2017

Synthesis of Bismuth Ferrite for Photoelectrochemical Water Splitting

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Synthesis of Bismuth Ferrite for Photoelectrochemical Water Splitting

Fagr Albagle

**Thesis submitted to the
Benjamin M. Statler College of Engineering and Mineral Resources
at West Virginia University
in partial fulfillment of the requirements for the degree of Mechanical
Engineering**

**Master of Science
in
Mechanical Engineering**

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**Morgantown, West Virginia
2017**

Keywords: solar energy, photocatalysis, water splitting, hydrogen generation,
photoelectrochemical, bismuth ferrite oxide, semiconductor

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ABSTRACT

Synthesis of Bismuth Ferrite for Photoelectrochemical Water Splitting

by Fagr Albagle

Converting solar energy to chemical fuels is one of the alternative solutions to address the sustainable energy challenges in the world. This can be achieved through photocatalytic conversion of solar energy to chemical energy stored in hydrogen (H_2) via photoelectrochemical water splitting. It still remains a significant challenge in developing semiconductors as photoelectrodes for photoelectrochemical water oxidation. The objective of this project is to develop and synthesize a semiconductor-based material for photoelectrochemical water splitting. A perovskite bismuth ferrite oxide ($BiFeO_3$) thin film has been synthesized and deposited onto a fluorine-doped tin oxide (FTO) coated glass substrate by the sol-gel process. The thickness of thin film has been tuned by applying different spin coating cycles. The photoelectrochemical properties of the bismuth ferrite oxide (BFO) film have been investigated. The BFO photoanode exhibits the n-type behavior with a flat band potential of 0.36 V versus the reversible hydrogen electrode (RHE). The BFO film possesses a band gap about 2.0 eV, which is favorable for photoelectrochemical water splitting. Among the three BFO thin film samples prepared, five spin cycles achieved the highest photocurrent. The results show that the BFO film photoanode is very stable and capable of generating hydrogen through photoelectrochemical water splitting. However, an improvement in the photocurrent needs to be studied through the use of co-catalyst and metal transition doping. The knowledge obtained from our findings can be used for development of metal oxide based materials for solar fuel generation.

ACKNOWLEDGMENTS

I would like to thank all the people who contributed in some way the work done in this thesis. First and foremost, I must thank my academic advisor Dr. Nianqiang (Nick) Wu, first for accepting me into his group and being part of it throughout my 2 years as gradated student at West Virginia University. His constant guidance, patience, and encouragement for this research project and without his help this thesis would never reached completion.

A Special thanks to Dr. Ayyakkannu Manivannan for his support, help, and motivation and laying out necessary details for the proposed project.

I must also sincerely thank my parents for believing in me and providing me with unfailing support throughout my years of study. Without their support and continuous encouragement, I wouldn't be standing where I am right now. To my siblings and friends, thanks all for keeping up with me and supporting me throughout my academic journey.

I would also like to thank my groupmates, Sujan Kasani, Joey Bright, Peng Zheng, Dr. Haibin Tang, for their considerable help during my Master Study.

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1. INTRODUCTION

1.1. Background

The continuous increase in world population has led to significant growth in the global energy consumption. As reported by the U.S Energy Information Administration, the total world consumption of marketed energy will increase from 549 quadrillion British thermal units (Btu) in 2012 to 629 quadrillion Btu in 2020 reaching 815 quadrillion Btu by 2040, as shown in Fig. 1.1.

Figure 1.1 World Energy consumption from 1990-2040¹

In the past decade more than 80% of the world's overall energy is supplied by fossil fuels ². It is mainly used for transportation, industrial processes, and electricity generation. However, there are noticeable side effects for using fossil fuels as an energy source. When burning fossil fuels,

carbon dioxide is produced and therefore greenhouse gases are released in the atmosphere contributing to global warming which affect climate conditions worldwide ³. In addition, the amount of fossil fuel on the Earth is limited and subjected to depletion ^{3,4}. Based on the current situation, our intention is to find an environmentally friendly, and renewable energy resource to reduce the growing consumption of fossil fuel and therefore reduce the content of any hazardous byproduct released in the atmosphere. There are many alternative energy resources introduced with low or free carbon dioxide emission these include wind power, hydropower, and solar energy, accounting for 1.44%, 6.79%, and 0.45% respectively, of the world total energy consumption as of 2015 shown in Fig. 1.2 ¹⁵. Although wind is considered a free and clean energy source used to produce mechanical power and electricity, it faces difficulties regarding wind storage. Likewise, the major challenge of hydropower is that it is very expensive energy resource and causes geological and ecological damage ³. As a result, a renewable, clean, and inexpensive energy source must be adapted to solve the issues behind climate change and the world's increasing energy demands. Solar energy is considered a promising solution. Converting solar energy to chemical fuels is one of alternative solution to address the world's sustainable energy challenges. Solar energy can be directly converted into solar fuel using photocatalysis via photoelectrochemical water splitting into hydrogen (H_2) and oxygen (O_2) ^{5,6}. The introduction of the first photoelectrochemical device by Fujishima and Honda have opened up a new pathway for developing an alternative fuel resources using solar energy conversion. In a typical photocatalytic water splitting process, a semiconductor absorbs incident light of energy larger than its band gap to excite electrons from the valence band to the conduction band, creating

electron-hole pairs. The excited electron-hole pairs must be separated to drive a redox reaction and split water into H₂ and O₂.

Figure 1.2 World total energy from 2005-2015 (6.97% hydropower, 1.44% wind power, and 0.45% solar energy as of 2015) ¹⁵

Over the past years, many semiconductor-based photocatalysts have been reported for photoelectrochemical water splitting. Among the many studied materials, TiO₂-based photocatalysis is considered an interesting material for water splitting, however its wide band gap limits its absorption to ultraviolet (UV) light only. As a result, numerous work is still being done to develop photocatalytic material with optimal band gap in order to extend the photo-absorption of the material from UV light to visible light. Perovskite metal oxide semiconductors have attracted great interest and is recognized to be a good candidate for solar light responsive photocatalysts due to its narrow band gap and their visible light absorption of the solar spectrum. More specifically, perovskite BiFeO₃ with band gap of ~2.2 eV is expected to be an interesting material for photocatalytic water splitting. Several groups have synthesized different

nanostructures of BiFeO₃ and studied their photoelectrochemical properties. Joshi *et al.* reported the photo-induced water oxidation activity of single crystalline BiFeO₃ nanocubes suggesting that BFO could act as a promising material for photocatalytic applications³⁹. Another group studied the behavior of epitaxial ferroelectric BiFeO₃ thin films via unassisted photocatalytic water splitting where a considerable photocurrent were observed at a magnitude of 10 $\mu\text{A}/\text{cm}^2$ ⁹⁴. Subsequently, BiFeO₃ thin films were prepared via simple chemical vapor deposition proving the high photocurrent density of BFO films for water oxidation⁶³.

1.2. Motivation and Objectives

Solar energy, the most abundant and clean energy source, can provide enormous power to meet the energy demand needed for our future. Among the many solar energy methods, solar-to-hydrogen conversion is known to be a promising process where clean fuel is produced, stored, and transported with zero emission. The research and development of solar hydrogen fuel is of great interest, therefore, many national laboratories such as (National Renewable Energy Laboratory and Sandia National Laboratories) of the Department of Energy (DOE) have been extensively working on hydrogen production from renewable energy sources^{7,8}.

Photoelectrochemical (PEC) water splitting using semiconductor-based photocatalyst is considered one of the many routes used for hydrogen fuel production^{9,10}. In particular, PEC water splitting is a process in which solar energy is converted into chemical energy using natural solar light (i.e. sunlight) and water only to produce clean H₂ fuel⁹⁻¹¹. The basic principle of photoelectrochemical water splitting is illustrated in Fig. 1.3 and briefly described as follows. When a semiconductor photocatalyst is irradiated by sunlight or illuminated light source, it

absorbs the photons with energy greater than the band gap (E_g). Next, electrons are excited to the conduction band leaving holes in the valence band. These excited electrons and holes separate and migrate to the surface of the photocatalyst and used as reducing and oxidizing agents to produce H_2 and O_2 respectively^{10,13-14}. Though, after excited charges are generated a portion of photogenerated charge carriers is subjected to both bulk and surface recombination, which limits the solar-to-chemical energy conversion efficiency⁸⁹. Hence, efficient electron-hole separation, fast electron-hole transport, and less charge recombination are three important fundamentals must be considered when designing an efficient photocatalysis for water splitting. In order to maintain an efficient water splitting process, the bandgap of the semiconductors should be larger than the water electrolysis potential of 1.23 eV and less than 3.0 eV to harvest visible light and possess proper band structure. Moreover, the conduction band must be lower than (0 V vs. RHE), and the valence band must be higher than (1.23 eV vs. RHE)^{13,14}.

Figure 1.3 Processes in photocatalytic water splitting

For the semiconductor to act as photocatalyst for water splitting, it must follow certain requirements. First, the semiconductor must have a sufficiently narrow bandgap to harness visible light of the solar spectrum. Second, the ability to reduce charge recombination during the reaction. Third, maintaining high efficiency of charge separation. Based on the above conditions, semiconductor-based materials act as promising photocatalysis used to overcome the three barriers including charge recombination, poor charge separation, and large band gap. Therefore, $BiFeO_3$ was chosen as semiconductor-based photocatalytic material to gain more understanding of the photocatalytic activity of perovskite metal oxides materials and their applications in photoelectrochemical water splitting. As it is known for its narrow bandgap (~ 2.0 eV) comparing

to other transition metal oxide semiconductors, also its ability to absorb light in the visible light region of the solar spectrum. Therefore, this study was carried out to develop and synthesize perovskite BiFeO_3 thin film photocatalyst for solar hydrogen generation. Also to provide more understanding of BiFeO_3 material, its optical characteristics and the photocatalytic activity in PEC water splitting. We were able to fabricate BFO thin film using sol-gel method and test the photoelectrochemical performance of this material. Our results indicate that BFO semiconductor is very stable which acts as a promising material for long-term solar energy applications.

1.3. Significance

Of all energy sources provided in the industries, solar energy have been proven to be the most reliable and clean energy source. The ultimate goal of our research is to find a stable semiconductor material with optimum band gap used as photocatalyst to generate hydrogen fuel via photoelectrochemical water splitting. In the present study, the synthesis of BiFeO_3 and its photoelectrochemical water splitting properties are investigated. This work will gain fundamental understanding of perovskite bismuth ferrite oxide. The knowledge obtained will promote the application of BiFeO_3 thin films in solar-to-hydrogen conversion.

2. LITERATURE REVIEW

2.1. Introduction

Hydrogen generation is a key source for carbon-free environment and can be produced without any hazardous byproduct. The reaction, as shown in Equation (2.1) occurs when hydrogen reacts with oxygen, where water is then formed as the only byproducts using semiconductor catalysis to achieve water-splitting reaction¹⁸.

Currently, most of the hydrogen produced is based on fossil fuel such as steam reforming process, whereas only 4% is produced using water electrolysis^{18,21}. Until now two main processes are investigated and studied for photocatalytic production of hydrogen fuel. The first approach is splitting water into hydrogen (H₂) and oxygen (O₂) by converting solar energy into chemical energy. The second approach is photo-reforming of organic compounds¹⁸. Our main focus is to develop an effective photocatalyst for water oxidation to generate clean hydrogen fuel using water and sunlight only. The generated hydrogen fuel can be then stored and used for many energy applications.

Photoelectrochemical water splitting associated with semiconductor photocatalysts is a promising technology for our future, since large quantities of clean hydrogen fuel can be produced. The first experiment of photocatalytic water splitting was discovered by Honda and Fujishima using TiO₂ and Pt electrodes irradiated with UV light to drive the water splitting reaction^{16-17,19-22}. Since then, the search for semiconducting photoelectrode materials have gained great interest especially for energy applications and solar fuel production⁹². Semiconducting

materials such as oxides, sulfides, (oxy)nitrides, and III-V compounds have shown promise for PEC water splitting. Yet, these materials have to satisfy many requirements in order to achieve efficient solar hydrogen generation. More detailed overview on PEC water splitting will be discussed in section 2.3.

2.2. General introduction to hydrogen fuel generation

85% of the global energy supply comes from fossil fuels, as a result greenhouse emission such as carbon dioxide (CO_2) emissions have been contributed to global warming which have serious effect on our environment²⁴. The use of energy is a key factor for the development of the modern-day technology. Since energy production from fossil fuels results in increasing climate change and greenhouse gases, it is our mission to find an alternative solution to decrease the use of fossil fuels. This can be achieved by relying on the development of other hydrogen generation technologies using renewable energy sources.

Here comes the use of solar energy as an ideal type of renewable energy source due to its availability in most parts of the world as shown in Fig. 2.1. Since hydrogen acts as an ideal energy carrier it appears to be the best solution for reaching a carbon-free society and its production plays an important role in achieving an environmentally friendly and sustainable energy source.

Our intention is to use solar energy for generating solar hydrogen fuel from water, sunlight, and semiconductor photocatalyst. There are many benefits for using hydrogen as an energy carrier listed as follows²⁴, a) ease of production from water with no emissions, b) high energy conversion efficiencies, c) abundance, d) different forms of storage. As previously

mentioned, the world's hydrogen is currently produced from fossil resources such as coal, natural gas, and steam reforming process, in addition to renewable resources such as biomass, wind, solar and many other resources^{3,21,25-26}. Using steam reforming process and fossil resources for hydrogen production will result in the use of excess energy as well as producing large amount of CO₂ as byproduct. Therefore, solar energy is considered a promising energy source used to produce clean hydrogen fuel.

Figure 2.1 The world map of potential utilization of solar power²⁷

2.2.1. Hydrogen fuel production from fossil fuels

Hydrogen is currently produced from most of the fossil fuels, mainly natural gas and coal, where carbon dioxide is produced as by-product. Hydrogen production from natural gas is divided into three different chemical processes such as steam reforming, partial oxidation, and

autothermal reforming. Steam reforming process involves two steps. The first step involves the conversion of methane (used as fuel) and water vapor into hydrogen and carbon monoxide as the byproduct as shown in Equation 2.2, at temperatures (700 °C-900 °C) and pressure of (3-25 bar). The second step shown in Equation 2.3 involves the shift reaction where carbon monoxide (CO) reacts with more steam to produce more hydrogen and carbon dioxide (CO₂)^{3,25-2}.

2.2.2. Hydrogen fuel production from solar energy

Hydrogen fuel produced from solar energy can be divided into four different categories: (1) thermochemical water splitting, (2) photobiological water splitting, (3) photovoltaic (PV) electrolysis, and (4) photocatalytic water splitting²⁴⁻²⁵. Among the different hydrogen generation processes, we will mainly focus on the use of photocatalytic water splitting process with brief description of the other technologies.

2.2.2.1. Thermochemical water splitting

The basic principle of thermochemical water splitting is to use high temperature heat (500 °C-2000 °C) in addition to water and some catalyst for example, ZnO to drive the chemical reaction as shown in Equation 2.4 and 2.5. As a result, hydrogen and oxygen are produced and all chemical used except for water can be recycled and used in each reaction^{3,24,28}

2.2.2.2. Photobiological water splitting

This process involves the use of sunlight and specialized biological systems such as green microalgae or cyanobacteria to split water into oxygen and hydrogen ions. Photobiological water splitting technology is in the very early stages of research and it faces some challenges regarding hydrogen production. Therefore, researchers are still working hard to develop and increase the rate of hydrogen production using this process.

2.2.2.3. Photovoltaic (PV) electrolysis

Electrolysis of water is one of the methods used for hydrogen production from renewable resources. This process involves the use of electricity to split water into hydrogen and oxygen²⁹. Hydrogen produced via electrolysis of water result in zero greenhouse emission.

2.3. Principle of photocatalytic water splitting

Photocatalytic water splitting process is the conversion of solar energy into chemical energy used to drive the production of hydrogen and oxygen. This process is achieved when the photocatalyst absorbs natural solar light (i.e. sunlight) while dispersed in water, then electron-hole pairs migrate to the surface of the photocatalyst to generate and produce H₂ and O₂.

In the early 1970s, Fujishima and Honda discovered the first photoelectrochemical water splitting experiment using TiO₂ electrode^{17-19,22}. In this experiment, TiO₂ and platinum (Pt) electrodes were irradiated with UV light so electron and hole pairs can be generated. The photo-generated electrons reduced water to form H₂ on the Pt counter electrode and holes oxidized water to produce O₂ on the TiO₂ working electrode. Ever since the discovery of photoelectrochemical water splitting, the search of an efficient photocatalytic material for water

splitting under visible light is still on going. When dealing with photocatalytic materials for water splitting, three main points must be taken into consideration, (1) narrow band gap of semiconductor material to harness visible light, (2) reduction of electron/hole pairs recombination, and (3) increase the efficiency of charge separation³²⁻³³. Thus, many studies and researches have been done on finding an efficient material to overcome the three points mentioned above.

2.3.1. Process of photocatalytic water splitting

For a general photoelectrochemical (PEC) water splitting, light is absorbed by semiconductor photoelectrode where electron-hole pairs are created and separated by internal electric fields if the photon energy is greater than or equal to the semiconductor bandgap (E_g) energy¹⁴. This absorption creates holes in the valence band (VB) of the semiconductor and excited electrons on the conduction band (CB) of the semiconductor. Later, holes drive water oxidation reaction where oxygen (O_2) is formed at the photoanode and electrons drive water reduction reaction where hydrogen (H_2) is formed at the photocathode. The reaction involves separating the oxidation and reduction processes into two half reactions, where photo-generated electrons (e^-) and holes (h^+) migrate to the surface of the photocatalyst without recombination^{13,14}.

Equations (2.6) and (2.7) shows the two half-cell reactions of both oxidation and reduction process, respectively with the corresponding standard reduction potential (E^0) with respect to the standard hydrogen electrode (SHE). The overall reaction is shown in Equation (2.8) where the positive Gibbs energy (ΔE^0) is an indication that water splitting is a thermodynamically uphill process³⁴.

2.3.2. Fundamental theory of photocatalytic water splitting

Many researchers have been extensively working on the fundamentals of photocatalysis and its application in the production of hydrogen fuel, due to its crucial necessity in solving global energy and environmental issues associated with fossil fuel. Therefore, tremendous effort have been devoted to develop stable and efficient semiconductor-based photocatalytic materials that can absorb visible light and split water at the same time. To achieve an efficient water splitting reaction, there are many requirements to be considered when choosing the appropriate semiconductor photocatalyst material. The band gap of any semiconductor used for water splitting must be less than 3.0 eV (~420 nm) and greater than 1.23 eV corresponding to water splitting potential^{16-17,35-36}. It is worth mentioning that even semiconductors with optimized band gap can produce low efficient hydrogen due to many factors such as: 1) quick electron-hole recombination on the surface of the semiconductor or in the bulk which leads to low quantum efficiency of photocatalysis, 2) quick back reaction of oxygen and hydrogen, and 3) semiconductor is unable to utilize the visible light region. To overcome these barriers, loading noble metal on the semiconductor can solve the electron-hole recombination problem. Likewise,

adding sacrificial reagents such as alkaline sodium presulphate⁵², sodium sulfite¹⁰², and many others into the reaction could improve quantum efficiency and reduce charge recombination.

Figure 2.2 the band gap positions for different traditional semiconductors relative to the redox potential of water²⁰

Another important requirement to be considered is that the conduction band (CB) and valence band (VB) levels should satisfy the energy requirements of the reduction and oxidation potentials of water as shown Fig. 2.2. Furthermore, the semiconductor photocatalyst conduction band (CB) must have a more negative potential than the reduction potential of H^+/H_2 (0 V vs. NHE), whereas its valence band (VB) must have a more positive potential than the oxidation potential of $\text{O}_2/\text{H}_2\text{O}$ (1.23 V vs. NHE)^{14,16}. If the above conditions are met, photogenerated electrons and holes will reduce water to hydrogen (H_2) and oxidize water to oxygen (O_2) as shown in Fig. 2.3. Since photocatalyst materials with wide band gap can only respond to the UV light, our goal is to find a photocatalytic material that drives water-splitting reaction and utilizes visible light of the solar spectrum ($400 \text{ nm} < \lambda < 800 \text{ nm}$). By finding a semiconductor photocatalyst that is capable

of utilizing visible light up to 600 nm, the conversion efficiency could be improved to 16% comparing with 2% efficiency when only UV light is utilized. Moreover, reaching 800 nm wavelength would raise the efficiency up to 32%^{19,21}.

*Figure 2.3 Schematic of water splitting principle using semiconductor photocatalysts*³⁷

The search for semiconductor photocatalysts capable of splitting water under visible light is still ongoing. The redox potential of water, suitable band gap, charge separation, overpotential, photogenerated electrons and holes recombination are all very important factors must be taken into consideration for the design of photocatalysts for water splitting. Introducing BiFeO₃-type material as good candidate for photocatalytic activity under visible light due to its narrow band gap (~2.0 eV) and less recombination of photogenerated charge carriers, which can eventually increase the conversion efficiency³⁸⁻³⁹. For that reason, bismuth ferrite oxide based material can serve as water oxidation photocatalyst for hydrogen fuel generation from water splitting. More details on BiFeO₃ photocatalyst is reviewed in the following section.

2.4. Perovskite metal oxide materials as photocatalysts

2.4.1. Structure of perovskite metal oxide

Semiconductor materials are of great importance especially as photocatalytic materials, where large number of semiconductor materials have been developed and investigated for photoelectrochemical process. However, the formation of semiconductor photocatalyst that can drive efficient photocatalytic water splitting while facilitating charge separation and charge carrier transfer is still ongoing. TiO_2 -based material is known to be one of the best photocatalytic material due to its low cost, long-term stability, and high photocatalytic activity⁴⁰. Owing to the wide band gap energy of TiO_2 (~3.2 eV) it can only absorb UV light and thus, its photocatalytic activity can be limited^{21,42}. As a result, tremendous effort is being done to find a photocatalytic material that can efficiently absorbs visible light of the solar spectrum. Among the many visible light activated photocatalyst, perovskite metal oxides have attracted considerable attention due to their narrow bandgap, high thermal stability, low price, and excellent photocatalytic activity.

The mineral perovskite was first discovered in 1839 by German chemist Gustav Rose, named after a Russian mineralogist called Count Lev Aleksevich von Perovski⁴³⁻⁴⁴. Perovskite was initially used to describe the mineral calcium titanium oxide (CaTiO_3), however it is now applied for a general group of oxides having ABO_3 structure⁴³⁻⁴⁵. A perovskite oxide is any compound that has the same crystal structure as calcium titanium oxide (CaTiO_3) with ABO_3 general formula, where the size of A-site is larger than the B-site^{43,46-47}. Fig. 2.4 shows the ideal ABO_3 structure, where A-site is occupied by 12-fold coordination with oxygen atoms and the B-site is occupied by 6-fold coordination⁴⁷⁻⁴⁸. In these perovskite metal oxide with the ABO_3 structure, A-cation can be

filled by M^+ such as (Na, K), M^{2+} (Ca, Sr, Ba), and M^{3+} (Fe, La, Gd). On the other hand, B-site can be filled by M^{5+} such as (Nb, W), M^{4+} (Ce, Zr, Ti), and M^{3+} (Fe, Mn, Co, Ga)⁴³. The final material can be either semiconducting, insulating, or ionic conducting based on the different combination of the A-/B-site. As a result, the final combination can be used for different applications such as, sensor devices, electronic components, catalysis for hydrogen production and many other applications⁴³.

Figure 2.4 Schematic of Ideal ABO₃ perovskite crystal structure¹⁰⁶

2.4.2. Perovskite materials in photocatalysis

Many researches were conducted to discover and design other metal oxide photocatalysts that are capable of splitting water under UV light and visible light irradiation. Even though TiO₂ photocatalyst is widely used for such approach, yet the large band gap of TiO₂ (~3.0 eV) limits its absorption of light to UV light only. As a result the wide band gaps (~3.0 eV) of transition

metal oxides make it insufficient photocatalyst material under visible light irradiation⁵². As previously mentioned, the absorbed photon energy needed for water splitting must be around 1.23 eV or larger in order to generate hydrogen fuel based on the following reactions^{32-33,48,51}:

Hence, it is essential to fabricate and tailor photocatalytic materials with narrow band gap in order to increase their visible response and thus increase solar-hydrogen production. The advantage of using multiferroic materials for photoelectrochemical water splitting is mainly due to their relatively small band gaps where it can absorb the majority of solar radiation in the visible light, as well as its ability to enhance the separation of photo-generated charge carriers^{38-39,49}. Bismuth ferrite oxide (BFO) is a typical perovskite type of multiferroic material that has been recently used for photoelectrochemical applications. Comparing with TiO₂ photocatalysts, BFO has attracted much attention in the solar applications due to its narrow band gap (~2.2 eV), which can act as efficient photocatalyst under visible light for water oxidation via PEC water splitting³⁸⁻³⁹. This is considered a very important approach because 48% of the total solar energy is occupied by visible light, whereas UV light accounts for only 4% of the overall solar energy⁵⁰.

2.5. Perovskite Bismuth ferrite oxide

Bismuth ferrite based material is a promising photocatalyst for photoelectrochemical water splitting. It has been reported that photogenerated charged carriers could be separated due to the depolarization of electric field of the ferroelectric materials, which helps in reducing electron-

hole recombination during transmission process^{23,53}. Another advantage of bismuth ferrite materials, is the large visible light absorption covering up to 750 nm. The following sections will present an overview of BiFeO₃ perovskite material mainly, (i) crystal structure of BFO, (ii) synthesis methods of fabricating BFO, and (iii) photocatalytic applications of BiFeO₃

2.5.1. Structure of bismuth ferrite oxide

Perovskite bismuth ferrite oxide (BFO) exhibits a narrow direct band gap of (~2.2 eV) with large visible light absorption up to 750 nm therefore, BFO is considered an ideal material for photocatalytic and photoelectrochemical water splitting for water oxidation^{33,53,57}. Bismuth ferrite oxide is one of the important single phase perovskite material, its crystal structure possesses a rhombohedral distorted perovskite structure with R3c space group at room temperature, as shown in Fig. 2.5⁵⁴⁻⁵⁶. Furthermore, bismuth ferrite material has a unique high ferroelectric Curie temperature ($T_C = 1103 \text{ K} \approx 830 \text{ }^\circ\text{C}$) and antiferromagnetic Neel temperature ($T_N = 643 \text{ K} \approx 367 \text{ }^\circ\text{C}$) which makes it suitable for high temperature applications.

Figure 2.5 Crystal structure of perovskite BiFeO_3 ⁵⁸

2.5.2. Synthesis of bismuth ferrite oxide by different routes

There are numerous methods used for the fabrication of nanostructured, bulk, and thin film BFO. These routes include sol-gel method^{58-61,70-75}, pulsed-laser deposition (PLD) method⁶¹⁻⁶², chemical vapor deposition (CVD)^{61,63}, and many others. Table 2.1 summarizes the most commonly used methods for the preparation of BiFeO_3 material with different morphologies. Among the many chemical route processes, sol-gel and hydrothermal synthesis are being commonly used to fabricate low-dimensional BFO materials. Therefore, in this dissertation we will focus on the fabrication of BFO thin film samples via sol-gel method. We will start with

brief introduction to sol-gel synthesis process for more understanding on the principle and procedure of this method.

Table 2.1 Synthesis routes of bismuth ferrite oxide

Synthesis method	Morphologies/Structure	Ref.
Sol-gel	Thin films, nanoparticles, nanowires, nanotubes	58-61,70-75
PLD	Thin films, nanoparticles	58, 61-62
CVD	Thin films	61,63
Hydrothermal	Nanoparticles	64,74,80
Sputtering	Thin films	31

Sol-gel is one of the earliest chemical route synthesis methods used to prepare metal oxides especially 0-D, 1-D, and 2-D perovskite materials^{66,68-69}. The fabrication process of any perovskite material structure starts with chemical solution known as the precursor, which consists of a metal source, a solvent, and chelating agent. The precursor solution is then converted into “gel” when applying the appropriate heating conditions. As shown in Fig. 2.6, by using different deposition approaches such as, spin-coating, dip-coating, electrodeposition and many other, we can easily fabricate the desired material structure. In this work, BiFeO₃ thin film

was fabricated using sol-gel process and deposited on FTO glass substrate by spin-coating technique due to its ease of setup, inexpensive method, and flexible control.

Figure 2.6 preparation of different material structure using sol-gel method ⁶⁶

Many researchers and various groups have been working on the synthesis of BiFeO_3 thin film using different techniques. However, our focus is to search for studies done on the synthesis of BFO thin film using sol-gel techniques. Zohra *et al* focused on preparing BiFeO_3 thin films using sol-gel route where bismuth nitrate, ferric chloride, acetic acid, and ethylene glycol were used to synthesize the BFO precursor⁷⁰. The film was deposited on copper substrate using spin-coating technique. The XRD analysis revealed the formation secondary phases in addition to pure BFO phase. Thus they concluded that obtaining pure BFO phase could be a difficult approach. Yilmaz *et al* reported the synthesis of BiFeO_3 thin film and its performance in visible light activity using sol-gel method and deposition of thin film on FTO glass substrate via spin-

coating method ⁷¹. Their study showed an improvement in the photocatalytic activity of the p-type BFO photocatalyst. Another study was conducted by Dash *et al* using sol-gel process to prepare BiFeO₃ thin film followed by spin-coating deposition on ITO and Si (100) substrate⁷². XRD analysis revealed the effect of annealing temperature on the phase of the as-deposited films. Increasing the annealing temperature could reduce the formation of secondary phases, thus pure BFO phase was achieved during annealing temperature of 600 °C.

3. BISMUTH FERRITE OXIDE THIN FILM SYNTHESIS AND CHARACTERIZATION

3.1 Introduction

As mentioned in chapter 2, perovskite metal oxide materials have been widely studied in recent years due to their wide range of applications in catalysis, fuel cells, and electrochemical sensing⁷⁹. Due to their good stability, low cost, and flexibility, perovskite materials have been utilized for photoelectrochemical water splitting due to their narrow band gap, large absorption of visible light, and efficient charge carrier separation. Bismuth iron oxide (BFO) is very interesting material used for energy-related applications especially hydrogen generation via photoelectrochemical water splitting due to its narrow band gap (~2.2 eV) and large absorption of visible light^{33,53,57}. Various method routes are being studied for BFO synthesis including pulsed laser deposition (PLD)⁵³, hydrothermal synthesis^{66,74,80}, co-precipitation⁵³, and sol-gel process⁶⁶. In our present work, we have synthesized BFO thin films using the sol-gel route due to its ease of preparation and low cost. The following work tends to investigate the crystal structure, surface morphology and optical properties of BFO thin films, which has implication on the photocatalytic activity of BiFeO₃ for water splitting.

3.2 Experimental section

3.2.1 Preparation of BiFeO₃ precursor

BFO thin film were synthesized by sol-gel method, following the procedure developed by Yilmaz *et al*⁷¹. The BFO precursor solution was prepared by mixing 8 grams of Bismuth Nitrate pentahydrate (BiN₃O₉.5H₂O, Alfa Aesar =98%) and 6 grams of Iron (III) Nitrate nanohydrate

($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Alfa Aesar = 98%) in 20ml of 2-methoxyethanol ($\text{C}_3\text{H}_8\text{O}_2$, Alfa Aesar, 99%) by magnetic stirring for 30 min at room temperature, until all powders are completely dissolved. 0.1 ml of ethanolamine ($\text{C}_2\text{H}_7\text{NO}$, Alfa Aesar, 98%) was added to adjust the viscosity of the solution. Upon the addition of 10 ml of acetic anhydride ($\text{C}_4\text{H}_6\text{O}_3$, Alfa Aesar =99%) and stirring for additional 60 min, the precursor color went from light red to very dark red (Fig. 3.1a-b). This process was prepared in ambient atmosphere and at room temperature.

3.2.2 Deposition of BiFeO_3 thin film

Prior to deposition, the FTO glass substrates were cleaned thoroughly by sonication with commercial washing up detergent. Then cleaned with ethanol, acetone, diluted hydrochloric acid (9% w/w), and DI water (15-30 min for each step). Thin films were deposited onto (2 by 2 cm^2) FTO glass substrates by spin coating method. Small part of the FTO was covered by scotch tape to ensure that FTO surface is clean for later electrical contact preparation for photoelectrochemical testing. The BFO sol was deposited onto the FTO substrates ($\sim 150 \mu\text{l}$ using micropipette) via spin coating at 3000 rpm for 60 seconds. Next, the as-prepared samples were pre-fired by placing the samples onto a hot plate at 150 $^\circ\text{C}$ for 10 min before transferred onto another hot plate at 350 $^\circ\text{C}$ for additional 10 min. This step was repeated after every coating layer to improve the crystallinity of the BFO thin film. The prepared samples were cooled at room temperature before starting the next coating layer. Fig. 3.1c shows the three different samples prepared with different number of coating layers (3, 5, and 7 layers). We investigated the effect of film thickness on the photoelectrochemical performance of the BFO thin film samples. Finally, the prepared samples were sintered in air at 550 $^\circ\text{C}$ for 2 h using box furnace.

Figure 3.1(a) BFO precursor before adding acetic anhydride, (b) after adding acetic anhydride, and (c) BFO thin film grown on FTO substrate [(i) 3 spin cycles, (ii) 5 spin cycles, (iii) 7 spin cycles]

3.3 Characterization of the BFO thin film

All samples were characterized using different analytical spectroscopic techniques discussed below. Scanning electron microscope (SEM, JOEL 7600F) was used to observe surface morphology as well as the film thickness of the sample. X-ray photoelectron spectroscopy (XPS, PHI 5000 Versa Probe System, Physical Electronics, MN) was used to analyze the surface states of Bi and Fe. The binding energy of all XPS measurements was calibrated according to the reference of C 1s peak at 284 eV. The crystal structure of the BFO

thin film was characterized by X-ray diffraction (XRD, X' Pert Pro PW3040-Pro, Panalytical Inc.) with Cu K α radiation. UV-Vis spectra were recorded under absorption mode over the range of 350nm-850nm and equipped with thin film holder (UV 2401/2, Shimadzu).

3.4 Results and discussion

3.4.1 Morphology and crystal structure of the BiFeO₃ thin film

Fig. 3.2 displays the SEM images of BFO thin films annealed at 550 °C with different number of spin coating layers (3, 5, and 7 layers). Clearly BFO thin films are formed on the FTO glass substrate for all three samples. Films prepared with 3 spin cycles (Fig. 3.2a) consist of fine smooth grains, flat surface morphology with almost void-free structure. Whereas, BFO thin film with 5 spin cycles in Fig. 3.2b showed dense grain structure with some obvious pores in the film. On the other hand, Fig. 3.2c represents BFO-7 sample that consists of inhomogeneous grains and irregular shape with few voids in between the grains comparing to BFO-3 sample. The film morphology is consistent with previously reported studies of BiFeO₃ thin films^{71,75}. The formation of voids within bismuth ferrite thin films could be attributed to the volatile of Bi during thermal treatment, which lead to the formation of secondary phases^{95,96}, this can be further confirmed by XRD data. The volatilization of Bi is a well-known phenomenon that affects the stoichiometry via the appearance of bismuth and oxygen vacancies⁹⁵. This is confirmed in terms of Kroger-Vink notation according to the following reaction:

Furthermore, the thickness of each sample was measured via cross-section SEM images. The BFO film thickness was measured to be 525 nm for BFO-3, 750 nm for BFO-5, and 950 nm for BFO-7, see Fig. 3.2.

Figure 3.2 SEM images of BFO thin film samples for different spin coating cycles (a) 3 spin cycles, (b) 5 spin cycles, and (c) 7 spin cycles. [BFO-3, BFO-5, BFO-7 correspond to 3, 5, and 7 spin cycles, respectively.]

Numerous work and research have been carried out on the BFO material and the issues associated with the presence of secondary phases. They acknowledged the difficulties of obtaining pure BFO phase without the formation of impurity phases such as $\text{Bi}_2\text{Fe}_4\text{O}_9$, Bi_2O_3 , and $\text{Bi}_{25}\text{FeO}_{39}$ ^{52,63,70-71,76-77}. Therefore, the crystal structure of the BFO thin film samples were examined using X-ray diffraction (XRD) to detect what impurity phases are formed in our samples. Fig. 3.3 shows the XRD pattern of BFO-5 and BFO-7 samples. The presence of the (014) and (110) peaks at $2\theta \approx 31.5^\circ$ and 32° reveal a perovskite BFO phase belonging to rhombohedral $R3c$ space group^{52,97}, which is present in both samples treated under the same thermal conditions. In addition, a small amount of a secondary phase in the film was detected along with the pure BFO peaks is assigned to Bi_2O_3 , which is in agreement with previous reported study^{91,95}. Many literatures have studied the crystal structure of BFO thin films

deposited on different substrates. Among them, Xu *et. al*⁸¹ conducted a study to compare the behavior of BFO thin films prepared by so-gel spin-coating technique and deposited on three different substrates. Their XRD patterns of BFO thin film on FTO substrate is consistent with our XRD results as shown in Fig. 3.4.. From our XRD data it could be noted that there is no major difference in the peak intensity between BFO-7 and BFO-5, which means that the peak intensity is independent of the film thickness. There are many factors that could affect the crystal structure of the BFO resulting in the formation of secondary phases. These must be addressed to enhance the crystallinity of the films and minimize the formation of impurity phases. The two major factors are, annealing time and temperature and their effect on the growth of BFO thin films. Raj and his group studied the effect of annealing time on the formation of crystalline phases of the BFO thin films⁶¹. Their results have revealed that annealing the BFO films at 500 °C and increasing heat dwell time to 9 h can enhance the crystallinity of the films and minimize the formation of secondary phases compared to 3 and 6 h annealing time. Another study by Moniz *et. al*⁵² has suggested annealing the BFO films at 550 °C to limits the formation of secondary phases such as Bi₂Fe₄O₉ and Bi₂₂FeO₄. Nevertheless, the impurity phase detected in our samples is very minor with very low intensity, thus the effect of such phase on the photoelectrochemical water splitting performance is very minimal.

Figure 3.3 XRD patterns of BFO thin film samples prepared by sol-gel method with after annealing temp of 550 $^{\circ}\text{C}$ (a) BFO-7 (b) BFO-5

Figure 3.4 XRD pattern of BFO thin film using different substrate from Ref. 81

3.4.3 Chemical state and electronic structure of BiFeO_3 films

XPS measurements were performed to further study the electronic structure and surface state of BFO thin films. XPS spectra of Fe, Bi, and O elements are shown in Fig. 3.4.4 for BFO-5 sample only. The two peaks detected from C 1s (Fig. 3.5a) spectra could be very well attributed to carbon contamination either during the sample fabrication or from the XPS instrument. From the O 1s XPS spectrum (Fig. 3.5b) the peak is deconvoluted into two peaks at 529.5 and 531.3 eV that corresponds to metal oxides and the surface hydroxyl (OH) group, respectively where similar values are reported for BiFeO_3 thin films^{49, 52,73,81}. Two peaks of Bi 4f state were observed from the spectrum at binding energies of 163.3 and 158.6 eV as shown in Fig. 3.5c. The higher binding energy corresponds to $4f_{5/2}$ whereas the lower binding energy corresponds to

4f_{7/2}, which indicates the presence of bismuth in the +3 oxidation state of BiFeO₃^{49,52,83}. The Fe 2p core level is split into two main peaks, Fe 2p_{3/2} and Fe 2p_{1/2} at binding energies of about ~710.4 and 723.9 eV, respectively. These two major peaks reveal the existence of iron in the +3 oxidation state in BiFeO₃. A broad shakeup satellite peak is usually observed at binding energy a little higher than the Fe 2p_{3/2} and in the range of 718-722 eV due to the presence of Fe³⁺ state in the sample, in our spectra it is observed at binding energy of 718.4 eV that is 8 eV above the Fe 2p_{3/2} peak which is consistent with reported values in the literature^{49,83,84,86}. Additionally, there exist another satellite peak around 731.9 eV and based on reported literature this peak could be attributed to Fe 2p_{1/2} of Fe³⁺ this peak is in agreement with XPS spectra of α -Fe₂O₃^{87,85}.

Figure 3.5 XPS patterns for BFO-5 samples (a) C 1s, (b) O 1s, (c) Bi 4f, and (d) Fe 2p.

3.4.4 Optical absorption of BiFeO₃ thin film

Figure 3.6. UV-visible absorption spectra of BFO thin films

Fig. 3.6 shows the UV-visible absorption spectra of BiFeO₃ films with different spin cycles. The film thickness was measured to be 950 nm for BFO-7 sample, 750 nm for BFO-5 sample, and 525 nm for BFO-3 sample. Our results showed that the thickest BFO film of the 7-spin cycle has the highest light absorption comparing to the other two samples. The significant absorption in the visible light region is due to the narrow band gap of BFO. All three spectrums display the typical BiFeO₃ absorbance curve, indicating that both indirect and direct band gap are

possible for BFO thin film corresponding to the optical absorption cut-off of 590 nm and 476 nm respectively, these values are in good agreement with previous reports¹⁰⁴⁻¹⁰⁵. The absorption edge correspond to optical band gap values of 2.1 eV and 2.6 eV for indirect and direct respectively, which is comparable with reported values obtained from previous literatures^{38-39,52,71}. This can be confirmed by replotting the absorption curve using Tauc plot, Fig. 3.7. The following equation was used to estimate the exact optical band gap of BiFeO₃ thin films:

$$\alpha h\nu = A (h\nu - E_g)^n \quad (3.2)$$

Where α is the absorption coefficient, $h\nu$ is incident photon energy, A is a constant (relative to the material), E_g is the band gap, and n is can be taken as $\frac{1}{2}$ for indirect and 2 for direct band gap. By Linear extrapolation of $(\alpha h\nu)^n$ to zero, the direct band gap of BFO is found to be around 2.6 eV whereas the indirect band gap is 2.15 eV.

Figure 3.7 Tauc plot for (a) indirect band gap and (b) direct band gap of BFO thin films

4. PHOTOELECTROCHEMICAL TESTING OF BISMUTH FERRITE OXIDE THIN FILMS

4.1 Introduction

As previously mentioned, hydrogen generation via photoelectrochemical/photocatalytic water splitting is a promising approach to generate environmentally friendly solar fuel. This approach is a potential solution for the ever-increasing energy demands^{22,37,88}. Owing to the small fraction of the ultraviolet light region (~4%) with respect to the solar spectrum in comparison to (46%) of the visible light region, we have developed a semiconductor photocatalyst with narrow band gap to extend the photocatalytic activity into the visible light region so it can serve as efficient photocatalyst towards hydrogen generation. Charge separation and transfer, electron-hole recombination, mobility, and lifetime of photogenerated electrons and holes are all factors that influence the overall photoelectrochemical water splitting performance^{89,92}. In this regard, Bismuth ferrite oxide was used as photocatalyst due to its relatively narrow band gap of (~2.2 eV), low cost, and stability where it serve as a very interesting material for photoelectrochemical water splitting under visible light irradiation^{38-39,52}. Therefore, we have conducted a photoelectrochemical test on BiFeO₃ thin films to study their photocatalytic activity under visible light. In this study, different aqueous electrolyte solutions were used to test the performance of BFO thin films and to study the effect of each electrolyte on the photocatalytic enhancement of the prepared samples.

Figure 4.1 Experimental set up for photoelectrochemical water splitting testing (a) WE, BiFeO_3 sample, (b) RE, $\text{Ag}|\text{AgCl}$, and (c) CE, Pt wire

4.2 Photoelectrochemical testing and setup

All photoelectrochemical measurements including linear sweep voltammetry (J-V curve), Mott-Scottky (M-S plot), and incident photon-to-current efficiency (IPCE) were performed in a three-electrode electrochemical system using glass cell with quartz window as shown in Figure 4.1 and measured with a potentiostat (Gamry instrument Reference 3000TM). A platinum wire (Pt), silver-silver chloride electrode ($\text{Ag}|\text{AgCl}$), and BFO sample were used as counter, reference, and working electrodes respectively. The measured potential (vs. $\text{Ag}|\text{AgCl}$) is converted to the reversible hydrogen electrode (vs. RHE) scale based on the conversion diagram (Fig. 4.2) and according to the Nernst equation:

$$E_{RHE} = E_{Ag/AgCl} + (0.059 * pH) + E^o_{Ag/AgCl} \quad (4.1)$$

Figure 4.2 Reference electrode potential conversion

where E_{RHE} is the calculated potential with respect to the reversible hydrogen electrode, $E_{Ag|AgCl}$ is the measured potential with respect to an Ag | AgCl reference electrode, $E^o_{Ag|AgCl}$ is the standard potential of an Ag/AgCl reference electrode with respect to standard hydrogen electrode which is +0.199V at 25 °C. The test was performed twice using two different aqueous electrolyte solutions, 0.5 M Na₂SO₄ (pH=6.5) was used for the first test and 0.5 M Na₂SO₃ (pH=9) was used as hole scavenger for the second test. Both electrolyte solutions were purged with nitrogen to remove dissolved oxygen before PEC testing. A commercial solar light simulator (300W Xe lamp, Newport, USA) equipped with AM 1.5G filter was used to illuminate the photoelectrode at calibrated light intensity of 100 mW/ cm². The scan rate used in PEC test is 10 mV/s.

4.3 BiFeO₃ thin film Photoelectrode preparation

The electrical contact of the BFO thin film samples were prepared as follows: a 4 cm long copper foil was thoroughly cleaned with diluted hydrochloric acid (9% w/w) for several minutes, rinsed with DI water, and dried with air to ensure a clean surface. Next, indium gallium metal was used for electrical contact between the copper foil and FTO glass side of the BFO thin film then mounted together with scotch tape to ensure good contact between copper foil and FTO substrate. Finally, the sample was sealed with quick-setting epoxy glue, while illuminated area about 0.64 cm² of the BFO thin film kept without sealing for photoelectrochemical testing as shown in Fig. 4.3. The samples were kept overnight to cure before testing.

Figure 4.3 A photoelectrode sample of BFO thin film

4.4 Surface Photovoltage (SPV/SPS)

Surface Photovoltage is a contactless method of characterizing semiconductors. This technique was discovered experimentally by Becquerel in 1839¹⁰⁷. It is used to measure the surface potential of the semiconductor by generating electron-hole pairs with a light source. The knowledge of photovoltaic effect at metal-semiconductor and semiconductor-semiconductor junctions is very important, where light is converted to electricity. Due to its technological importance, SPV became a powerful characterization tool in semiconductor field. SPV measurements are performed mainly of Metal Insulator semiconductor arrangement. SPV spectroscopy is the change of surface potential induced by optical generation of free carriers followed by their space redistribution in the sample¹⁰⁸. The difference between the surface potential under illumination V_s^* and that in dark V_s using the following equation:

$$\delta V_s = V_s^* - V_s \quad (4.2)$$

Figure 4.4 (a) SPV sample set up (b) band bending diagram of n-type semiconductor

4.4.1 SPV analysis of BiFeO₃ Thin Films

Figure 4.5 (a) SPV amplitude spectrum, (b) SPV signal

Fig. 4.5a shows the surface photovoltage response starting from 560nm (2.21 eV) to 310 nm (4.1 eV). The spectrum peaks of BFO thin film sample centered about 350 nm (3.45 eV), 455 nm (2.72 eV) and 525 nm (2.36 eV). The peak at 455nm is intense indicating band to band transition due to electron transitions between O 2p to Fe 3d. This is indicative of high charge separation at this certain wavelength. The response at 525 nm is caused by the charge transfer excitations between the adjacent Fe³⁺ ions¹⁰⁹. BFO is both direct and indirect band gap semiconductor, with band gaps of 2.7 eV and 2.36 eV respectively. Thus, in SPV all the peaks above direct band gap can be ignored which are caused by super band transitions, dependent on light intensity.

Fig. 4.5b display the X and Y signal of SPV which is an indication of instantaneous and delay charge coming on the surface. The dominant signal of SPV amplitude is cause by delayed charge (Y) which is positive. This is an explanation of how holes are moving towards the surface and electrons into the bulk. Therefore, the surface charge of BFO thin films is positive and mainly

and caused by the holes. Because of the dominant signal, that is delayed charge, BFO thin film possessed slow charge separation mechanism.

4.5 Photoelectrochemical measurements of BiFeO₃ thin film samples

The conductivity and the flat-band potential of any photoelectrode must be determined before carrying out any photoelectrochemical test. Both properties can help to elucidate the band structure of the BiFeO₃ semiconductor which therefore, confirm the ability of the BiFeO₃ thin films to drive efficient water splitting. To estimate the flat band potential (E_{fb}) of the BFO thin film, Mott-Schottky measurements was performed on BFO-5 thin film sample under dark conditions. A plot of the capacitance ($1/C^2$) as a function of the applied potential (V) is shown in Fig. 4.6 using the following equation:

$$\frac{1}{C_{SC}^2} = \frac{2}{\epsilon\epsilon_0 e N_D} \left(E - E_{fb} - \frac{kT}{e} \right) \quad (4.3)$$

where ϵ is the dielectric constant of the semiconductor, ϵ_0 is the dielectric permittivity of the vacuum, e is the elementary electric charge, k is the Boltzman of the vacuum, N_D is the donor density and $kT/e = 0.0257$ V at 25 °C.

It has been reported that BiFeO₃ exhibits both p- and n-type conductivity based on its element deficiencies. Oxygen vacancies result in n-type conductivity whereas Bi and Fe vacancies result in p-type conductivity⁷¹. Based on the M-S plot, n-type behavior was exhibited by the BFO thin film where electrons are the majority charge carriers and it is confirmed by the positive slope of the curve. The flat band potential can be determined by extrapolating the linear

region to the x-axis. By applying different frequencies, the flat band potential was estimated to be around 0.36 V vs. reversible hydrogen electrode, RHE) at frequency of 1 kHz.

Figure 4.6 Mott-Schottky plot for BFO-5 thin film at different frequencies in dark in 0.5M Na_2SO_3 (pH=9)

Figure 4.7 Schematic illustration of the estimated conduction band (CB) and valence band (VB) bands in BiFeO_3

For n-type semiconductors the flat band potential (E_{fb}) is located close to the conduction band and the valence band is more positive comparing to the oxidation potential of $\text{O}_2/\text{H}_2\text{O}$ (1.23 V vs. RHE)⁶³. Therefore, the band position diagram shown in Fig. 4.7 is constructed based on the obtained band gap of BiFeO_3 from UV-visible absorption spectra (~ 2.1 eV) and the flat band potential from the M-S plot. This result indicate that BiFeO_3 thin films benefits the separation of photo-generated e^-/h^+ pairs and serve as a promising candidate for photocatalytic water oxidation.

We have also studied the photoanodic activity of BiFeO_3 thin film samples via PEC measurements using two different electrolyte solutions separately. First, the photoelectrochemical test was performed using 0.5 M Na_2SO_4 electrolyte (pH=6.5). Fig. 4.8 shows the J-V curve obtained from BFO-5 thin film photoelectrode deposited onto FTO glass, under 1 Sun (100 mW cm^{-2}) using AM 1.5G illumination. It can be clearly seen that the sample

doesn't produce any marked photocurrent under illumination. This can be due to the insufficient separation and slow transport of photo-generated electron-hole pairs, which therefore increase the rate of electron-hole recombination. Based on this observation, it can be assumed that BFO material is very poor photocatalyst for water oxidation. Consequently, to date many studies were conducted to improve and enhance the photocatalytic activity of many semiconductor materials. These studies include (a) doping transition metal or rare earth in BFO⁹⁷⁻⁹⁸, (b) co-catalysts loading onto the surface of BiFeO₃ thin film⁹⁹, and (c) using sacrificial reagent to act as hole scavenger¹⁰⁰⁻¹⁰¹.

Figure 4.8 J-V curve for BFO-5 thin film in Na₂SO₄ electrolyte (pH 6.5)

Among the various solutions studied for enhancing the photocatalytic performance of semiconductor materials, a sacrificial reagent was used in this study, which acts as hole scavenger to prohibit and reduce rapid electron-hole recombination. Since sulfite is thermodynamically and kinetically more favorable than water oxidation, Na_2SO_3 electrolyte solution was used instead of Na_2SO_4 . Na_2SO_3 acts as hole scavenger since sulfite is oxidized to sulfate in a two-electron redox reaction much faster than the four-electron water oxidation reaction¹⁰². The presence of Na_2SO_3 electrolyte could promote rapid electron-hole transport and enhances charge carrier separation and therefore maintaining high photocurrent density. In addition, Na_2SO_3 can improve the stability of the BiFeO_3 thin film over long period of time. This is confirmed from the study done by Mali *et al.*¹⁰¹ where the effect of Na_2SO_3 electrolyte showed an enhancement in the photocurrent density of BiVO_4 films due to the favorable kinetics and thermodynamics of the sulfite oxidation.

As a result, we have studied the photoelectrochemical performance of BiFeO_3 thin film samples under BFO-side illumination (front illumination) and FTO-side illumination (back illumination). From Fig. 4.9, it can be clearly observed that the dark photocurrents density of all samples were insignificant. Whereas, all BFO thin film samples show photoanodic performance under both back and front illumination. From Fig. 4.9(a), the lowest photocurrent was obtained from BFO-3 sample, generated under front illumination ($20 \mu\text{A cm}^{-2}$ at 1.0V vs. RHE) and back illumination ($40 \mu\text{A cm}^{-2}$ at 1.0V vs. RHE). The highest photocurrent density was obtained from BFO-5 sample, shown in Fig. 4.9(b) giving ($140 \mu\text{A cm}^{-2}$ at 1.0V vs. RHE) for back illumination and ($120 \mu\text{A cm}^{-2}$ at 1.0V vs. RHE) for front illumination. These values are higher than the photocurrent reported for BFO films deposited *via* PLD onto platinized silicon substrates (~ 90

$\mu\text{A cm}^{-2}$ at 1.0 V vs. Ag/AgCl)⁷⁶, and higher than the photocurrent obtained by Moniz *et al.*⁵² for BiFeO₃ thin film synthesis via CVD route ($\sim 100 \mu\text{A cm}^{-2}$ at 1.0 V vs. Ag/AgCl).

Figure 4.9 (a-c) J-V curves for BiFeO₃ thin films with different spin coating cycles under dark and illumination (a) BFO-3 (525 nm), (b) BFO-5 (750 nm), (c) BFO-7 (950 nm), and (d) J-T curve for BFO-5 measured at an applied potential of 0.4 V vs. Ag|AgCl. All PEC test performed in 0.5M Na₂SO₃

Moreover, it is substantially higher than epitaxial BFO films deposited onto SRO buffered STO(001) substrate via sputtering ($10 \mu\text{A cm}^{-2}$ at $0.64 \text{ V vs. Ag} | \text{AgCl}$)⁹⁴. In addition, BFO-7 sample (Fig. 4.9c) shows a significant photocurrent difference between back and front illumination. The photocurrent density obtained from back illumination ($\sim 120 \mu\text{A cm}^{-2}$ at 1.0 V vs. RHE) is four times higher than the photocurrent density obtained from front illumination.

Our results show that for all BiFeO_3 thin film samples, the back illumination exhibits higher photocurrent than that under front illumination. This could be ascribed to the effect of film thickness on charge carrier transport and separation during the PEC test. With increasing the film thickness, the photocurrent density increases to a certain value and then decreases again. When the film thickness is 525 nm , both front and back illumination photocurrent density values are close to each other. Since photocurrent density is dominated by the light absorbance, thicker films will absorb more light which therefore, produces higher photocurrent density. The front and back illumination photocurrent density of both BFO-5 and BFO-7 samples exhibit different trends (Fig. 4.9b-c). However, the BFO-5 sample produces higher photocurrent density under back illumination than the BFO-7, which is an indication of excellent charge carrier separation and transport. As a result, the optimal BFO film thickness is estimated to be 750 nm to reach an efficient photoelectrochemical water splitting performance.

Furthermore, the transient photocurrent response of BFO photocatalysts was investigated to study the separation and transport efficiency of the photogenerated carriers. Fig. 4.9(d) shows the transient photocurrent spectra over period of time for BFO-5 sample measured via several on/off cycles under chopped AM 1.5G illumination. The present I-T curve confirms the high photocurrent density obtained from BFO-5 sample, which indicates much more efficient charge

separation and transfer with no obvious electron-hole recombination. This is attributed to the excellent hole scavenger in SO_3^{2-} ions that capture holes and minimize electron/hole recombination. More importantly BFO-5 thin film possesses long lifetime of the photogenerated charge carrier. To further confirm the stability of the BFO thin film sample, a transient photocurrent was recorded at 0.4 V vs. Ag | AgCl for three hours measurement under full irradiation. Fig. 4.10(a) shows a very excellent stability for BiFeO_3 photocatalyst, where the photocurrent density exhibited steady increase ($\sim 120 \mu\text{A cm}^{-2}$ at 1.0 V vs. RHE) without any noticeable photocurrent drop during the test. Our results are in good agreement with the study by Moniz *et al.*⁵² where BiFeO_3 film deposited via LPCVD revealed very good stability during the three hours test.

To further measure the light harvesting efficiency for the BiFeO_3 photocatalyst, the incident photo-to-electron conversion efficiency (IPCE) was measured using a monochromator under an applied potential of 1.0 V vs. RHE (~ 0.4 V vs. Ag | AgCl) and calculated based on the following equation¹⁰³:

$$IPCE = \frac{h \cdot C \cdot J}{\lambda P} = \frac{1240 J}{\lambda P} \quad (4.3)$$

Where, J is the photocurrent density ($\mu\text{A cm}^{-2}$), λ is the wavelength (nm), P is the power intensity of the incident light ($\mu\text{W/cm}^2$), h is Planks constant = 6.626×10^{-34} Joules sec, and C is speed of light = 3.0×10^8 meter/sec, where $h \cdot C = 1240$ eV nm. The wavelength was varied from 325 nm to 600 nm with an interval of 25 nm. The IPCE curve of the BFO thin film photoelectrode at the applied potential is given in Fig. 4.10(b). If we compare it with the UV-visible absorption spectra, BFO absorbs light mostly in the range of 350-600 nm. Therefore, the

maximum IPCE of about 4.5% was recorded at wavelength of approximately 350 nm. This result is similar to the IPCE value obtained by Chen *et al.*⁷⁶ at an applied potential of 0.5 V vs. Ag | AgCl.

Figure 4.10 (a) J-T curve for BiFeO₃ thin film measured under AM 1.5G illumination at an applied potential of 1.0 V vs. RHE for 3 hrs (b) IPCE vs. UV-visible absorption spectrum measured at 1.0 V vs. RHE

5. CONCLUSION AND FUTURE WORK

The following conclusions are drawn from our investigation of perovskite BiFeO_3 semiconductor:

First, synthesis of single BiFeO_3 phase is still under debate where secondary phases such as $\text{Bi}_2\text{Fe}_4\text{O}_9$, $\text{Bi}_{25}\text{FeO}_{39}$, and Bi_2O_3 are commonly detected along with pure perovskite BFO phase. Our results have showed that the appearance of Bi_2O_3 secondary phase is attributed to the volatilization of Bi during thermal treatment. This phenomenon is known to affect the stoichiometry due to the appearance of bismuth and oxygen vacancies. However, the intensity of such phase is very low and thus the effect of this phase on the PEC water splitting performance is very minimal.

Second, based on the UV-Visible spectra the BiFeO_3 thin film has been found to possess a narrow band gap, which leads to significant visible light absorption in the range of (350 nm-600 nm) of the solar spectrum. Both indirect and direct band gap characteristics have been observed for our BFO thin film with band gaps of 2.1 eV and 2.6 eV, respectively. Furthermore, the electrical band gap of BFO was also analyzed using SPV. An Indirect band gap of 2.36 eV at high wavelength ($\sim 525\text{nm}$) is indicative of high charge separation. On the other hand, direct band gap of 2.7 eV at lower wavelength ($\sim 455\text{ nm}$) is due to charge transfer excitations. As a result, the narrow band gap of BiFeO_3 is favorable for photoelectrochemical water splitting and lead to enhancement of photocatalytic water oxidation.

Third, we have further examined the photoelectrochemical performance of BiFeO₃ thin films for water splitting. Our results have indicated that BiFeO₃ photocatalyst exhibit n-type behavior is due to the oxygen vacancies with flat band potential of 0.36 V vs. RHE. Based upon the value determined for the band gap of BiFeO₃ and the band diagram constructed previously, the results indicate that BiFeO₃ has significant overpotential for photocatalytic water oxidation. Furthermore, the photoanodic activity of BiFeO₃ thin film has been studied using two different aqueous electrolytes. The results have showed that using Na₂SO₄ (pH 6.5) lead to insufficient separation and slow transport of electron-hole pairs. Therefore, the BFO didn't show any anodic photocurrent during illumination. As a result, Na₂SO₃ (pH 9) was used as hole scavenger to reduce surface recombination and improve the performance of BFO for photocatalytic water splitting. Among the three BFO thin film samples prepared, the highest photocurrent density of 140 $\mu\text{A cm}^{-2}$ at 1.0V vs. RHE was achieved from five spin cycles sample with optimal film thickness of 750 nm. In addition, the BFO film photoanode is found to be very stable over long period of time with high charge separation and low electron-hole recombination. The photocurrent is limited by the low conductivity and insufficient catalytic activity toward water oxidation.

Overall, the knowledge obtained from this thesis has developed strategies for understanding how metal oxide based materials can be used for solar fuel generation. Besides, the information gained will allow for further improvement of BiFeO₃ photocatalyst through the use of co-catalyst and metal transition doping, which can be studied in our future work.

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