag/rGO[187]	Hydrothermal Growth	BiVO ₄ /Ag/rGO:0.129
BiVO ₄ and	Electrospinning method	BiVO ₄ : 0.066
CdS/BiVO ₄ [188]		CdS/BiVO ₄ : 0.792

Although BiVO₄ powder system was well construed as above, thin film option is always more appealing when it comes to practical usage as it can be more easily implemented onto self-cleaning surfaces and require much less effort in recycling. BiVO₄ thin film with monoclinic scheelite structure was also successfully synthesized by a simple spin coating approach at calcination temperature as low as 300°C, lower than the most of reported works. Post annealing from 350°C to 500 °C for 1 hour in dry air was applied to improve the crystallinity. SPV response confirmed that as-fabricated thin film started to be photo-active at 520 nm. BiVO₄ thin film annealed at 450 °C exhibited the fastest SPV response of at least 3 times larger than BiVO₄ annealed at other temperatures and the most efficient photocurrent

generation of at least 5 times larger. The enhancement in 450 °C annealed thin film was attributed to the lone-pair distortion in local crystal structure as revealed by the blue-shift in Raman band position. The photocatalytic performance was also studied and established to be one of few reported works on direct use of BiVO₄ thin film for photocatalytic reaction.

7.2 Future Work Recommendations:

This thesis work has laid the ground work for the following future works:

7.2.1 Continual Improvement on KP Measurement System

In this work, it was demonstrated that KP system was able to measure SPV response under constant/chopped light illumination at different wavelength. However, a more comprehensive SPV spectrum can be obtained with incorporation of monochromator to provide insight of SPV response in a broader light spectrum. Other system improvements like reducing noise level in the CPD measurement and increasing sampling frequency can be further explored to make transient SPV study more accurate.

7.2.2 Continual Improvement on Charge Separation for BiVO₄ Nano-particles Synthesized by High Energy Ball Mill Approach

In this work, the formation of p-CuO/n-BiVO₄ heterojunction was successfully demonstrated by high energy ball mill approach. Other p-type semiconductors, such as Co₃O₄, proven to be efficient by heteronuclear complexing approach [31] and Bi₂O₃, proven to be efficient by homogeneous precipitation method [34] are worth exploring. Other than p-type semiconductors, noble metal such as Au and Ag [30, 32] are also of interest. The ease in the preparation procedure and its high throughput make high energy ball milling appealing for practical applications. Hence it is worthy to explore other semiconductor composite structure for enhanced photo energy conversion efficiency.

7.2.3 Extended works on BiVO₄ Thin Film Fabrication

This work has merely demonstrated an easy and effective approach to synthesize BiVO₄ thin film for photocatalytic applications; however the work is far from complete. Firstly, different precursors of Bismuth and Vanadium can be used to study the effect on surface morphology and particle size control as researches did in the line of powder synthesis. Secondly, thin film fabrication of BiVO₄ coupling with p-type semiconductor or noble metal of choice is worth trying for further enhancement in photocatalytic efficiency

Author's Publication

Journal Papers

1. L. Zhang, **Q. Luo**, X. F. Chen, M. S. Tse, O. K. Tan, et al., “ Mechanochemically synthesized CuO/m-BiVO₄ composite with enhanced photoelectrochemical and photocatalytic properties”, *RSC Adv*, vol. 6 (69), pp. 65038-6504, 2016.
2. **Q. Luo**, L. Zhang, X. F. Chen, O. K. Tan , K.C. Leong, “Mechanochemically synthesized m-BiVO₄ nano-particles for visible light photocatalysis”, *RSC Adv*, vol. 6 (19), pp. 15796-15802, 2016.

International Conferences

1. **Q. Luo**, X. F. Chen, M. D. Han, O. K. Tan, M. S. Tse, *RhB degradation and Photo-response performances of sol-gel BiVO₄ thin films*, *International Conference on Materials for Advanced Technologies(ICMAT)*, Singapore 2013.
2. **Q. Luo**, X. F. Chen, M. D. Han, O. K. Tan, M. S. Tse, *Preparations and Photo Response Studies of Photocatalytic BiVO₄ Thin Films*, 4th International Conference on Semiconductor Photochemistry (SP4), Prague 2013
3. **Q. Luo**, X. F. Chen, M. D. Han, O. K. Tan, M. S.Tse, *Influence of doping and surface loading CuO on photocatalytic properties of high energy ball-milled BiVO₄ nano-particles*, *International Conference of Young Researchers on Advanced Materials*, Singapore 2012.
4. **Q. Luo**, X. F. Chen, M. D. Han, O. K. Tan, M. S. Tse, *Photocatalytic degradation of RhB by high energy ball-milled BiVO₄ nano-particles*, 5th MRS-S Conference on Advanced Materials, Singapore 2012.

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