

Understanding and Improving the Charge Kinetics of BiVO₄

Author:

Tan, Hui Ling

Publication Date:

2017

DOI:

<https://doi.org/10.26190/unsworks/19659>

License:

<https://creativecommons.org/licenses/by-nc-nd/3.0/au/>

Link to license to see what you are allowed to do with this resource.

Downloaded from <http://hdl.handle.net/1959.4/57829> in <https://unsworks.unsw.edu.au> on 2024-05-04



Understanding and Improving the Charge Kinetics of BiVO_4

A thesis submitted to The University of New South Wales in partial
fulfillment of the degree of Doctor of Philosophy

By
Hui Ling Tan

School of Chemical Engineering
The University of New South Wales

May 2017

PLEASE TYPE**THE UNIVERSITY OF NEW SOUTH WALES
Thesis/Dissertation Sheet**Surname or Family name: **TAN**First name: **HUI LING**

Other name/s:

Abbreviation for degree as given in the University calendar:

PhDSchool: **School of Chemical Engineering**Faculty: **Engineering**

Title:

Understanding and Improving the Charge Kinetics of BiVO₄**Abstract 350 words maximum: (PLEASE TYPE)**

Visible-light-active BiVO₄ particles with different morphologies were synthesized and studied for their photocatalytic activities, relating the charge kinetics (i.e., charge separation, transport, and transfer) to the surface and bulk properties of the material.

The work started with the synthesis of dual-faceted BiVO₄'s with distinctly different dominant exposed facets, one which was {010}-dominant and the other {110}-dominant. Despite {010} and {110} being proven as the respective active reduction and oxidation sites of BiVO₄, the photooxidation activities of {010}-dominant BiVO₄ were found to be higher than {110}-dominant BiVO₄. This was due to the presence of larger {010} facets to facilitate electron transfer, which was found to be crucial not only for photoreduction, but also for photooxidation reactions.

Subsequently, the influence of the {010}/{110} relative exposure extent on the charge interactions between BiVO₄ and reduced graphene oxide (RGO) was investigated. The degree of BiVO₄ photocurrent enhancement in the presence of RGO was found to correlate to the exposure extent of {010} facets, attributing to improved charge transfer ability. Density functional theory calculations revealed that charge transfer across graphene/BiVO₄{010} interface is more favorable than across the graphene/BiVO₄{110} interface due to their different electronic properties.

Following these findings, the practicability of Argon (Ar) annealing to improve charge separation and transport of dual-faceted BiVO₄ was examined. In addition to reduced band gap, greater local structure distortion, and improved crystallinity, Ar annealing was also shown to effectively instigate formation of oxygen vacancies, which enhance electron transport in BiVO₄.

The last section of the work explored the prospect of dual-faceted BiVO₄ microcrystal in comparison to the generally more desirable smaller (or nanosized) particles for water oxidation in powder suspension (PS) and photoelectrochemical (PEC) systems. Although faceted BiVO₄ microcrystal falls short of providing short interparticle distance and good photocatalyst/substrate contact for efficient charge transport in the PEC system, the higher crystallinity and the more significant band-bending-mediated built-in electric field present in the micro-sized crystal allowed it to outperform the smaller BiVO₄ particles for photocatalytic O₂ evolution.

Declaration relating to disposition of project thesis/dissertation

I hereby grant to the University of New South Wales or its agents the right to archive and to make available my thesis or dissertation in whole or in part in the University libraries in all forms of media, now or here after known, subject to the provisions of the Copyright Act 1968. I retain all property rights, such as patent rights. I also retain the right to use in future works (such as articles or books) all or part of this thesis or dissertation.

I also authorise University Microfilms to use the 350 word abstract of my thesis in Dissertation Abstracts International (this is applicable to doctoral theses only).

.....
Signature.....
Witness Signature.....
Date**FOR OFFICE USE ONLY**

Date of completion of requirements for Award:

COPYRIGHT STATEMENT

'I hereby grant the University of New South Wales or its agents the right to archive and to make available my thesis or dissertation in whole or part in the University libraries in all forms of media, now or here after known, subject to the provisions of the Copyright Act 1968. I retain all proprietary rights, such as patent rights. I also retain the right to use in future works (such as articles or books) all or part of this thesis or dissertation.

I also authorise University Microfilms to use the 350 word abstract of my thesis in Dissertation Abstract International (this is applicable to doctoral theses only).

I have either used no substantial portions of copyright material in my thesis or I have obtained permission to use copyright material; where permission has not been granted I have applied/will apply for a partial restriction of the digital copy of my thesis or dissertation.'

Signed

Date

AUTHENTICITY STATEMENT

'I certify that the Library deposit digital copy is a direct equivalent of the final officially approved version of my thesis. No emendation of content has occurred and if there are any minor variations in formatting, they are the result of the conversion to digital format.'

Signed

Date

ORIGINALITY STATEMENT

'I hereby declare that this submission is my own work and to the best of my knowledge it contains no materials previously published or written by another person, or substantial proportions of material which have been accepted for the award of any other degree or diploma at UNSW or any other educational institution, except where due acknowledgement is made in the thesis. Any contribution made to the research by others, with whom I have worked at UNSW or elsewhere, is explicitly acknowledged in the thesis. I also declare that the intellectual content of this thesis is the product of my own work, except to the extent that assistance from others in the project's design and conception or in style, presentation and linguistic expression is acknowledged.'

Signed

Date

Abstract

Charge kinetics, which includes separation of photogenerated electrons and holes, charge transport to reaction sites, and interfacial charge transfer for chemical reactions, critically determines the photochemical conversion efficiency of a photocatalyst. While various efforts have been invested in the production of photocatalysts with different morphologies or alteration of photocatalysts properties via post-synthesis treatment, fundamental understanding of charge kinetics in relation to the surface and bulk properties of photocatalyst is essential for development of a highly effective photocatalyst. For this purpose, a range of visible-light-active BiVO_4 particles with monoclinic scheelite phase were produced using solid-liquid state reaction and studied for their photocatalytic activities, primarily on water oxidation reaction.

The work started with an investigation on the influence of $\{010\}/\{110\}$ relative exposure extent on the photooxidation ability of BiVO_4 with respect to the charge transfer efficiency of the material. Two dual-faceted BiVO_4 's with distinctly different dominant exposed facets, one which was $\{010\}$ -dominant and the other $\{110\}$ -dominant, were synthesized. Despite $\{010\}$ and $\{110\}$ being proven as the respective active reduction and oxidation sites of BiVO_4 , the photooxidation activities of $\{010\}$ -dominant BiVO_4 were found to be higher than $\{110\}$ -dominant BiVO_4 for water oxidation and 2,4-dichlorophenoxyacetic acid degradation. The presence of larger reduction functional $\{010\}$ facets was shown to facilitate electron transfer, which is crucial not only for photoreduction, but also for photooxidation reactions.

The BiVO_4 particles with varying $\{010\}/\{110\}$ relative exposure extents were further studied for the facet-dependent charge transfer interactions between BiVO_4 and reduced

graphene oxide (RGO). While improvement of photoelectrochemical (PEC) photocurrent was apparent for all BiVO₄ samples in the presence of RGO, the degree of enhancement was revealed to correlate to the exposure extent of {010} facets, attributing to improved charge transfer ability. The experimental results were supported by density functional theory calculations, whereby different electronic properties between graphene/BiVO₄{010} and graphene/BiVO₄{110} interfaces were predicted to facilitate charge transfer across the former.

Following these findings, the practicability of Argon (Ar) annealing as a post-synthesis treatment to optimize the charge separation and transport aspects of dual-faceted BiVO₄ for water oxidation was examined. In addition to reduced band gap, greater local structure distortion, and improved crystallinity, Ar annealing was also shown to effectively instigate formation of oxygen vacancies, which enhance electron transport in BiVO₄. The extent of improvements however, was dependent on the annealing temperature.

The last section of the work explored the prospect of dual-faceted BiVO₄ microcrystal in comparison to the generally more desirable smaller (or nanosized) particles for water oxidation in powder suspension (PS) and PEC systems. Contrary effects of particle size were displayed in the two systems: larger particles evolved greater amount of O₂ in the PS system, whereas particulate electrode made of smaller particles led to higher PEC photocurrent. These findings highlight the different governing factors of the two systems, that is, charge transport for PEC system and charge separation for PS system. Although faceted BiVO₄ microcrystal falls short of providing short interparticle distance and good photocatalyst/substrate contact for efficient charge transport predominantly needed in the PEC system, the higher crystallinity and the more

significant band-bending-mediated built-in electric field present in the micro-sized crystal facilitated charge separation and allowed it to outperform the smaller BiVO_4 particles for photocatalytic O_2 evolution.

Acknowledgements

I would first like to express my gratitude to my supervisors, Prof. Rose Amal and Dr. Yun Hau Ng. The completion of this work would not have been possible without their tireless guidance, support, valuable advices, and helpful discussions throughout my research. I would also like to thank Dr. Yun Hau Ng for sharing his invaluable skills and experiences these past few years.

My sincere thanks also go to Dr. Bill Gong for assisting in XPS measurements; Dr. Yu Wang for his guidance in XRD analyses; Mr. Sean Lim, Ms. Sigrid Fraser, and Mr. Yin Yao for providing trainings and helps on TEM and SEM; Dr. Anne Rich for training and assistance in Raman spectroscopy measurements; Dr. Rabeya Akter and Dr. Dorothy Yu for performing the ICP analyses. I acknowledge Ms. Alexandra T. De Denko and Prof. Frank E. Osterloh from the Department of Chemistry at University of California, United States for performing the SPS measurements; Dr. Hassan A. Tahini and Prof. Sean C. Smith from the Integrated Materials Design Centre for conducting the DFT calculations.

I would like to extend my appreciation to Ms. Ik Ling Lau, Ms. Sandra Twoney, Ms. Ann Moore, Dr. Robert Chan, Ms. Ee Meen Iliffe, Mr. Phil Thompson, and Mr. Paul Brockbank for their administrative and technical supports. Special thanks go to Dr. Mandalena Hermawan and Dr. Victor Wong for being attentive and responsive in procuring chemicals and lab apparatus.

I am grateful to all the past and present members of the Particles and Catalysis Group. Thank you for their support, encouragement, share of joy and laughter that made my

PhD journey a pleasant and memorable one. I am particularly indebted to Roong Jien Wong and Hendra Wibawa Saputera for their assistance in parts of my experimental works. I have been very fortunate to have the companionship from Dr. Charlene Ng, Dr. Lipson Chin, Dr. Mega Ng, Dr. Ee Teng Kho, and Dr. Tze Hao Tan, who constantly helped and supported me in various ways. I would also like to thank Dr. Gary Low for his inspiration, wise advices, and great sense of humor.

The financial support from the University of New South Wales via the University International Postgraduate Award (UIPA) is gratefully acknowledged.

Last but not least, I would like to thank my parents, brothers, and sister. I am truly blessed to have their encouragement, understanding, and unconditional love.

List of Publications

Journal Publications from this Thesis

1. Tan, H. L.; Wen, X.; Amal, R.; Ng, Y. H., BiVO₄ {010} and {110} Relative Exposure Extent: Governing Factor of Surface Charge Population and Photocatalytic Activity. *J. Phys. Chem. Lett.* **2016**, 7 (7), 1400-1405.
2. Tan, H. L.; Tahini, H. A.; Wen, X.; Wong, R. J.; Tan, X.; Iwase, A.; Kudo, A.; Amal, R.; Smith, S. C.; Ng, Y. H., Interfacing BiVO₄ with Reduced Graphene Oxide for Enhanced Photoactivity: A Tale of Facet Dependence of Electron Shuttling. *Small* **2016**, 12 (38), 5295-5302.
3. Tan, H. L.; Amal, R.; Ng, Y. H., Exploring the Different Roles of Particle Size in Photoelectrochemical and Photocatalytic Water Oxidation on BiVO₄. *ACS Appl. Mater. Interfaces* **2016**, 8 (42), 28607-28614.
4. Tan, H. L.; Suyanto, A.; Denko, A. T. D.; Saputera, W. H.; Amal, R.; Osterloh, F. E.; Ng, Y. H., Enhancing the Photoactivity of Faceted BiVO₄ via Annealing in Oxygen-Deficient Condition. *Part. Part. Syst. Character.* **2017**, 34 (4), 1600290.

Other Journal Publications

1. Jing, L.; Tan, H. L.; Amal, R.; Ng, Y. H.; Sun, K.-N., Polyurethane Sponge Facilitating Highly Dispersed TiO₂ Nanoparticles on Reduced Graphene Oxide Sheets for Enhanced Photoelectro-Oxidation of Ethanol. *J. Mater. Chem. A* **2015**, 3 (30), 15675-15682.
2. Tang, Y.; Traveerungroj, P.; Tan, H. L.; Wang, P.; Amal, R.; Ng, Y. H., Scaffolding an Ultrathin CdS Layer on a ZnO Nanorod Array using Pulsed Electrodeposition for Improved Photocharge Transport under Visible Light Illumination. *J. Mater. Chem. A* **2015**, 3 (38), 19582-19587.
3. Tan, H. L.; Denny, F.; Hermawan, M.; Wong, R. J.; Amal, R.; Ng, Y. H., Reduced Graphene Oxide Is Not a Universal Promoter for Photocatalytic Activities of TiO₂. *Journal of Materiomics* **2017**, 3 (1), 51-57.
4. Toe, C. Y.; Tan, H. L.; Boyer, C.; Rawal, A.; Thickett, S. C.; Scott, J.; Amal, R.; Ng, Y. H., Photo-Driven Synthesis of Polymer-Coated Platinized ZnO Nanoparticles with Enhanced Photoelectrochemical Charge Transportation. *J. Mater. Chem. A* **2017**, 5 (9), 4568-4575.
5. Tan, H. L.; Du, A.; Amal, R.; Ng, Y. H., Decorating Platinum on Nitrogen-Doped Graphene Sheets: Control of the Platinum Particle Size Distribution for Improved Photocatalytic H₂ Generation (in preparation)

Conference Presentations

1. Tan, H. L., Amal, R., Ng, Y. H. Influence of BiVO₄ Crystal Facets on Its Charge Interaction with Graphene. *Energy Future Conference*, 3-5 November 2014, The University of New South Wales, Sydney, Australia.
2. Tan, H. L., Ng, Y. H., Amal, R. Tuning the Deposition of Platinum by Doping Nitrogen into Graphene. *The Royal Australian Chemical Institute (RACI) National Congress*, 7-12 December 2014, Adelaide Convention Centre, Adelaide, Australia.
3. Tan, H. L., Wen, X., Amal, R., Ng, Y. H. Interrelationship between Carrier Dynamics and Photoactivities in Facet-Controlled BiVO₄, *International Conference on Nanoscience and Nanotechnology (ICONN 2016)*, 7-11 February 2016, National Convention Centre, Canberra, Australia.
4. Tan, H. L., Wen, X., Amal, R., Ng, Y. H. Role of Crystal Facet in Governing Surface Charge Population and Photoactivity of BiVO₄, *9th European meeting on Solar Chemistry and Photocatalysis: Environmental Applications (SPEA9)*, 13-17 June 2016, Strasbourg Convention Centre, Strasbourg, France.
5. Tan, H. L., Denko, A. T. D., Osterloh, F. E., Amal, R., Ng, Y. H. Oxygen Vacancies in BiVO₄ and Their Impacts on Photocatalytic Water Oxidation. *Energy Future Conference*, 4-6 July 2016, The University of New South Wales, Sydney, Australia.

Table of Contents

Thesis/Dissertation Sheet.....	i
Copyright Statement.....	ii
Originality Statement.....	iii
Abstract	iv
Acknowledgements.....	vii
List of Publications.....	ix
Table of Contents	xii
Chapter 1 Introduction	1
1.1. Background	1
1.2. Aims and Objectives	3
1.3. Thesis Outline	5
1.4. References.....	6
Chapter 2 Literature Review.....	11
2.1. Introduction.....	11
2.2. Photocatalysis	12
2.2.1. Basic Principles of Photocatalytic Reactions.....	13
2.2.2. Oxide Semiconductor Photocatalysts.....	16
2.3. Bismuth Vanadate (BiVO ₄)	17
2.3.1. Crystal Structure and Phase Transition	18
2.3.2. Electronic Structure.....	20
2.4. Photocatalytic Applications of BiVO ₄ under Visible Light.....	24
2.4.1. Organic Degradations.....	25
2.4.2. Water Splitting	27
2.4.2.1. Powder Suspension System	28

2.4.2.2.	Photoelectrochemical System	36
2.4.2.3.	Difference in Charge Separation Mechanisms in PS and PEC Systems	38
2.4.3.	Limitations of BiVO ₄	41
2.5.	Strategies for Improving the Charge Kinetics of BiVO ₄	46
2.5.1.	Crystal Facet Engineering	47
2.5.2.	Compositing with Graphene	53
2.5.3.	Annealing Treatment.....	59
2.5.4.	Nanoscaling.....	64
2.6.	Summary	69
2.7.	References.....	71
Chapter 3	BiVO₄ {010} and {110} Relative Exposure Extent: Governing Factor of Surface Charge Population and Photoactivity	95
3.1.	Introduction.....	95
3.2.	Experimental.....	97
3.2.1.	Synthesis of BiVO ₄	97
3.2.2.	Photocatalytic Reactions	97
3.2.2.1.	Photocatalytic O ₂ Evolution.....	97
3.2.2.2.	2,4-Dichlorophenoxyacetic Acid Degradation	98
3.2.3.	Material Characterization.....	99
3.2.4.	Electrochemical Impedance Spectroscopy Measurements	100
3.3.	Results and Discussion	101
3.3.1.	Morphological, Structural and Optical Properties	101
3.3.2.	{010} as the Active Reduction Functional Facet of BiVO ₄	105
3.3.3.	Photocatalytic O ₂ Evolution and 2,4-D Degradation	107
3.3.4.	Photoluminescence and Electrochemical Impedance Measurements	109
3.3.5.	Proposed Crystal-Facet-Dependent Charge Transfer Kinetics	114

3.4.	Summary	118
3.5.	References.....	119
Chapter 4 Interfacing BiVO₄ with Reduced Graphene Oxide for Enhanced Photoactivity: A Tale of Facet Dependence of Electron Shuttling ...		125
4.1.	Introduction.....	125
4.2.	Experimental.....	128
4.2.1.	Synthesis of Graphene Oxide.....	128
4.2.2.	Synthesis of BiVO ₄ and RGO-BiVO ₄	129
4.2.3.	Material Characterization.....	129
4.2.4.	Photoelectrochemical Measurements.....	130
4.2.4.1.	Photocurrent Measurements.....	130
4.2.4.2.	Electrochemical Impedance Spectroscopy Studies.....	130
4.2.5.	Theoretical Calculations.....	131
4.3.	Results and Discussion	131
4.3.1.	Physical and Optical Properties of Bare BiVO ₄	131
4.3.2.	Preparation of RGO-BiVO ₄ Composites	136
4.3.2.1.	Morphological Properties.....	136
4.3.2.2.	Surface Chemical States and Optical Properties.....	138
4.3.2.3.	Structural Properties.....	139
4.3.2.4.	Photoelectrochemical Photocurrent	141
4.3.2.5.	Photoluminescence Measurements	142
4.3.3.	Effect of BiVO ₄ {010}/{110} Relative Exposure Extent on Photoelectrochemical Performance	144
4.3.4.	Density Functional Theory Calculations.....	147
4.4.	Summary	151
4.5.	References.....	152
Chapter 5 Enhancing the Photoactivity of Faceted BiVO₄ via Annealing in Oxygen-Deficient Condition.....		158

5.1.	Introduction.....	158
5.2.	Experimental.....	161
5.2.1.	Synthesis of BiVO ₄	161
5.2.2.	Photocatalytic O ₂ Evolution.....	161
5.2.3.	Photoelectrochemical Measurements.....	161
5.2.4.	Facet-Selective Photodepositions of Pt/MnO _x	162
5.2.5.	Material Characterization.....	162
5.2.6.	Surface Photovoltage Spectroscopy.....	163
5.3.	Results and Discussion	164
5.3.1.	Photocatalytic O ₂ Evolution and Photoelectrochemical Photocurrent....	164
5.3.2.	Structural, Physical, and Optical Properties at Different Annealing Temperatures.....	165
5.3.3.	Surface Photovoltage Spectroscopy.....	169
5.3.4.	X-ray Photoelectron and Electron Paramagnetic Resonance Spectroscopies.....	172
5.3.5.	Effects of Ar Treatment on the Structural, Electronic, and Morphological Properties of Dual-Faceted BiVO ₄	174
5.4.	Summary.....	181
5.5.	References.....	182
Chapter 6	Exploring Different Roles of Particle Size in Photoelectrochemical and Photocatalytic Water Oxidation on BiVO₄	188
6.1.	Introduction.....	188
6.2.	Experimental.....	191
6.2.1.	Synthesis of BiVO ₄	191
6.2.2.	Material Characterization.....	192
6.2.3.	Preparation of Electrodes	192
6.2.4.	Photoelectrochemical Measurements (PEC System).....	192
6.2.5.	Photocatalytic Reaction (PS System).....	193

6.3.	Results and Discussion	193
6.3.1.	Morphological, Structural and Optical Properties	193
6.3.2.	Surface Chemical States.....	198
6.3.3.	Photoelectrochemical Measurements.....	200
6.3.4.	Effect of Particle Size on Interparticle and Particle/FTO Contacts in BiVO ₄ Particulate Electrode	204
6.3.5.	Photocatalytic O ₂ Evolution.....	207
6.3.6.	Different Governing Factors in Powder Suspension and Photoelectrochemical Systems.....	208
6.4.	Summary.....	211
6.5.	References.....	212
Chapter 7	Conclusion & Recommendations.....	218
7.1.	Conclusion	218
7.2.	Recommendations.....	222
7.2.1.	Dual-Faceted BiVO ₄ : Further Studies, Material Optimization and Potential Application	222
7.3.	References.....	226

Chapter 1

Introduction

1.1. Background

While the industrial and agricultural revolutions have spurred human population and economic growth, they have also contributed to the ever-growing energy demand and environment destruction. Excessive burning of fossil fuels as the main energy supply leads to rapid depletion of the natural resources along with CO₂ emission, which is the major contributor to global warming.¹⁻² Meanwhile, industrial wastewater and agrochemical products contribute to environment pollutions and jeopardizing the ecosystems. These energy and environmental concerns have driven the research community into photocatalysis, in the hopes of mitigating the issues for achieving sustainable development.

The interest in the field of photocatalysis is attributable to the numerous appealing features of the process: (1) it exploits (renewable) solar energy; (2) it works at near ambient temperature; and (3) a wide variety of compounds can be chemically transformed or decomposed through photomediated redox transformations.³ Given the inexhaustible nature of solar energy, it is by far the most promising energy source with the least negative impacts on the environment.⁴ In photocatalysis, the abundant, renewable, and freely available solar energy can be directly harvested to initiate chemical processes on semiconductor materials, forming the basis of various useful photocatalytic applications.

Of the broad applications of photocatalysis, water splitting and organic degradation are the two most significant reactions, directed respectively towards H_2 production and environment pollutant abatement.⁵ As the simplest chemical bond with water as the only waste product upon combustion, H_2 is the ultimate clean energy carrier which is highly desirable to replace fossil fuels.^{4, 6} Although there are manifold ways to produce H_2 such as steam reforming, biomass reformation, and electrolysis, utilization of sunlight to drive the thermodynamically uphill reaction of water splitting to gaseous H_2 and O_2 is indisputably the most ideal approach.⁷⁻⁸ The pioneering work on photocatalytic water splitting was reported by Fujishima and Honda in 1972, in which TiO_2 electrode was employed as the photoactive anode for water oxidation in conjunction with platinum as the cathode for water reduction.⁹ Following this discovery, the scientific and engineering interest in oxide semiconductors heightened, particularly on binary metal oxides that are composed of earth-abundant elements. The functionality of photocatalysis was also further expanded into water and air purification, whereby the proven ability of oxide materials to transform or degrade a large variety of organics (a major constituent of environment pollutants) into less harmful substances suggests photocatalysis as a green approach for environmental remediation and amelioration.^{3, 10-}

14

Oxide semiconductors, which are generally cheap, easy to fabricate, chemically and photocatalytically stable,¹⁵ are promising photocatalyst candidates. However, the implementation of most binary metal oxides such as TiO_2 and ZnO is strictly restricted to ultraviolet (UV) light due to their large band gap energies arising from the deep valence bands consisting of O 2p orbitals.¹⁶⁻¹⁷ While UV radiation constitutes merely 5 % of the solar irradiation incident on the Earth's surface, nearly half of the spectrum (40 %)

falls within the visible region.¹⁸ Development of semiconductor materials capable of visible light absorption is therefore necessary for efficient utilization of solar energy. Although some non-oxide semiconductors such as sulfides and nitrides are responsive toward visible light, they are generally unstable.¹⁶ In this regard, ternary metal oxides emerge as a new class of material that has garnered great attention. This is not only due to their common merits with oxide semiconductor as stated above, but their valence bands formed by atomic orbitals of more than one element also allow fine tuning of their band gap energies.¹⁹ Recently, bismuth vanadate (BiVO_4) with a favorable band gap of 2.4 – 2.5 eV has been widely demonstrated to be a promising candidate for water splitting (including photocatalytic water oxidation,²⁰⁻²¹ photoelectrochemical water splitting,²²⁻²⁴ and Z-scheme water splitting²⁵⁻²⁶) and organic degradations²⁷⁻²⁹ under visible light irradiation.

The photochemical conversion efficiency of a photocatalyst is fundamentally determined by three key steps related to charge kinetics, which are charge separation, transport, and transfer.³⁰ All of these are affected by the surface and bulk properties of the photocatalysts such as the types of exposed crystal facet,³¹⁻³² particle size,³³⁻³⁴ crystallinity,³⁵ crystal structure,³⁶ and induction of mid gap states.^{19, 37} Advancement of photocatalysis has thus contributed to the interdisciplinary nature of the field, integrating semiconductor physics, physical chemistry, materials science, and surface sciences to name a few.⁵ Bridging of multidisciplinary knowledge is indispensable to further propel the growth of photocatalysis field.

1.2. Aims and Objectives

The overall aim of this thesis is to understand and improve the charge separation, transfer, and transport aspects of photocatalyst with respect to the material's

characteristics ensuing from the variation in morphology (i.e., exposed facets and particle size) and application of post-synthesis heat treatment. BiVO_4 , which is a promising visible-light-responsive ternary metal oxide semiconductor, is chosen as the model photocatalyst in this study due to the ease of preparation of this material with controllable exposed facets and particle size.

Dual-faceted BiVO_4 with exposed $\{010\}$ and $\{110\}$ has been demonstrated to assist in charge separation during which photogenerated electrons and holes are spatially driven to the respective exposed facets.³² In order to understand the influence of the two facets on the charge transfer efficiency of BiVO_4 , dual-faceted BiVO_4 samples with different relative exposure extents of $\{010\}/\{110\}$ facets are synthesized and compared for their photooxidation activities.

Additionally, the dependence of BiVO_4 's charge transfer efficiency on the relative exposure extent of $\{010\}/\{110\}$ facets is studied in a composite structure, where the BiVO_4 is coupled with reduced graphene oxide (RGO) that is known as a good electron mediator. This is to understand and verify the origin of the crystal-facet-dependent interfacial charge interactions between BiVO_4 and RGO.

Dual-faceted BiVO_4 is also subjected to heat treatment in an oxygen-deficient environment. The main objective here is to assess the efficiency of oxygen-deficient Argon (Ar) atmosphere in altering the physicochemical, optical, and electronic properties, targeting at optimizing the charge separation and transport efficiencies of the dual-faceted BiVO_4 for water oxidation reactions.

Given that the dual-faceted BiVO_4 particles are large in size (microcrystals) contradict the generally more desirable nanosized materials, the water oxidation performances of

faceted BiVO₄ microcrystal is also compared to smaller BiVO₄ particles in different systems: photoelectrochemical (PEC) and power suspension (PS). The key attributes of the BiVO₄ with different particle sizes that control the efficiencies of the two systems are also identified.

1.3. Thesis Outline

This thesis explores the relationship between the charge kinetics of BiVO₄, encompassing charge separation, transport, and transfer, to the surface and bulk properties of the material. Firstly, Chapter 2 provides the basic principles of photocatalysis, followed by the fundamental properties and photocatalytic applications of BiVO₄ as well as the current state-of-the-art to improve the photoactivity of BiVO₄. The following two chapters are devoted to study the effects of {010}/{110} relative exposure extent on the charge transfer efficiency of BiVO₄. Specifically, Chapter 3 investigates the dependence of the surface electron and hole populations on the exposure extent of the {010} and {110} facets to affect the photooxidation performance of BiVO₄, whereas Chapter 4 examines the electron transfer ability between RGO and BiVO₄ with the presence of {010} and {110} of different relative exposure extents. In Chapter 5, the efficacy of Ar annealing on optimizing the charge separation and transport properties of the faceted BiVO₄ in relation to the annealing temperature is detailed. Chapter 6 presents the prospect of the dual-faceted BiVO₄ microcrystals in comparison to smaller BiVO₄ particles for water oxidation in the PS and PEC systems. The influence of particle size on charge separation and transport properties, which respectively form the governing factors in the PS and PEC systems are described. Lastly, a summary on the major findings in this work together with recommendations on future work are given in Chapter 7.

1.4. References

1. Lashof, D. A.; Ahuja, D. R., Relative Contributions of Greenhouse Gas Emissions to Global Warming. *Nature* **1990**, *344*, 529-531.
2. Solomon, S.; Plattner, G.-K.; Knutti, R.; Friedlingstein, P., Irreversible Climate Change Due to Carbon Dioxide Emissions. *Proc. Natl. Acad. Sci. U. S. A.* **2009**, *106* (6), 1704-1709.
3. Carp, O.; Huisman, C. L.; Reller, A., Photoinduced Reactivity of Titanium Dioxide. *Prog. Solid State Chem.* **2004**, *32* (1), 33-177.
4. Walter, M. G.; Warren, E. L.; McKone, J. R.; Boettcher, S. W.; Mi, Q.; Santori, E. A.; Lewis, N. S., Solar Water Splitting Cells. *Chem. Rev.* **2010**, *110* (11), 6446-6473.
5. Teoh, W. Y.; Scott, J. A.; Amal, R., Progress in Heterogeneous Photocatalysis: From Classical Radical Chemistry to Engineering Nanomaterials and Solar Reactors. *J. Phys. Chem. Lett.* **2012**, *3* (5), 629-639.
6. Ashokkumar, M., An Overview on Semiconductor Particulate Systems for Photoproduction of Hydrogen. *Int. J. Hydrogen Energy* **1998**, *23* (6), 427-438.
7. Kudo, A.; Miseki, Y., Heterogeneous Photocatalyst Materials for Water Splitting. *Chem. Soc. Rev.* **2009**, *38* (1), 253-278.
8. Bard, A. J.; Fox, M. A., Artificial Photosynthesis: Solar Splitting of Water to Hydrogen and Oxygen. *Acc. Chem. Res.* **1995**, *28* (3), 141-145.
9. Fujishima, A., Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature* **1972**, *238*, 37-38.
10. Fox, M. A.; Dulay, M. T., Heterogeneous Photocatalysis. *Chem. Rev.* **1993**, *93* (1), 341-357.

11. Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W., Environmental Applications of Semiconductor Photocatalysis. *Chem. Rev.* **1995**, 95 (1), 69-96.
12. Herrmann, J.-M., Heterogeneous Photocatalysis: Fundamentals and Applications to the Removal of Various Types of Aqueous Pollutants. *Catal. Today* **1999**, 53 (1), 115-129.
13. Kamat, P. V.; Huehn, R.; Nicolaescu, R., A “Sense and Shoot” Approach for Photocatalytic Degradation of Organic Contaminants in Water. *J. Phys. Chem. B* **2002**, 106 (4), 788-794.
14. Gouvea, C. A.; Wypych, F.; Moraes, S. G.; Duran, N.; Nagata, N.; Peralta-Zamora, P., Semiconductor-Assisted Photocatalytic Degradation of Reactive Dyes in Aqueous Solution. *Chemosphere* **2000**, 40 (4), 433-440.
15. Ni, M.; Leung, M. K. H.; Leung, D. Y. C.; Sumathy, K., A Review and Recent Developments in Photocatalytic Water-Splitting using TiO_2 for Hydrogen Production. *Renewable Sustainable Energy Rev.* **2007**, 11 (3), 401-425.
16. Abe, R., Recent Progress on Photocatalytic and Photoelectrochemical Water Splitting under Visible Light Irradiation. *J. Photochem. Photobiol., C* **2010**, 11 (4), 179-209.
17. Kudo, A., Photocatalyst Materials for Water Splitting. *Catal. Surv. Asia* **2003**, 7 (1), 31-38.
18. Zayat, M.; Garcia-Parejo, P.; Levy, D., Preventing UV-Light Damage of Light Sensitive Materials using a Highly Protective UV-Absorbing Coating. *Chem. Soc. Rev.* **2007**, 36 (8), 1270-1281.
19. Wang, G.; Ling, Y.; Lu, X.; Qian, F.; Tong, Y.; Zhang, J. Z.; Lordi, V.; Rocha Leao, C.; Li, Y., Computational and Photoelectrochemical Study of

- Hydrogenated Bismuth Vanadate. *J. Phys. Chem. C* **2013**, *117* (21), 10957-10964.
20. Kudo, A.; Ueda, K.; Kato, H.; Mikami, I., Photocatalytic O₂ Evolution under Visible Light Irradiation on BiVO₄ in Aqueous AgNO₃ Solution. *Catal. Lett.* **1998**, *53* (3-4), 229-230.
21. Kudo, A.; Omori, K.; Kato, H., A Novel Aqueous Process for Preparation of Crystal Form-Controlled and Highly Crystalline BiVO₄ Powder from Layered Vanadates at Room Temperature and Its Photocatalytic and Photophysical Properties. *J. Am. Chem. Soc.* **1999**, *121* (49), 11459-11467.
22. Sayama, K.; Nomura, A.; Zou, Z.; Abe, R.; Abe, Y.; Arakawa, H., Photoelectrochemical Decomposition of Water on Nanocrystalline BiVO₄ Film Electrodes under Visible Light. *Chem. Commun.* **2003**, (23), 2908-2909.
23. Sayama, K.; Nomura, A.; Arai, T.; Sugita, T.; Abe, R.; Yanagida, M.; Oi, T.; Iwasaki, Y.; Abe, Y.; Sugihara, H., Photoelectrochemical Decomposition of Water into H₂ and O₂ on Porous BiVO₄ Thin-Film Electrodes under Visible Light and Significant Effect of Ag Ion Treatment. *J. Phys. Chem. B* **2006**, *110* (23), 11352-11360.
24. Liang, Y.; Tsubota, T.; Mooij, L. P.; van de Krol, R., Highly Improved Quantum Efficiencies for Thin Film BiVO₄ Photoanodes. *J. Phys. Chem. C* **2011**, *115* (35), 17594-17598.
25. Kato, H.; Hori, M.; Kato, R.; Shimodaira, Y.; Kudo, A., Construction of Z-Scheme Type Heterogeneous Photocatalysis Systems for Water Splitting into H₂ and O₂ under Visible Light Irradiation. *Chem. Lett.* **2004**, *33* (10), 1348-1349.

26. Sasaki, Y.; Nemoto, H.; Saito, K.; Kudo, A., Solar Water Splitting using Powdered Photocatalysts Driven by Z-Schematic Interparticle Electron Transfer without an Electron Mediator. *J. Phys. Chem. C* **2009**, *113* (40), 17536-17542.
27. Martinez-de La Cruz, A.; Pérez, U. G., Photocatalytic Properties of BiVO₄ Prepared by the Co-Precipitation Method: Degradation of Rhodamine B and Possible Reaction Mechanisms under Visible Irradiation. *Mater. Res. Bull.* **2010**, *45* (2), 135-141.
28. Kohtani, S.; Koshiko, M.; Kudo, A.; Tokumura, K.; Ishigaki, Y.; Toriba, A.; Hayakawa, K.; Nakagaki, R., Photodegradation of 4-Alkylphenols using BiVO₄ Photocatalyst under Irradiation with Visible Light from a Solar Simulator. *Appl. Catal., B* **2003**, *46* (3), 573-586.
29. Kohtani, S.; Hiro, J.; Yamamoto, N.; Kudo, A.; Tokumura, K.; Nakagaki, R., Adsorptive and Photocatalytic Properties of Ag-loaded BiVO₄ on the Degradation of 4-n-Alkylphenols under Visible Light Irradiation. *Catal. Commun.* **2005**, *6* (3), 185-189.
30. Bai, S.; Jiang, J.; Zhang, Q.; Xiong, Y., Steering Charge Kinetics in Photocatalysis: Intersection of Materials Syntheses, Characterization Techniques and Theoretical Simulations. *Chem. Soc. Rev.* **2015**, *44* (10), 2893-2939.
31. Pan, J.; Liu, G.; Lu, G. Q. M.; Cheng, H. M., On the True Photoreactivity Order of {001},{010}, and {101} Facets of Anatase TiO₂ Crystals. *Angew. Chem. Int. Ed.* **2011**, *50* (9), 2133-2137.
32. Li, R.; Zhang, F.; Wang, D.; Yang, J.; Li, M.; Zhu, J.; Zhou, X.; Han, H.; Li, C., Spatial Separation of Photogenerated Electrons and Holes Among {010} and {110} Crystal Facets of BiVO₄. *Nat. Commun.* **2013**, *4*, 1432.

33. Hong, S. J.; Jun, H.; Borse, P. H.; Lee, J. S., Size Effects of WO₃ Nanocrystals for Photooxidation of Water in Particulate Suspension and Photoelectrochemical Film Systems. *Int. J. Hydrogen Energy* **2009**, *34* (8), 3234-3242.
34. Osterloh, F. E., Nanoscale Effects in Water Splitting Photocatalysis. In *Solar Energy for Fuels*, Springer International Publishing: **2015**, pp 105-142.
35. Iwase, A.; Kudo, A., Photoelectrochemical Water Splitting using Visible-Light-Responsive BiVO₄ Fine Particles Prepared in an Aqueous Acetic Acid Solution. *J. Mater. Chem.* **2010**, *20* (35), 7536-7542.
36. Tokunaga, S.; Kato, H.; Kudo, A., Selective Preparation of Monoclinic and Tetragonal BiVO₄ with Scheelite Structure and Their Photocatalytic Properties. *Chem. Mater.* **2001**, *13* (12), 4624-4628.
37. Wang, G.; Wang, H.; Ling, Y.; Tang, Y.; Yang, X.; Fitzmorris, R. C.; Wang, C.; Zhang, J. Z.; Li, Y., Hydrogen-Treated TiO₂ Nanowire Arrays for Photoelectrochemical Water Splitting. *Nano Lett.* **2011**, *11* (7), 3026-3033.

Chapter 2

Literature Review

2.1. Introduction

BiVO_4 is an emerging n-type semiconductor that has been proven to be a promising ternary metal oxide material for various photocatalytic processes. Not only does BiVO_4 capable to induce photodegradation of organic compounds, it is also highly active for water splitting, both of which are the most significant applications of photocatalysis for environmental remediation and energy supply. With band gap energy of 2.4 – 2.5 eV, the light absorption ability of BiVO_4 outperforms that of the typical binary metal oxides such as TiO_2 , ZnO , and WO_3 with the respective band gap energies of 3.0 – 3.2,¹ 3.2 – 3.3,² and 2.7 eV,³ in which a larger proportion of the solar spectrum including visible region can be utilized. However, the solar conversion efficiency achieved with BiVO_4 to date is far below from the theoretical value. In light of this, over the past few years, development of novel ideas and techniques has been devoted to improve the understanding on the mechanistic aspects and the efficiency of this material.

This chapter reviews the experimental and computational breakthroughs achieved so far for BiVO_4 -based materials. The first part of this chapter will provide the fundamentals of photocatalysis to understand the selection criteria for photocatalysts, followed by the crystal and electronic structures of BiVO_4 that are closely related to the photoactivity of the material. Subsequently, the application of BiVO_4 in visible-light-triggered photocatalytic reactions, the related mechanisms and limitations of BiVO_4 will be discussed, in which emphasis is placed on water splitting. Lastly, recent approaches to

address one or more of the limitations to boost the efficiency of BiVO₄-based materials will be reviewed which include crystal facet engineering, formation of graphene composite, annealing treatment, and nanoscaling. The gaps existing in such strategies and the possible advancements will also be evaluated and explored.

2.2. Photocatalysis

Due to the presence of infinite number of atoms, the closely spaced orbitals render the energy levels in a solid to be presented as continuous band. The highest occupied energy band forms the valence band, whereas the lowest unoccupied band is denoted as the conduction band. It is the energy difference between the top of the valence band and the bottom of the conduction band (i.e., the band gap, which is measured in the units of electron volts (eV)) that categorizes solids into three main groups: metal, semiconductor and insulator.⁴

For metals, the band gap is negligible because of the overlapping valence and conduction bands (Figure 2.1). For insulators, the band gap is large enough to make the promotion of electrons from the valence band to the conduction band unviable. On the contrary, the band gap in semiconductors is not as large and hence provision of external energy (either thermally or photochemically) can excite electrons to the conduction band. Following an electron promotion, a positively charged vacancy is formed in the valence band, which is referred to as a hole. The activation of a semiconductor utilizing solar energy to generate electron-hole pairs for the ensuing chemical redox reactions is thus generally known as photocatalysis.

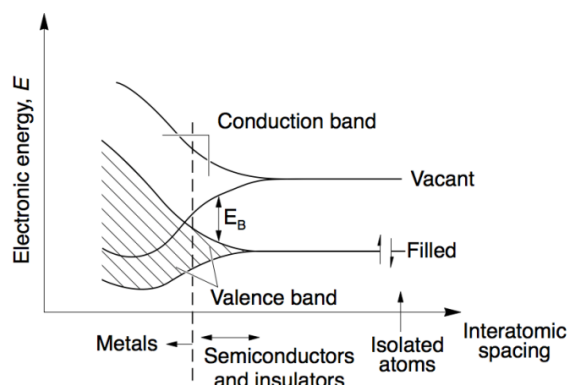


Figure 2.1. Electronic energy structure for solids.⁴

2.2.1. Basic Principles of Photocatalytic Reactions

Photocatalysis on semiconductor particles encompasses three main steps: (1) charge generation (electron-hole pairs) via absorption of photons with energies equivalent to or greater than the semiconductor band gap (as illustrated by the enlarged section of Figure 2.2); (2) charge separation and migration to the semiconductor surface; (3) charge transfer of electrons and holes to the electron acceptors and donors (represented by Pathway C and D in Figure 2.2), respectively, on the semiconductor surface for chemical reactions.

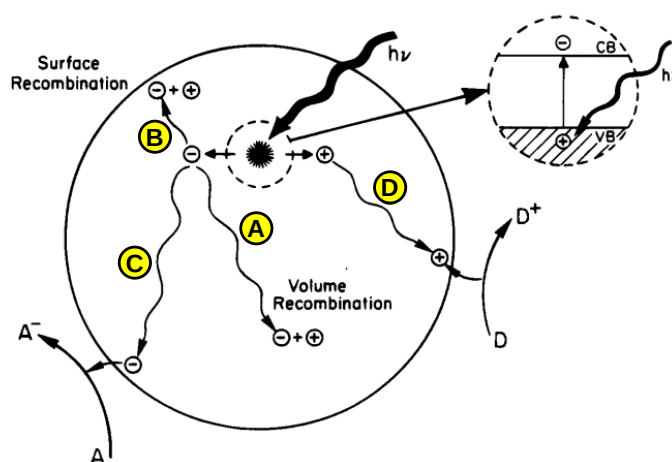


Figure 2.2. Kinetics of the photogenerated electrons and holes in a semiconductor upon excitation. Adapted from Linsebigler et al.⁵

As photon absorption is the initial process for photocatalysis by semiconductor, solar energy conversion efficiency of a semiconductor is principally affected by the width of its band gap. Given that merely 5 % of the solar spectrum is made up of UV light but a larger proportion (40 %) within the visible region,⁶ a semiconductor with sufficiently small band gap (i.e., < 3.0 eV) which is responsive towards visible light absorption is essential for effective harvesting and utilization of solar energy. Based on the standard solar spectrum and the assumption of 100 % quantum efficiency (i.e., complete absorption of the incident light), utilization of all UV light up to 400 nm by a photocatalyst for photocatalytic water splitting would result in a maximum solar conversion efficiency (i.e., maximum theoretical solar-to-hydrogen (STH) efficiency) of only 2 %, as illustrated in Figure 2.3. However, further extension of light utilization into the visible region would significantly improve the conversion efficiencies to 16 and 32 % for light absorption up to 600 and 800 nm, respectively.⁷

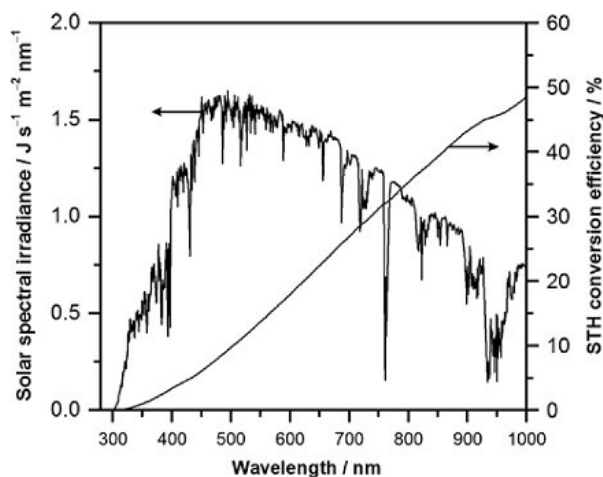


Figure 2.3. Distribution of standard solar spectrum (AM 1.5) and the maximum theoretical STH conversion efficiency as a function of the wavelength.⁸

Following light absorption, another important aspect that affects the photoconversion efficiency of a semiconductor is its charge separation efficiency, which controls the mobility and lifetime of the photogenerated electrons and holes. Upon band gap excitation, the electrons and holes generated within the semiconductor bulk have to separate and migrate to the surface to be active for subsequent redox reactions. Recombination of the electrons and holes that is detrimental for charge separation can occur both in the bulk (Pathway A depicted in Figure 2.2) and on the surface (Pathway B) of the semiconductor, reducing the number of free electrons and holes available on the surface. The charge separation efficiency of the semiconductor is highly dependent on the bulk and surface properties of the material such as crystallinity, particle size, number of surface active sites, and exposed crystal facets.⁹ Details will be reviewed in Section 2.5.

On the other hand, the ability of a semiconductor to drive oxidation and/or reduction reactions is governed by the band edge positions of the conduction and valence bands of the semiconductor with respect to the redox potentials of the reactants. While the energy level of the bottom of the conduction band determines the reducing ability of the photogenerated electrons, the top of the valence band defines the oxidizing potential of the holes. Typically, photoreduction of the reactants is thermodynamically possible if their reduction potentials lie below (more positive than) the conduction band edge. Whereas, photooxidation is feasible if the oxidation potentials of the reactants lie above (more negative than) the valence band edge.^{1, 5}

Therefore, for a semiconductor to be highly functional for the targeted applications with high solar conversion efficiency, it has to fulfill the following stringent requirements:

- Narrow band gap (i.e., < 3.0 eV) such that it can be activated by visible light
- Suitable bulk and surface properties to reduce recombination for efficient charge separation
- Appropriate conduction and valence band positions (i.e., potentials of the conduction and valence bands)

2.2.2. Oxide Semiconductor Photocatalysts

Although it is essential to satisfy the above-mentioned requirements, from the practicability and economical points of view, an ideal semiconductor photocatalyst also has to be chemically and photocatalytically stable, cheap, and easy to produce. Oxide semiconductors with high chemical and photostability, low cost, and ease of fabrication thus appear to be the promising photocatalyst materials. Earlier studies have been focused exclusively on binary metal oxides that are made up of earth-abundant elements such as ZnO,¹⁰⁻¹² TiO₂,^{5, 13-14} WO₃,¹⁵⁻¹⁷ and α -Fe₂O₃.¹⁸⁻²⁰ However, most of these binary metal oxides fall short of visible light absorption, attributing to their intrinsic highly positive valence bands that consist of O 2p orbitals located at ca. +3.0 V vs. NHE (normal hydrogen electrode).²¹ Despite α -Fe₂O₃ having a narrow band gap in the range of 2.0 – 2.2 eV, it is limited by short carrier lifetime and diffusion length to result in rapid charge recombination.²² The conduction bands of oxide semiconductors are generally composed of empty orbitals (known as the lowest unoccupied molecular orbitals, LUMOs) of metal cations with d^0 and d^{10} configurations. Given that the energy levels of these conduction bands are not significantly negative, lowering of these bands is thermodynamically undesirable. Instead, a new valence band formed by orbitals of other elements not associated with O 2p is imperative to reduce the band gaps of oxide

semiconductors by upshifting of the valence band edge, as schematically illustrated in Figure 2.4. This would help to design visible-light-driven oxide photocatalysts.

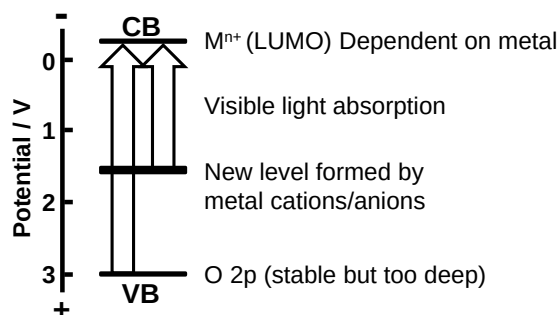


Figure 2.4. Valence band-controlled approach to design visible-light-driven oxide photocatalysts. Adapted from Kudo and Miseki.²³ CB and VB represent the conduction and valence bands, respectively.

In this regard, ternary metal oxides with their valence bands formed by atomic orbitals of more than one element offer better control of their band structure (i.e., band potentials and band gap energies), depending on the stoichiometric ratio of the elements and the crystal structure.²⁴ The orbitals of Bi 6s in Bi^{3+} , Ag 4d in Ag^+ , Pb 6s in Pb^{2+} , and Sn 5s in Sn^{2+} can contribute to valence bands formation above the valence band formed by O 2p orbitals in oxide photocatalysts.²³ Therefore, ternary metal oxides containing Bi, Ag, Pb, or Sn element such as BiVO_4 (particularly monoclinic scheelite structure),²⁵ Bi_2WO_6 ,²⁶ AgNbO_3 ,²⁷ PbCrO_4 ,²⁸ and SnNb_2O_6 ²⁹ have relative narrower band gap and they show photocatalytic activities under visible light irradiation.²³

2.3. Bismuth Vanadate (BiVO_4)

Originally BiVO_4 -based compounds were extensively studied as the potential substitutes for the lead-, cadmium-, and chromate-based pigments that are widely used in the coating and plastics industry, because of their non-toxic nature.³⁰ Over the past

four decades, the interest on BiVO_4 was mainly focused on its various technological properties such as ferroelasticity,³¹⁻³⁶ acousto-optical,³³ and ionic conductivity.³⁷ These properties are strongly dependent on the crystal structures of BiVO_4 . More recent research interest on BiVO_4 , however, is driven by its photocatalytic activity which also depends on the crystal structures with different electronic structures.^{25, 38} As previously discussed in Section 2.2., while BiVO_4 shares the common merits with other oxide semiconductors by being highly stable, abundant, and cheap, contribution of Bi 6s in Bi^{3+} toward valence band formation renders a relatively smaller band gap energy of this material, in particular the monoclinic scheelite BiVO_4 (2.4 – 2.5 eV). Such band gap reduction can potentially improve the STH efficiency to ca. 9 %, ³⁹⁻⁴¹ which is significantly greater than those typically achieved by binary metal oxides such as TiO_2 , ZnO , and WO_3 (< 5 %).⁴¹⁻⁴³ This makes BiVO_4 a promising photocatalyst candidate, which subsequently attracted profound research interest. A concise overview of the different crystal structures available for BiVO_4 and their corresponding optical properties and electronic structures are discussed in this section to facilitate understanding of the structure-dependent photocatalytic activity of BiVO_4 .

2.3.1. Crystal Structure and Phase Transition

Naturally occurring BiVO_4 exists as the mineral pucherite with orthorhombic structure. Nevertheless, normal laboratory synthesis routes do not produce BiVO_4 of the similar form. Three other main crystal structures are more commonly obtained: scheelite structure with tetragonal and monoclinic phases and zircon structure with tetragonal phase.^{31, 44} In all three structures, each V ion is coordinated by four O atoms in a tetrahedral site and each Bi ion is coordinated by eight O atoms. The distinction between scheelite and zircon structures is that each Bi ion is bounded to eight VO_4

tetrahedral units in the former structure, while the latter only has six VO_4 around one Bi ion (Figure 2.5).⁴⁵ For the scheelite structure, BiVO_4 with tetragonal and monoclinic phases are dissimilar as the local environments of V and Bi ions are notably distorted in the latter. Hence, the V-O bonds in tetragonal scheelite BiVO_4 (Figure 2.5 a) are all of equal length (1.72 Å), while two different V-O bond lengths (1.77 Å and 1.69 Å) are present in monoclinic scheelite BiVO_4 (Figure 2.5 b).⁴⁶

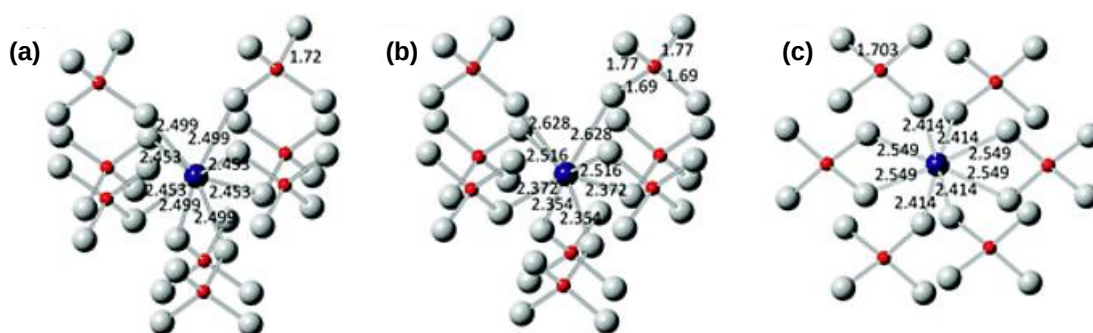


Figure 2.5. Local coordination of V (red), Bi (purple), and O (grey) atoms in (a) tetragonal scheelite, (b) monoclinic scheelite, and (c) tetragonal zircon BiVO_4 structure, in which the both lengths are shown in Å.⁴⁵

In general, low temperature synthesis such as precipitation at room temperature produces zircon-structured BiVO_4 , while high temperature syntheses (e.g., solid-state and melting reactions) result in the formation of monoclinic scheelite BiVO_4 .²⁵ However, the crystal structure of the obtained BiVO_4 is highly determined by the preparation method. Scheelite BiVO_4 with tetragonal and monoclinic phases were also reported to be selectively attainable via aqueous process at room temperature depending on the preparation time.³⁸ While tetragonal scheelite BiVO_4 was initially obtained from the dissolution and recrystallization process, further aging of the process resulted in the formation of monoclinic scheelite BiVO_4 . This suggests that the formation of tetragonal scheelite BiVO_4 is kinetically favorable, while monoclinic scheelite is a more thermodynamically stable form of BiVO_4 at room temperature. The phase transitions are

also possible via heat treatment (Figure 2.6): transformation of scheelite BiVO_4 with monoclinic and tetragonal phases occurs reversibly at 528 K;³¹ tetragonal zircon BiVO_4 irreversibly transforms into monoclinic scheelite at 670 – 770 K.²⁵ Irreversible transition from tetragonal zircon to monoclinic scheelite has also been demonstrated to be viable through mechanical crushing.³⁶

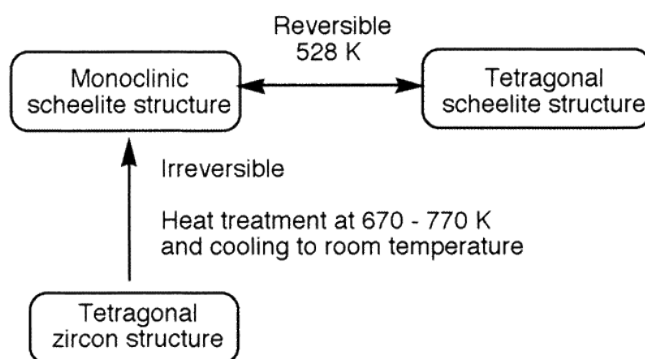


Figure 2.6. Phase transitions of BiVO_4 via heat treatment.³⁸

2.3.2. Electronic Structure

On the basis of the comparable band gap energies between tetragonal scheelite (2.34 eV) and monoclinic scheelite (2.41 eV) BiVO_4 , Tokunaga et al. suggested that the electronic structures of these scheelite-structured BiVO_4 's are similar.³⁸ However, they found that monoclinic scheelite BiVO_4 showed significantly higher activity for O_2 evolution from aqueous AgNO_3 solution (i.e., water oxidation reaction with Ag^+ as sacrificial reagent) compared to tetragonal scheelite BiVO_4 , under both UV and visible light irradiations.³⁸ The distinct difference in photocatalytic activity between the two BiVO_4 was attributed to the difference in the distortion of the local structure. In particular, distortion of the Bi-O polyhedron by the $6s^2$ lone pair of Bi^{3+} primarily in the monoclinic BiVO_4 improves charge separation and photocatalytic activity.

On the other hand, Kudo et al. demonstrated that the water oxidation activity of monoclinic scheelite BiVO_4 was higher than that of zircon-type BiVO_4 under visible light irradiation, in spite of their comparable activity under UV irradiation.²⁵ The different activities under visible light irradiation was revealed to be mainly due to the enhanced optical absorption of monoclinic scheelite BiVO_4 compared to tetragonal zircon BiVO_4 , as portrayed in Figure 2.7. Compared to zircon-type BiVO_4 , an additional valence band formed by 6s states of Bi^{3+} (i.e., Bi 6s orbitals) or a hybrid Bi 6s - O 2p orbitals was postulated to present above the O 2p orbitals in scheelite BiVO_4 . The electron transition from the Bi 6s or hybrid Bi 6s – O 2p valence band (that is of lower energy than the O 2p valence band) to the V 3d conduction band hence leads to smaller band gap energy of scheelite BiVO_4 (2.4 eV) in comparison to that of zircon BiVO_4 (2.9 eV) with V – O transition.²⁵

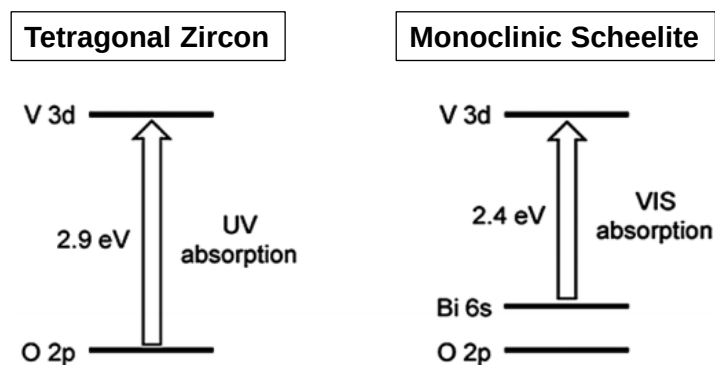


Figure 2.7. Band structures of tetragonal zircon and monoclinic scheelite BiVO_4 proposed by Kudo et al.²⁵

The findings by Tokunaga et al. and Kudo et al., as described above, collectively suggest that among the three structures, monoclinic scheelite is the most active phase of BiVO_4 for photocatalytic applications under visible light irradiation. Therefore, the electronic structure of monoclinic scheelite BiVO_4 based on computational and

experimental findings reported to date is further reviewed hereafter. Density functional theory (DFT) calculations by Walsh et al. indicated that the BiVO_4 is a direct band gap semiconductor with the conduction band mainly composed of V 3d states with contributions from O 2p and Bi 6p, whereas the top of the valence band consists of Bi 6s – O 2p antibonding state.⁴⁷ These structures were affirmed by Payne et al. using X-ray photoemission spectroscopy (XPS), X-ray emission spectroscopy (XES), and X-ray absorption spectroscopy (XAS),⁴⁸ corroborating hybridization of Bi 6s states and O 2p states at the valence band maximum of monoclinic BiVO_4 as suggested by Kudo et al.²⁵

However, a different structure was proposed by Zhao et al. according to their DFT calculations, in which the BiVO_4 was predicted as an indirect band gap semiconductor.⁴⁹ The top of the valence band was estimated to be predominated by the nonbonding states of O $2p_\pi$ and Bi 6s, whereas the bottom of the conduction band is primarily the nonbonding V $3d_{x^2-y^2}$ and $3d_{z^2}$ states. The relatively smaller band gap of this BiVO_4 was ascribed to the lone-pair distortion impact of Bi 6s, contributing to the upshift of the O 2p states to lower energy. A more recent study by Cooper et al. provides a comprehensive band structure of the BiVO_4 (Figure 2.8), which was derived from DFT calculations in conjunction with experimental evidences obtained via combination of X-ray spectroscopies, including XAS, XES, resonant inelastic X-ray scattering (RIXS), and XPS.⁵⁰ The valence band was found to primarily composed of O 2p states, whereby hybridized V 3d – Bi 6p and V 3d – O sp^2 orbitals contribute to the respective lowest and middle regions, whereas O $2p_\pi$ and Bi 6s contribute to the top region, in consistent with that reported by Zhao et al.⁴⁹ Likewise, the conduction band consists of V 3d states with dominant $d_{x^2-y^2}$ and d_{z^2} character at the lowest energy edge, but contains Bi 6p character at the upper region. The band gap energy was determined

to be 2.5 eV with the Fermi energy at the surface measured to be 2.0 eV above the valence band maximum, indicating that the BiVO_4 is an n-type semiconductor.

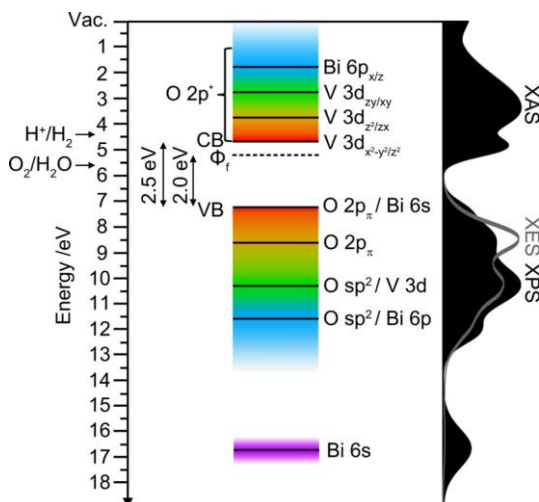


Figure 2.8. Energy level diagram representing the electronic structure of monoclinic scheelite BiVO_4 proposed by Cooper et al. based on DFT calculations and experimental spectra of XAS, XES, XPS, and RIXS. All energy levels are shown with respect to vacuum.⁵⁰

Consistently, the DFT calculations by Walsh et al.⁴⁷ and Zhao et al.⁴⁹ suggest that the effective masses of both holes and electrons in monoclinic scheelite BiVO_4 are smaller than other oxide materials. While Walsh et al. predicted a minimum effective mass of $0.3 m_0$ for both electrons and holes, Zhao and co-workers found the minimum effective masses of $0.9 m_0$ for electrons and $0.7 m_0$ for holes, where m_0 represents electron rest mass. Since the drift velocity of electrons and holes is inversely proportional to the effective mass,⁵¹ the smaller effective masses suggests easier charge separation and migration to reach the surface reaction sites, indicating the potential of monoclinic scheelite BiVO_4 as a photocatalyst.

2.4. Photocatalytic Applications of BiVO₄ under Visible Light

Depending on the change in Gibbs free energy, photocatalytic reactions can be classified into two types: downhill and uphill (Figure 2.9).⁹ Photooxidation of organic compounds (i.e., organic degradations) that occurs irreversibly using oxygen molecules is generally a downhill reaction. This type of reaction is regarded as a photoinduced reaction because it is instigated by the reactive oxygen species (ROS) formed by the redox reactions between photogenerated charge carriers and water molecules or dissolved oxygen. Meanwhile, water splitting into H₂ and O₂ involves the conversion of photon energy into chemical energy, accompanied by a large positive change in Gibbs free energy ($\Delta G^\circ = 273 \text{ kJ mol}^{-1}$). This reaction is similar to photosynthesis by green plants, which is also an uphill reaction. Therefore, water splitting is otherwise known as artificial photosynthesis.

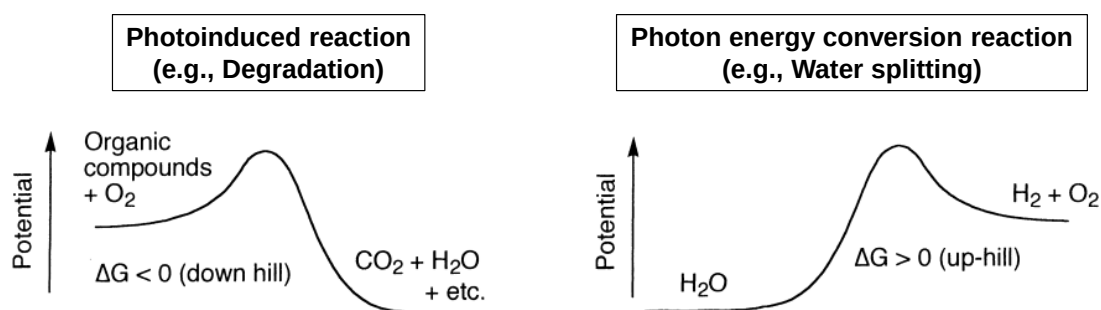


Figure 2.9. Two distinct classifications of photocatalytic reactions: downhill and uphill.⁹

This section will focus on the fundamental principles of the photocatalytic reactions of organic degradation and water splitting. The comparison of BiVO₄ as a potent visible-light-active photocatalyst alongside with other oxide materials on their respective functionalities in these applications is also covered. Given that monoclinic scheelite BiVO₄ is the only structure that shows high photoactivity under visible light, the BiVO₄ mentioned henceforth will refer to monoclinic scheelite BiVO₄, unless otherwise stated.

2.4.1. Organic Degradations

Environmental pollution (e.g., water and air) resulting from various anthropogenic and industrial activities is largely composed of organic compounds such as pesticides, dyes, chloro-organics and surfactants. Great research effort has been focused on photocatalysis as a viable option for environmental remediation since the functional groups of organic compounds may be oxidized, allowing transformation or degradation of the organic contaminants into less harmful substances.¹ Oxide semiconductors with highly positive valence band, in particular TiO_2 , have been extensively studied and shown to be effective in photooxidative degradation of numerous organic compounds.^{1,}

52

Organic degradation in aqueous phase or humid condition can generally proceed via two pathways: direct oxidation by holes and indirect oxidation by ROS such as superoxide ($\text{O}_2^{\bullet-}$) and hydroxyl ($\bullet\text{OH}$) radicals.²² $\bullet\text{OH}$, which is one of the most active and nonselective ROS, is highly oxidizing and formed by the reaction of photogenerated holes with the adsorbed H_2O or hydroxide groups present on the surface of oxide photocatalyst. Simultaneously, electrons in the conduction band are transferred to oxygen to generate $\text{O}_2^{\bullet-}$ that can trigger the subsequent formations of hydroperoxyl radicals ($\text{HO}_2^{\bullet}$) and hydrogen peroxide (H_2O_2), depending on the reaction conditions. These $\bullet\text{OH}$, $\text{O}_2^{\bullet-}$, $\text{HO}_2^{\bullet}$, and H_2O_2 are the important oxidant sources involve in the photocatalytic degradation of organics by TiO_2 .^{1, 52}

Despite having a considerably more negative valence band potential compared to that of TiO_2 , the thermodynamically weaker photooxidation power of BiVO_4 has also been reported to be highly efficient in the photodegradation of organic materials under visible light, including water-soluble and volatile organic compounds. The former includes

organic dyes (e.g., rhodamine B,⁵³⁻⁵⁵ methylene blue,⁵⁶⁻⁵⁷ and methyl orange⁵⁸⁻⁵⁹) and non-ionic surfactants (e.g., 4-n-nonylphenol,⁶⁰ nonylphenol,⁶¹ and 4-n-alkyl-phenol⁶²), while an example of the latter is ethylene.⁶³ In fact, the feasibility of photocatalytic organic degradation on BiVO₄ under visible light was shown to outperform that on TiO₂, which activity is strictly restricted to UV light.

Mechanistically, $\bullet\text{OH}$ radicals were proposed by several research groups as one of the active species to be involved in the photocatalytic oxidation of organic compounds by BiVO₄,^{53, 64} similar to that reported for TiO₂. For instance, on the basis of increased rhodamine B photodegradation rate with increasing pH value, one possible pathway for the photocatalytic decomposition of rhodamine B was attributed by Martinez-de La Cruz to the generation of $\bullet\text{OH}$ radicals on BiVO₄ (Figure 2.10).⁵³ At higher pH, a higher concentration of hydroxide (OH^-) ions is present in the aqueous solution. Adsorption of the OH^- ions on the surface of BiVO₄ and direct interaction with the photogenerated holes thus result in the formation of $\bullet\text{OH}$ radicals ($\text{OH}^- + \text{BiVO}_4(\text{h}^+) \rightarrow \bullet\text{OH} + \text{BiVO}_4$), which subsequently function as the oxidant to degrade the rhodamine B molecules available on the photocatalyst surface.

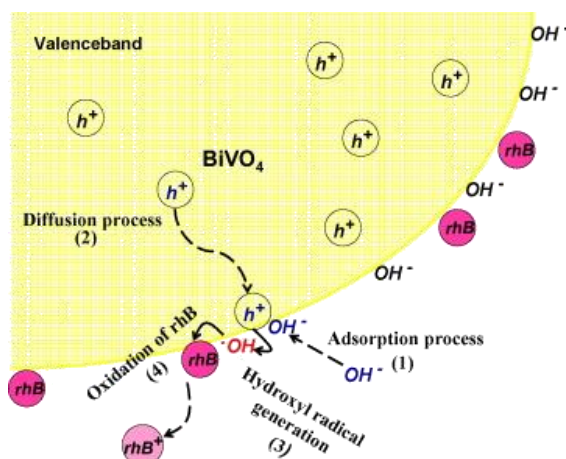


Figure 2.10. Schematic of the photocatalytic degradation pathway of rhodamine B (rhB) on BiVO₄ via $\bullet\text{OH}$ radical formation.⁵³

This generally accepted $\bullet\text{OH}$ -radical driven mechanism, however, was demonstrated by Kohtani et al. in their more recent investigation to be extraneous in the case of BiVO_4 .⁶⁵ Generation of $\bullet\text{OH}$ radicals was detected through its reaction with terephthalic acid to form the highly fluorescent 2-hydroxyterephthalic acid (TAOH). The amount of TAOH formed in the presence of BiVO_4 was found to be negligible in comparison to that of TiO_2 , suggesting the inefficiency of BiVO_4 to generate $\bullet\text{OH}$ radicals by hole oxidation of OH^- or water molecules. This phenomenon was ascribed to the negatively positioned valence band edge of BiVO_4 relative to the redox potential of $\bullet\text{OH}/\text{OH}^-$ (Figure 2.11), indicating that $\bullet\text{OH}$ generation is thermodynamically unfavorable on BiVO_4 .

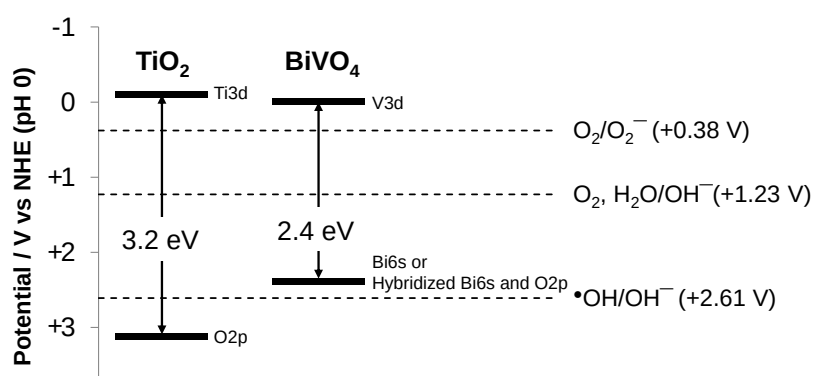


Figure 2.11. Energy diagrams of BiVO_4 in comparison to TiO_2 at pH 0. Adapted from Kohtani et al.⁶⁵

2.4.2. Water Splitting

Large-scale production of H_2 as clean (i.e., carbon-free) and renewable energy carrier is desirable to address the global energy and environmental issues. Combustion of H_2 generates heat and work with water as the only byproduct. However, present industrial production of H_2 mainly relies on steam reforming, in which fossil fuels (e.g., natural gas) are consumed to result in CO_2 emission.





One ideal way to solve the energy and environmental concerns is to utilize the renewable and freely available solar energy for H_2 generation from water, that is, solar water splitting. The potential of solar energy conversion to produce H_2 via photocatalytic decomposition of water was widely recognized after the discovery of Honda-Fujishima effect using TiO_2 electrode in 1972.⁶⁶ Since then, tremendous efforts have been devoted into investigating water splitting using semiconductor photocatalysts. Water splitting has generally been studied using two approaches: powdered photocatalyst and photoelectrode (i.e., photocatalyst immobilized on a conducting substrate), which are hereafter denoted as powder suspension (PS) and photoelectrochemical (PEC) systems, respectively.

2.4.2.1. Powder Suspension System

Solar water splitting using powdered photocatalyst shows promise for practical H_2 production in a large scale because of its simplicity and low cost. Typically, the photocatalyst powders only need to be dispersed in a water pool and then H_2 will be readily obtained by exposing the suspension to sunlight, as depicted in Figure 2.12. The photochemical reactions involved in solar water splitting include two half reactions: (1) oxidation of water molecules by holes for O_2 generation (equation 2.3) and (2) reduction of water molecules by electrons to form H_2 (equation 2.4).



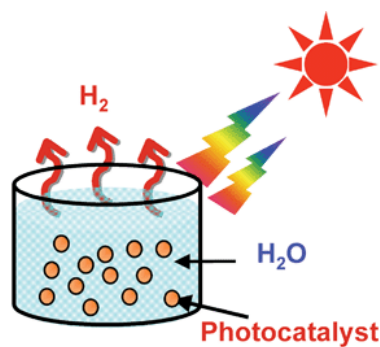


Figure 2.12. Schematic representation of powder suspension system for photocatalytic solar water splitting.²³

One strategy to drive an overall water splitting (i.e., simultaneous generation of H_2 and O_2 in stoichiometric amounts) is to use a single photocatalyst (single-step photoexcitation), as shown in Figure 2.13a. Thermodynamically, the bottom of the conduction band of a semiconductor photocatalyst has to be more negative than the redox potential of H^+/H_2 (0 V vs. NHE) and the top of the valence band be more positive than the redox potential of O_2/H_2O (1.23 V vs. NHE), in order to achieve overall water splitting.

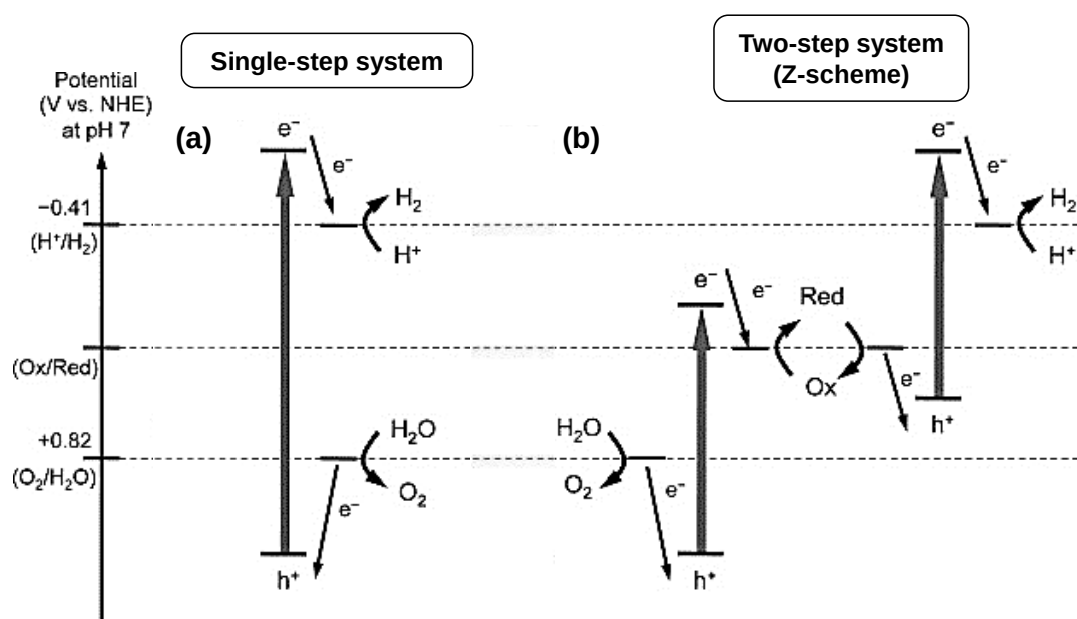


Figure 2.13. Schematic of (a) single- and (b) two-step photoexcitation systems for photocatalytic water splitting.⁷

Figure 2.14 exhibits the band potentials of various semiconductors relative to the redox potentials of water splitting. It is noteworthy that a number of oxide semiconductors such as TiO_2 , SrTiO_3 , Ta_2O_5 , KTaO_3 , and ZrO_2 have suitable band structures for splitting water into H_2 and O_2 . However, their application is primarily limited to UV light due to their intrinsically large band gaps, which is also the major demerit of tantalate photocatalysts that were shown to be active for overall water splitting.⁹ On the other hand, despite having suitable band potentials and a narrow band gap responsive to visible light, CdS is unstable and not active for overall water splitting because it is susceptible to photocorrosion. In the absence of a sacrificial electron donor, S^{2-} anions in CdS rather than H_2O molecules are preferentially oxidized by the photogenerated holes, resulting in the decomposition of CdS into Cd^{2+} and S according to the equation below:⁶⁷⁻⁶⁸



Such phenomenon of photocorrosion is commonly the limitation of metal sulfide photocatalysts.

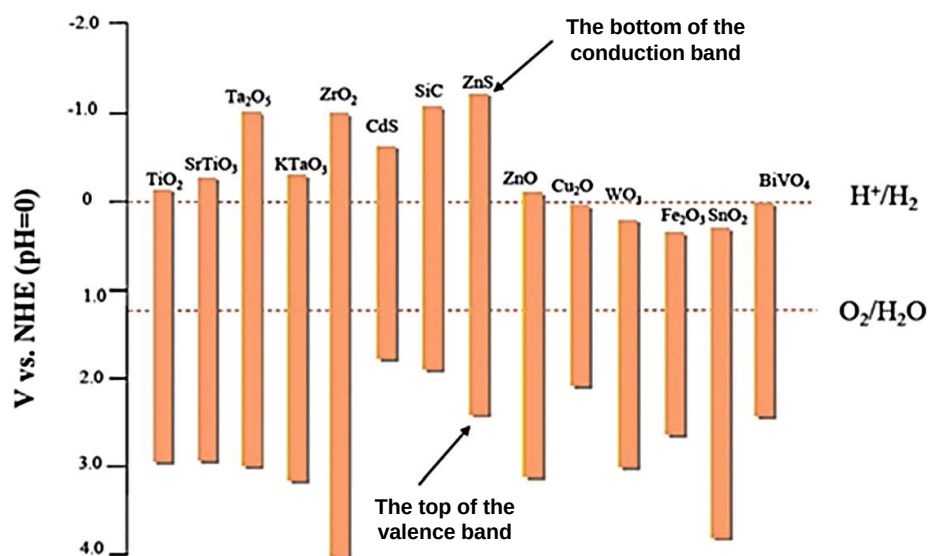


Figure 2.14. Comparison of the band structures of various photocatalysts with respect to the redox potentials of water splitting.⁶⁹

In fact, the number of semiconductors that are visible-light-active, photochemically stable and have appropriate conduction and valence band potentials for overall water splitting, are very limited. Band gap engineering of oxide photocatalysts is therefore essential for the development of new photocatalysts that are applicable for overall water splitting under visible light irradiation. For example, formation of midgap electron donor level via doping, introduction of a new valence band by element other than O 2p (e.g., oxynitrides and oxysulfides) and the production of solid solutions have been demonstrated to be efficient for band gap narrowing (Figure 2.15).^{7, 23} To date, $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ solid solution is one of the few visible-light-driven photocatalysts reported to be active for overall water splitting.⁷⁰

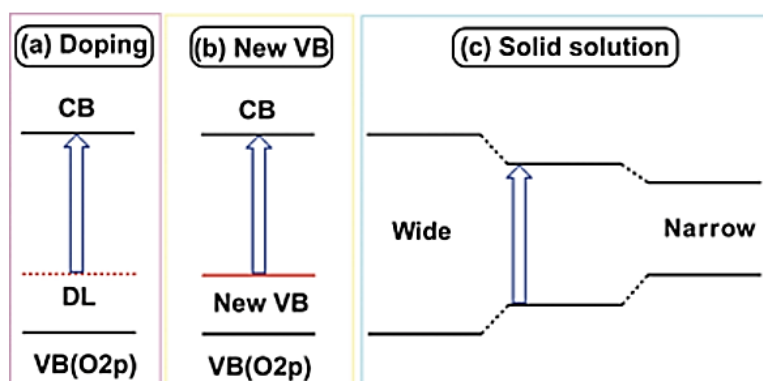


Figure 2.15. Band gap engineering approaches to design visible-light-active oxide photocatalysts.²³ CB, VB and DL represent the conduction band, valence band and electron donor level, respectively.

An alternative strategy for splitting water into H_2 and O_2 is to employ a two-step photoexcitation mechanism (Figure 2.13b), similar to that in natural photosynthesis by green plants and is known as the Z-scheme.^{7, 23, 71} This system was first introduced by Bard in 1979,⁷² which involves two different photocatalysts: one that is responsible for H_2 evolution and the other for O_2 evolution. A suitable electron mediator (e.g., redox

couple Red/Ox such as IO_3^-/I^- and $\text{Fe}^{3+}/\text{Fe}^{2+}$) is typically required to shuttle the photogenerated electrons from the O_2 -evolving photocatalyst to the H_2 -evolving photocatalyst. However, the presence of reversible ionic redox couple may promote undesirable backward reactions on the photocatalysts (Figure 2.16). For example, on the O_2 -evolving photocatalyst, the thermodynamically more favorable oxidation of reductant (Red) to oxidant (Ox) may compete with oxidation of water to O_2 . Likewise, reduction of Ox to Red may proceed preferentially over water reduction to H_2 on the H_2 -evolving photocatalyst.⁷ Such backward reactions suppress forward reactions (H_2 and O_2 generations), thus strongly hinder the efficiency of the Z-scheme system for overall water splitting. In regard to this, studies related to Z-scheme water splitting have also been directed towards using graphene as the solid-state electron mediator⁷³⁻⁷⁴ and promoting direct electron transfer between photocatalyst particles via electrostatic interaction without an electron mediator.⁷¹

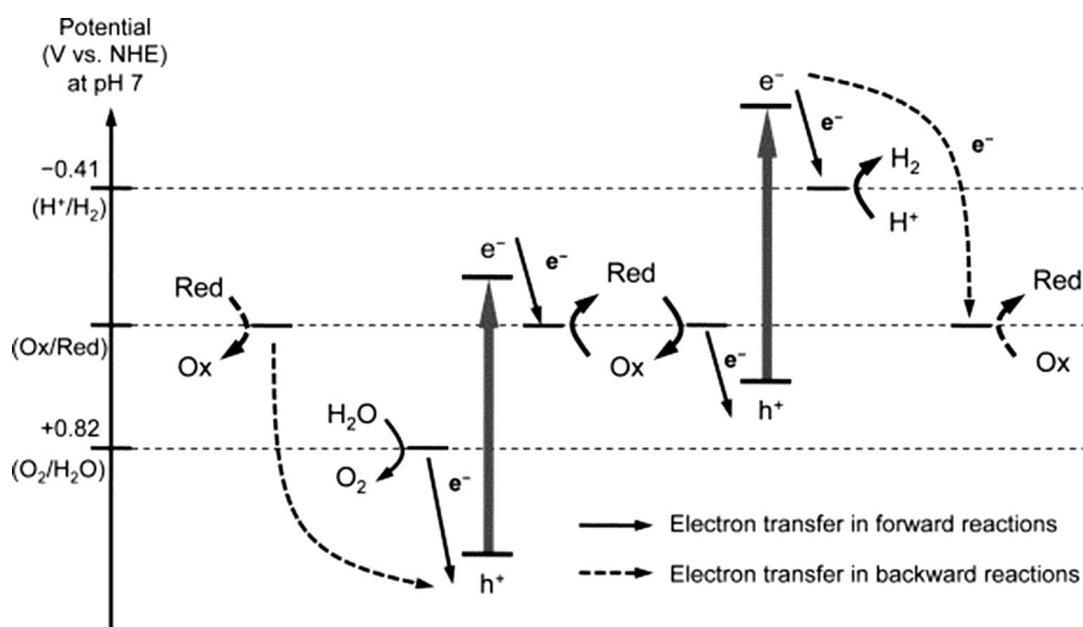


Figure 2.16. Schematic of the undesirable backward reactions along with the forward reactions in the two-step photoexcitation system.⁷

Z-scheme system offers a greater potential over the single-step system for water splitting under visible light. Visible-light-driven semiconductor photocatalysts that are active only for either water reduction or oxidation can potentially be employed for the construction of the Z-scheme. Consequently, the ability of a great variety of semiconductor photocatalysts for H_2 or O_2 evolution from water (i.e., half reactions of water splitting) has widely been conducted and evaluated in the presence of sacrificial reagents. Addition of a reducing reagent (i.e., hole scavenger) such as alcohol and sulfide ions promotes consumption of the photogenerated holes via oxidation of the reducing agent. This then enriches the electrons in the photocatalyst for an enhanced H_2 evolution reaction (Figure 2.17a). On the other hand, in the presence of an oxidizing agent (i.e., electron scavenger) such as Ag^+ and Fe^{3+} , the photogenerated electrons are readily used for reducing the oxidizing agent and results in an enhanced O_2 evolution reaction (Figure 2.17b). However, one should be aware that the photocatalysts tested to be active for the half reactions are not definite to be active for overall water splitting in the absence of sacrificial reagents.

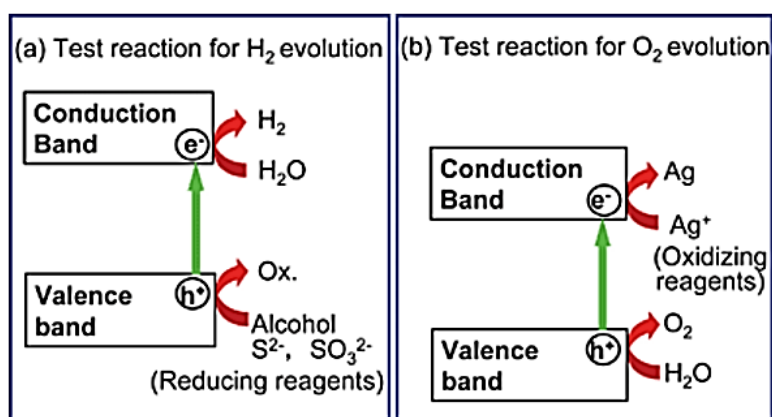


Figure 2.17. Photocatalytic H_2 or O_2 evolution from the aqueous solutions containing sacrificial reagents.²³

Although H_2 production is primarily the main focus of water splitting, the O_2 evolution half reaction plays an equally significant role in dictating the efficiency of the water splitting reaction since it supplies the electrons needed for water reduction to form H_2 . In fact, water oxidation is the more challenging half reaction for water splitting because it involves the abstraction of four electrons (refer to equation 2.3), whereas only two electrons are needed for water reduction (refer to equation 2.4). Among the visible-light-responsive oxide photocatalysts, WO_3 ⁷⁵ and BiVO_4 ^{25, 76} have been revealed to be active for O_2 generation from water in the presence of sacrificial reagent, attributing to their deep valence bands despite of the insufficient conduction band potential for water reduction, as presented in Figure 2.14. However, a greater attention is devoted to BiVO_4 because of its ability to absorb a larger portion of the solar spectrum, judging from its relatively smaller band gap (2.4 – 2.5 eV in comparison to 2.7 eV for WO_3).³ While the ability of BiVO_4 to oxidize water has been proven using Fe^{3+} as the oxidizing reagent,⁷⁷ the studies related to water oxidation on BiVO_4 are extensively executed using the electron-scavenging Ag^+ ions.^{25, 38, 46, 57}

Interestingly, the potential of BiVO_4 to function as the O_2 -evolving photocatalyst in visible-light-driven Z-scheme water splitting has also been demonstrated. The construction of the Z-scheme system constituting of BiVO_4 as the O_2 -evolving photocatalyst, $\text{Pt}/\text{SrTiO}_3\text{:Rh}$ (Rh-doped SrTiO_3) as the H_2 -evolving photocatalyst and $\text{Fe}^{3+}/\text{Fe}^{2+}$ as the redox couple was first reported by Kato et al. to be active for stoichiometric production of H_2 and O_2 (2:1) under visible light,⁷⁸ whereby the mechanism of overall water splitting is schematically displayed in Figure 2.18.

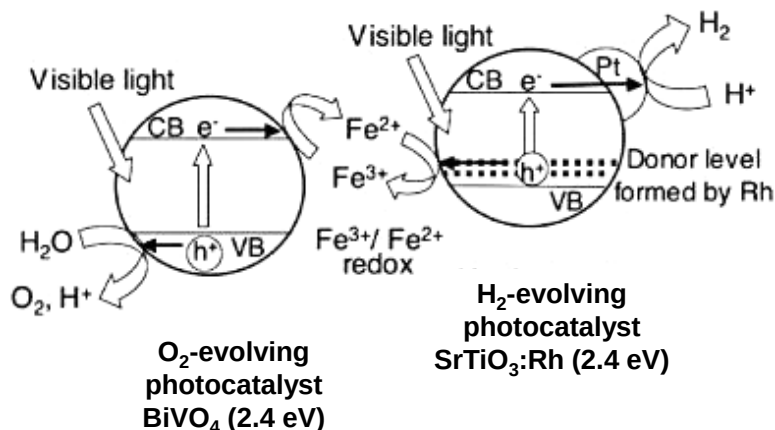


Figure 2.18. Mechanism of overall water splitting using the Z-scheme system constructed by BiVO_4 and $\text{Pt/SrTiO}_3\text{:Rh}$.⁷⁹

A subsequent study by Sasaki et al. showed that replacement of the Pt co-catalyst on the $\text{SrTiO}_3\text{:Rh}$ photocatalyst with Ru co-catalyst helped to suppress the undesirable backward reactions (e.g., water formation from H_2 and O_2 , oxidation of Fe^{2+} by O_2 and reduction of Fe^{3+} by H_2) particularly observed using $\text{Pt/SrTiO}_3\text{:Rh}$.⁷⁹ This study indicates that $\text{Ru/SrTiO}_3\text{:Rh}$ is a better H_2 -evolving photocatalyst to construct the $(\text{Ru/SrTiO}_3\text{:Rh})\text{-(BiVO}_4\text{)-(Fe}^{3+}/\text{Fe}^{2+}\text{)}$ Z-scheme system for overall water splitting under visible light. Such Z-scheme system composed of $\text{Ru/SrTiO}_3\text{:Rh}$ and BiVO_4 was also shown to split water into H_2 and O_2 by using $[\text{Co}(\text{bpy})_3]^{3+/2+}$ redox couple,⁸⁰ $[\text{Co}(\text{phen})_3]^{3+/2+}$ redox couple⁸⁰ or solid reduced graphene oxide (RGO)⁷³ as the electron mediator. On the other hand, overall water splitting was also observed to proceed in an electron-mediator-free $(\text{Ru/SrTiO}_3\text{:Rh})\text{-(BiVO}_4\text{)}$ Z-scheme system, in which the interparticle electron transfer was driven by the electrostatic interaction between the H_2 - and O_2 -evolving photocatalysts achieved via pH adjustment.⁷¹

Apart from $\text{Pt/SrTiO}_3\text{:Rh}$ and $\text{Ru/SrTiO}_3\text{:Rh}$, a very recent study by Iwase et al. also demonstrated photocorrosive metal sulfides as the potent H_2 -evolving photocatalysts in combination with CoOx-loaded BiVO_4 as the O_2 -evolving photocatalyst for Z-scheme

water splitting in the presence of RGO as the electron mediator.⁷⁴ Pt/CuGaS₂ and Pt/ZnGeS₄ were the only two metal sulfides found to be active in such system combination. As opposed to the Z-scheme systems containing Rh-doped SrTiO₃ as the H₂-evolving photocatalyst where stoichiometric water splitting was observed to proceed using bare BiVO₄ as the O₂-evolving photocatalyst, loading of CoOx as water oxidation co-catalyst on BiVO₄ was revealed to be necessary to promote electron injection from BiVO₄ to the metal sulfide via RGO for water splitting reaction to occur.

2.4.2.2. Photoelectrochemical System

The report of Honda-Fujishima effect in 1972 has formed the basis of PEC water splitting. As opposed to PS system, water reduction and oxidation reactions proceed on two physically separated electrodes in a PEC system. This allows separate production of H₂ and O₂ to prevent the backward reaction of the two gases to form water, which is the major setback in PS system. Another advantage of the PEC system is the immobilization of the photocatalyst particles on a conducting substrate, enabling easy removal and separation of the photocatalyst from water.

A basic PEC water splitting configuration includes single light-absorption component (i.e., a p-type or n-type semiconductor) and a counter electrode. Principally, the photoinduced minority carriers in the semiconductor are driven to the semiconductor-electrolyte interface due to the electric field at the interface, whereas the majority carriers are transported to the counter electrode (e.g., Pt) through an external circuit.⁸¹ In the case of n-type semiconductor, electrons as the majority carriers are transferred to the counter electrode to conduct water reduction for H₂ formation, while holes (the minority carriers) oxidize water to O₂ on the semiconductor surface, as illustrated in Figure 2.19a. Therefore, n-type semiconductor functions as the photoanode of the PEC cell. On the

contrary, p-type semiconductor with holes as the majority carriers works as the photocathode, in which water is being reduced on the semiconductor surface but being oxidized on the counter electrode (Figure 2.19b). However, given that most of the photochemically stable and visible-light-active semiconductors do not possess suitable thermodynamic potentials for water splitting into H_2 and O_2 , an external bias is generally needed to drive the overall water splitting. The provision of external bias by power supply is undesirable from the perspective of the energy consumption.

One ideal way to achieve visible-light-driven PEC water splitting without the need of electrical energy from an external source is to construct a tandem system composed of two light-absorption components as the photoanode and photocathode, as schematically shown in Figure 2.19c. Upon light illumination, both the photoanode and photocathode can be simultaneously excited to prompt spontaneous water redox reaction. Such a tandem system eliminates the stringent requirement of band potentials; the p-type semiconductor only needs to have a sufficiently negative conduction band to reduce water and the n-type semiconductor mainly requires a highly positive valence band to oxidize water. This suggests that a great variety of semiconductors with small band gaps can potentially be employed in such a PEC tandem system. However, Zhang et al. stated that the conduction band edge of the n-type semiconductor has to be more positive or of similar potential than the valence band edge of the p-type semiconductor,⁸² indicating careful selection of the semiconductor pair is crucial for the construction of the tandem system.

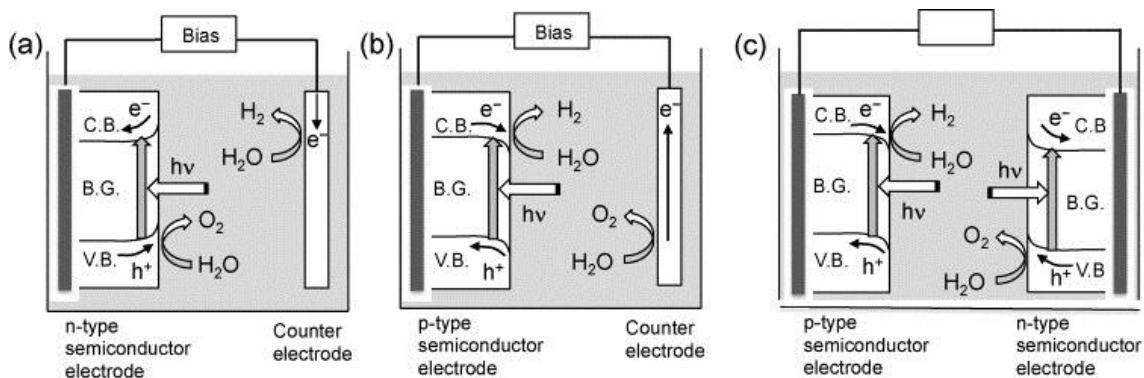


Figure 2.19. Configurations of PEC water splitting using (a) n-type semiconductor, (b) p-type semiconductor, and (c) both n-type and p-type semiconductors for a tandem system.⁷

BiVO_4 , which is an n-type semiconductor, has been recognized as one of the most promising photoanode materials.^{3, 39, 83} This is not only because of its small band gap of 2.4 – 2.5 eV and deep valence band, but also due to its conduction band edge that is only slightly below the redox potential for H^+/H_2 , which potential is relatively very negative compared to other visible-light-active n-type semiconductors. The potential of the photogenerated electrons that are used for water reduction at the cathode is determined by the conduction band position of the photoanode. A higher (i.e., more negative) conduction band position results in a more negative photocurrent onset potential at the anode half reaction, suggesting a lower external bias is needed and thus a higher cell efficiency can be achieved.⁴⁵

2.4.2.3. Difference in Charge Separation Mechanisms in PS and PEC Systems

When a semiconductor is brought into contact with a solution containing a redox couple, there exists a disparate electrochemical potential across the interface. In the case of n-type semiconductor that is immersed in a solution that contains strong oxidizing species (i.e., lower redox level ($E_{\text{F,redox}}$) than the Fermi energy (E_{F}) in the semiconductor), as illustrated in Figure 2.20, electrons will flow from the semiconductor into the solution

until the equilibrium is established ($E_F = E_{F, \text{redox}}$). The transfer of electrons away from the semiconductor causes band bending at the outer region of the semiconductor, in which the conduction and valence bands bend upward. Such a band bending develops an internal electric field (V_{sc}) within the semiconductor, whereby lesser electrons are present at the region of the semiconductor near the interface in comparison to the bulk. The depletion region is known as the space charge layer (SCL).

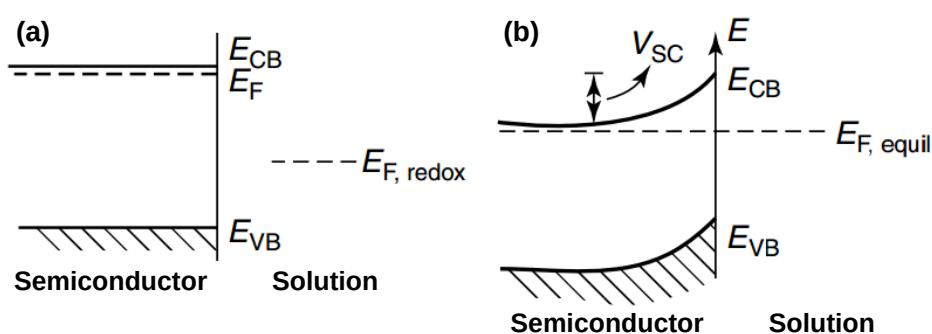


Figure 2.20. Schematic representation of the energy diagram of the semiconductor-solution interface (a) before and (b) after thermodynamic equilibration for a n-type semiconductor.⁸⁴

In the PS system, charge separation within the suspended semiconductor photocatalyst primarily relies on the SCL formation at the semiconductor-solution interface. For BiVO_4 that is n-type semiconductor, the built-in electric field in SCL drives the photogenerated electrons toward the bulk and holes are directed to the BiVO_4 -solution interface, promoting the separation of electrons and holes. The extent of electron-hole pair recombination within the bulk of the semiconductor (i.e., volume recombination) can be alleviated by the formation of SCL. However, the SCL thickness (d_{sc}) is restricted by the particle size since it cannot exceed the radius of the particle ($d_{sc} < d/2$).⁸⁵ As such, well-developed SCL is only present in large crystals but absent in nanosized particles, as portrayed in Figure 2.21.

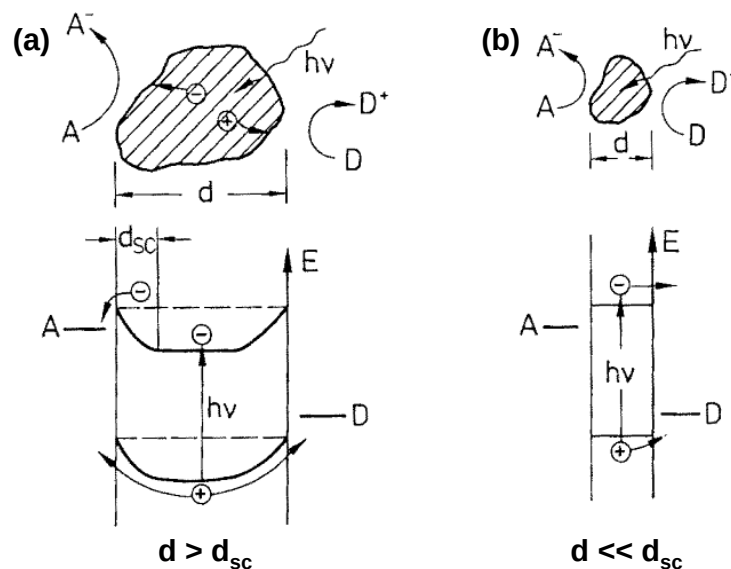


Figure 2.21. Formation of space charge layers in (a) large and (b) small semiconductor particles.⁸⁶

Additionally, since both the photogenerated electrons and holes have to be present on the surface of the same particle to conduct redox reactions, they can also be combined at the semiconductor surface (i.e., surface recombination). Therefore, the charge separation efficiency of suspended semiconductor photocatalyst in the PS system is determined by both the volume and surface recombination,⁸⁷ as schematically represented in Figure 2.22a.

On the other hand, charge separation in the PEC system is facilitated by the externally applied bias.⁸⁸ Given that the photogenerated electrons are transported to the cathode and physically separated from the holes at the anode, surface recombination of these charge carriers is not an issue in the PEC system. Instead, volume recombination arising from interparticle charge transport plays a critical role in governing the charge separation (Figure 2.22b).⁸⁷ Since the semiconductor particles are immobilized on a conducting substrate, the photogenerated electrons have to diffuse through the thickness

of the particle film to be collected at the back substrate, while holes have to migrate to the semiconductor-electrolyte interface to initiate oxidation reactions. Such migration of electrons and holes may result in their recombination at the grain boundaries.

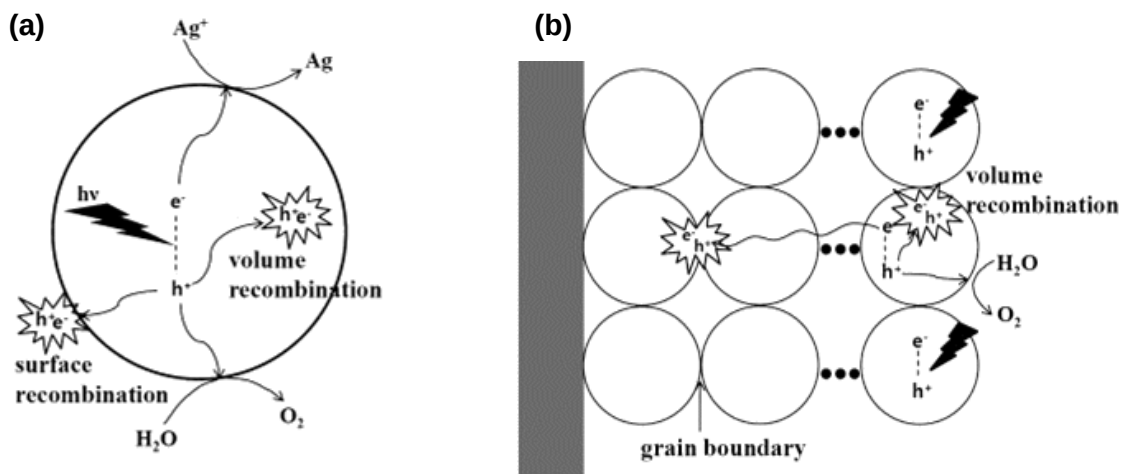


Figure 2.22. Schematics of the different charge separation mechanisms in the (a) PS and (b) PEC systems for water oxidation.⁸⁷

2.4.3. Limitations of BiVO₄

On the basis of 2.4 eV band gap, in which up to 11 % of the standard AM1.5 solar spectrum can be absorbed, BiVO₄ can theoretically produce a maximum photocurrent of 7.6 mA/cm² (assuming all incident photons with an energy greater than 2.4 eV are absorbed), corresponding to a solar-to-hydrogen energy efficiency of 9.3 %.³⁹ However, the actual energy conversion efficiency obtained by BiVO₄, reported to date, is far below its theoretical value. This is attributed to the poor electron transport,³⁹ slow water oxidation kinetics⁸⁹ and low carrier mobility,⁹⁰ contributing to the poor charge separation of BiVO₄.

Despite relatively small effective carrier masses have been predicted, the performance of BiVO₄ film was demonstrated by Liang et al. to be limited by poor electron

transport.³⁹ This was proven by the incident photon-to-electron conversion efficiency (IPCE) obtained from backside illumination of BiVO₄ photoelectrode (illumination through the substrate) was greater than that from the frontside illumination (illumination through the electrolyte), as presented in Figure 2.23a. Similar phenomenon was also observed by Zhong et al., where higher photocurrent densities were achieved with backside illumination of their BiVO₄ photoanodes, indicating that electron transport is slower than hole transport in the BiVO₄ films.⁹¹ The poor electron transport properties of BiVO₄ may be ascribed to the disconnected VO₄ tetrahedral units in the crystal structure of the material, suggesting that the photoexcited electrons in the V 3d conduction band have to hop between the VO₄ tetrahedra.³⁹ Indeed, the charge transport in BiVO₄ single crystals from 250 to 400 K has been proposed to be dominated by a small polaron hopping mechanism that is associated with low electron mobility.⁹² Poor wave function overlap between V 3d and Bi 6p orbitals at the conduction band of BiVO₄ to cause electron localization was also observed using DFT calculations.⁵⁰ In contrast, theoretical study on hole transport in BiVO₄ revealed a relatively weak hole localization in this material,⁹³ again signifying that the charge transport in BiVO₄ is primarily limited by electron mobility.

One approach that has been widely proven to effectively improve the electron transport in BiVO₄ involves introduction of impurity elements into the material, which is known as doping. Earlier efforts focused on BiVO₄ singly doped with metal. For example, Ye et al. demonstrated that among the various metal dopants (W, Fe, B, Cu, Zn, Ti, Nb, Sn, Co, Pd, Rb, Ru, Ag, Ga, Sr, and Ir), only W-doped BiVO₄ resulted in enhanced photocurrent and IPCE (obtained via frontside illumination) in comparison to undoped-BiVO₄.⁹⁴ Using backside illumination, significant enhancement of the IPCE spectrum of

BiVO₄ photoelectrode was also observed upon incorporation of 1 % W (Figure 2.23b), manifesting improved electron mobility ensuing from W-doping.³⁹ Subsequently, Luo et al. revealed that in addition to W, Mo is another metal dopant that can enhance the PEC performance of BiVO₄, while Ta, Zr, Si, Ti, La, Fe, Sr, Zn, and Ag are ineffective.⁹⁵ The beneficial role of W and Mo dopants to improve the electron transport in BiVO₄ was found to be due to increased carrier density,⁹⁴⁻⁹⁵ which is in accordance with DFT calculations that predict the two dopants as shallow electron donors.⁹⁶ Following these findings, BiVO₄ codoped with Mo and W has also been prepared and shown to outperform that of BiVO₄ singly doped with Mo or W.⁹⁷⁻⁹⁸

Another performance-limiting factor for BiVO₄ is slow hole transfer across the semiconductor-electrolyte interface (i.e., slow water oxidation kinetics). This is evidenced by about threefold enhancement of the photocurrent density of BiVO₄ in the presence of H₂O₂ (Figure 2.23c),^{40, 89} which is a highly efficient hole scavenger that has an oxidation kinetics at least 10 times faster than that of H₂O attributing to its lower reduction potential of +0.68 V with respect to +1.23 V vs. RHE for H₂O.⁹¹ The slow water oxidation kinetics of BiVO₄ can be overcome by modifying the surface with water-oxidation cocatalysts. While various transition metal catalysts such as IrO₂, RuO₂, and RhO₂ are known as good oxygen evolution catalysts,^{95, 99-100} materials based on earth-abundant elements are favorable. With regard to this, the potential of Co-Pi,^{40, 89, 91, 101-104} Co₃O₄¹⁰⁵⁻¹⁰⁶, CoO¹⁰⁷, FeOOH,¹⁰⁸⁻¹¹⁰ and NiOOH¹¹⁰ as the earth-abundant water-oxidation cocatalysts for BiVO₄ has recently been demonstrated. Of these cocatalysts, Co-Pi is the most commonly studied cocatalyst to improve the water oxidation kinetics of BiVO₄ in both the PEC and PS systems. Remarkably, the photocurrent densities of Co-Pi deposited BiVO₄ photoelectrodes were found to be

comparable to that of BiVO₄ performing H₂O₂ oxidation (Figure 2.23c),^{40, 89} indicating that Co-Pi is highly effective in capturing holes to promote water oxidation of BiVO₄ photoanode, whereby near-complete suppression of surface electron-hole recombination can be achieved.⁹¹ In spite of that, a significant fraction (60 – 80 %) of the photogenerated charge carriers still succumbs to recombination, as shown in Figure 2.23d.

In light of the different roles of doping and water-oxidation cocatalyst in improving BiVO₄ performance, as described above, Zhong et al. studied the performance of W-doped BiVO₄ interfaced with Co-Pi catalyst.⁹¹ In the tested potential range of 0.4 – 1.5 V vs. RHE (Figure 2.23e), although catalytic efficiencies of close to 100 % for surface water oxidation (ϕ_{ox}) on W-doped BiVO₄ can be achieved after Co-Pi modification, the resulting charge separation yields (ϕ_{sep}) still remain significantly low (approximately 0.1 – 0.3 (i.e., > 70 % of the electron-hole pairs are recombined)). The results thus suggest that bulk carrier recombination as the primary bottleneck limiting the efficiency of BiVO₄. Further development of BiVO₄ material should be focused on improving charge separation efficiency.

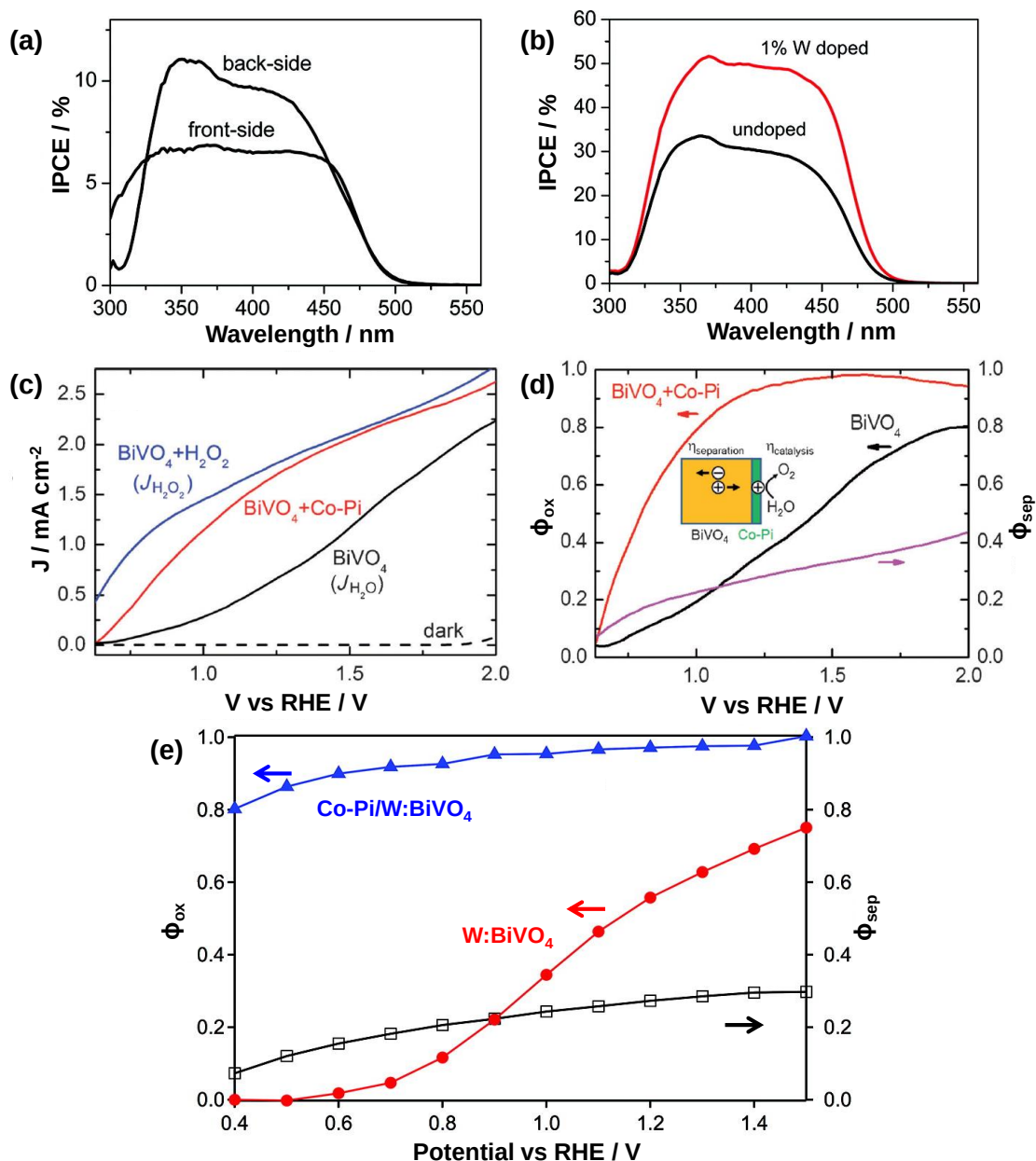


Figure 2.23. (a) IPCE spectra of BiVO₄ for frontside and backside illuminations.³⁹ (b) Comparison of the IPCE spectra of BiVO₄ and 1 % W-doped BiVO₄, both measured with backside illumination.³⁹ (c) Photocurrent-voltage curves of BiVO₄ (with and without the addition of H₂O₂ in the electrolyte), along with that of Co-Pi modified BiVO₄.⁴⁰ (d) Efficiencies of surface water oxidation catalysis (ϕ_{ox}) and charge separation (ϕ_{sep}) of BiVO₄ and Co-Pi modified BiVO₄ as a function of applied bias.⁴⁰ (e) ϕ_{ox} and ϕ_{sep} of W-doped BiVO₄ and Co-Pi modified W-doped BiVO₄ as a function of applied bias.⁹¹

The poor charge separation of BiVO₄ was revealed by Abdi et al. to be due to its intrinsic exceptionally low carrier mobility of $\sim 4 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (under ~ 1 sun illumination conditions).⁹⁰ However, the poor carrier mobility is compensated by the unexpectedly long carrier lifetime (40 ns) and diffusion length (70 nm), which are responsible for the high quantum efficiencies reported for BiVO₄. Table 2.1 compares the dynamic properties of BiVO₄ to typical metal oxides, such as Fe₂O₃, Cu₂O, and WO₃. Clearly, the carrier mobility of BiVO₄ is at least 1 – 2 orders of magnitude lower than that of the other metal oxides, while its carrier lifetime is 1 – 3 orders of magnitude longer.⁹⁰

Table 2.1. Comparison of the carrier mobility, lifetime, and diffusion length of BiVO₄ with that of several typical metal oxides.⁹⁰

Material	Carrier mobility, μ [$\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$]	Carrier lifetime, τ	Diffusion length, L [nm]
Fe ₂ O ₃	0.5	3 ps	2 – 4
Cu ₂ O	6	40 ps	25
WO ₃	10	1 – 9 ps	150 – 500
BiVO ₄	0.044	40 ns	70

2.5. Strategies for Improving the Charge Kinetics of BiVO₄

As described in Section 2.3. and 2.4., BiVO₄ possesses many features (e.g., visible band gap, deep valence band, and long carrier lifetime) that make it a highly promising oxide semiconductor photocatalyst for solar water oxidation and organic degradations. However, full exploitation of the valuable features of BiVO₄ is hindered by its intrinsic poor charge kinetics such as charge separation, transport, and transfer. While state-of-the-art BiVO₄ often incorporate n-type dopant (i.e., Mo and W) and water-oxidation cocatalyst to overcome the respective electron transport and water oxidation kinetics limitations of BiVO₄, the performance of BiVO₄ is still greatly hindered by poor charge

separation, particularly in the bulk. Exploration of other strategies, aside from doping and surface modification with water-oxidation cocatalyst, has shown the potentials of (1) morphology control, (2) formation of composite structure, (3) annealing treatment, and (4) nanoscaling to overcome the shortcomings of this material. This section aims to provide an overview of strategies 1–4, whereby relevant findings from our most recent studies will also be incorporated and discussed herein.

2.5.1. Crystal Facet Engineering

Given that photochemical redox reactions essentially proceed on the surface, the physicochemical and electronic properties of the exposed surfaces of a photocatalyst, which are dependent on the surface atomic arrangement and coordination, play a vital part in determining the reactivity and activity of the material. As such, design and morphological control of crystal facets is a strategy commonly employed to optimize the performance of various semiconductor photocatalysts.

On the one hand, the photoreactivity of different crystal facets exposed on a photocatalyst was demonstrated to vary because of the different surface atomic structures, surface electronic structures, and selective reactant adsorption.¹¹¹⁻¹¹⁶ These have been extensively studied for the benchmark oxide photocatalyst, TiO₂. Although anatase TiO₂ crystals obtained without addition of surfactant or directing agent in the synthesis processes are dominated by the thermodynamically stable {101} facets with minority {001} surfaces,¹¹⁷ both theoretical and experimental studies indicated that the latter being relatively more reactive than the former.¹¹⁸⁻¹²¹ The higher reactivity of {001} surface was conventionally ascribed to it having a higher percentage of surface undercoordinated Ti_{5c} atoms (100 %) in comparison to that of {101} with 50 % Ti_{5c} and 50 % Ti_{6c} atoms.^{112, 122} As opposed to the conventional understanding, Pan et al.

revealed that the photoreactivity order of the different facets on anatase TiO_2 is $\{001\} < \{101\} < \{010\}$ for $\bullet\text{OH}$ radical generation and H_2 evolution, accrediting to the cooperative attributes of surface unsaturated Ti_{5c} atom density and facet-specific conduction band potential.¹¹²

Likewise, BiVO_4 crystals with increased $\{010\}$ facets were shown to exhibit enhanced photocatalytic activity. Zhang et al. reported that BiVO_4 nanosheets with a preferred (010) surface orientation, synthesized in the presence of sodium dodecyl benzene sulfonate as the morphology-directing agent, showed faster degradation of N,N,N',N'-tetraethylated rhodamine than that of bulk BiVO_4 .¹²³ Xi et al. demonstrated that BiVO_4 nanoplates with exposed $\{010\}$ facets displayed enhanced degradation of Rhodamine B and photocatalytic O_2 generation in comparison to BiVO_4 nanorods and microcrystals.¹²⁴ By controlling the exposure extent of BiVO_4 (040) surface (corresponding to $\{010\}$ facets) using different amounts of TiCl_3 as the directing agent, Wang et al. revealed a correlation between the photocatalytic water oxidation activity of BiVO_4 with the $\{010\}$ facets, as exhibited in Figure 2.24.¹²⁵

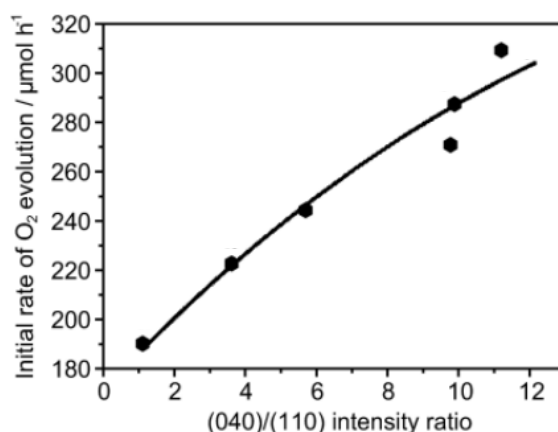


Figure 2.24. Correlation of the O_2 evolution rate of BiVO_4 with its exposure extent of $\{010\}$ facets, calculated via the XRD (040)/(110) peak intensity ratio. Adapted from Wang et al.¹²⁵

On the other hand, presence of different crystal facets on a photocatalyst polyhedron was demonstrated to drive spatial separation of photogenerated electrons and holes on the surface, which was proposed to be due to the difference in the potential energy levels of the conduction and valence bands of different facets arising from the varied surface electronic structures associated with them.¹²⁶⁻¹²⁷ Such phenomenon was first observed by Ohno et al. on TiO₂, in which formation of Pt deposits via photoreduction of Pt⁴⁺ primarily proceeded on the {110} facets of rutile and {101} facets of anatase, whereas PbO₂ particles resulting from photooxidation of Pb²⁺ were seen mainly on the {011} facets of rutile and {001} facets of anatase.¹²⁶ This study thus infers that rutile {110} and anatase {101} facets are the active reduction sites, while rutile {011} and anatase {001} facets function as the active oxidation sites. Using a single-molecule imaging and kinetic analyses of the fluorescence of redox-responsive fluorogenic dyes, Tachikawa et al. also demonstrated that the {101} facets of anatase TiO₂ are a more efficient reduction site than the {001} due to the preferential electron trapping on {101}.¹²⁸

The facet-selective metal and metal oxide depositions indicative of spatial separation of electrons and holes have also been demonstrated on other photocatalysts.^{127, 129} Particularly, Li et al. showed that the photoreduction of Au³⁺, Pt⁴⁺, and Ag⁺ ions to metal deposits and the photooxidation of Pb²⁺ and Mn²⁺ to metal oxide deposits took place selectively on the {010} and {110} facets of BiVO₄ crystal, respectively,¹²⁷ as depicted in Figure 2.25. The preferential occurrences of photoreduction reactions on the {010} facets and photooxidation on the {110} facets were attributed to the relatively lower conduction and valence band energy levels of the {010} facets (Figure 2.26a), which was supported by DFT calculations.¹²⁷ The difference in surface energy levels

suggests that electron transfer from $\{110\}$ to $\{010\}$ facets is thermodynamically feasible, leading to electron accumulation on the $\{010\}$ facets and hole on the $\{110\}$ (Figure 2.26b) for them to function as the redox functional facets.

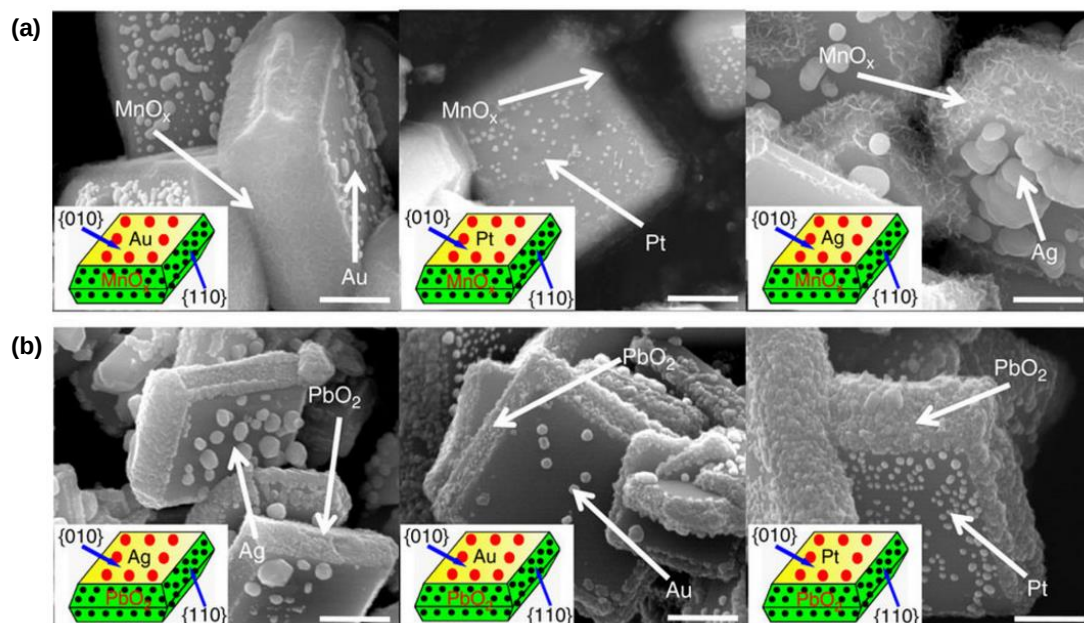


Figure 2.25. SEM images of the simultaneous depositions of metal (Au, Pt, or Ag) and metal oxide ((a) MnO_x or (b) PbO_2) on the surface of dual-faceted BiVO_4 .¹²⁷ Scale bar, 500 nm.

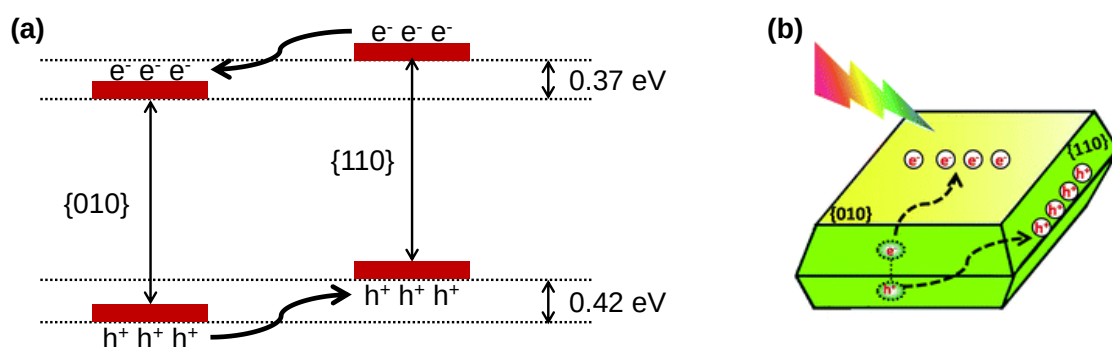


Figure 2.26. Schematic diagrams of (a) different conduction and valence band energy levels of the $\{010\}$ and $\{110\}$ facets of BiVO_4 ¹²⁷ and (b) spatial separation of electrons and holes on the two facets.¹⁰⁶

On the basis of the different energy structures of the {010} and {110} facets of BiVO₄, Li et al. designed two types of BiVO₄-TiO₂ heterojunctions by interfacing TiO₂ with either the {010} or the {110} facets of BiVO₄.¹³⁰ They revealed that the two heterojunctions have different activities for PEC photocurrent generation and photocatalytic degradation, owing to the different energy band alignments between TiO₂ and the two facets of BiVO₄. Meanwhile, the roles of {010} and {110} as the respective reduction and oxidation functional facets of BiVO₄ are further substantiated in numerous studies.^{106, 131} For instance, Li et al. presented that the reduction cocatalysts (Pt, Au or Ag) and oxidation cocatalysts (MnO_x or Co₃O₄) could be selectively deposited onto the {010} and {110} facets of BiVO₄ by sequential photodeposition method.¹⁰⁶ The deposition of cocatalysts on the right facets of the BiVO₄ (i.e., reduction cocatalyst on the electron-rich {010} facets and oxidation cocatalyst on the hole-rich {110} facets) was shown to be highly efficient to consume the photogenerated electrons and holes, resulting in enhanced photocatalytic activities with respect to the BiVO₄ with randomly distributed reduction and oxidation cocatalysts. For a Z-scheme comprises of the hybridization of platinized photosystem I (PSI) protein and BiVO₄, Kim et al. also demonstrated that photoreduction of Au³⁺ or Ag⁺ ions to the respective metal deposits occurred preferentially on the reduction functional {010} facets of BiVO₄ to allow selective extraction of electrons from BiVO₄ to be transferred to the PSI for H₂ generation reaction.¹³¹

Although the phenomenon of charge separation on the different facets of a semiconductor can be deduced from the results of selective photodepositions of metal and metal oxide and the DFT calculations, a direct evidence for the anisotropic charge transfer/separation on the surface of semiconductor is lacking. For this, Zhu et al.

employed spatially resolved surface photovoltage spectroscopy (SRSPS) on single dual-faceted BiVO_4 crystal and observed a highly anisotropic photogenerated hole transfer to the $\{110\}$ facets. This was indicated by the 70 times stronger SPS signal on the $\{110\}$ facets compared to that of $\{010\}$ facets.¹³² Tachikawa et al. studied the charge carrier dynamics of dual-faceted BiVO_4 using single-particle photoluminescence (PL) spectroscopy and discovered that trapped holes are favorably located on the $\{110\}$ facets of the BiVO_4 crystal, while electrons are uniformly distributed over the crystal.¹³³

The findings from the abovementioned experimental results of metal/metal oxide selective photodeposition, theoretical DFT calculations and in situ microscopic techniques consistently infer that photogenerated holes are preferentially transferred or accumulated on the $\{110\}$ facets of BiVO_4 relative to the $\{010\}$ facets, allowing $\{110\}$ to function as the active oxidation site. This may seem to be contradicting with the observations of the previously mentioned studies that suggest a correlation between the photooxidation performances of BiVO_4 (including degradation of organic molecules and water oxidation for O_2 evolution) with the $\{010\}$ facets,¹²³⁻¹²⁵ which are supposedly the reduction functional facet. However, it has to be noted that the BiVO_4 samples used for comparison in the said studies were of multiple morphological differences (e.g., particle size, types of exposed crystal facets and surface area). Therefore, the observed enhanced activity of BiVO_4 with preferentially exposed $\{010\}$ facets should not be solely attributed to the $\{010\}$ facets.

A theoretical study conducted by Yang et al. has indicated that water oxidation on the $\{010\}$ facets of BiVO_4 is more favorable than that on the $\{110\}$ facets because $\{010\}$ has higher charge carrier mobility, easier water adsorption and lower energy barrier.⁵¹ Despite these valuable computational calculations, the crystal facet effects on the charge

transfer efficiency of BiVO₄ to the reactants (electron donor/acceptor), which may be one of the underlying reasons for the crystal-facet-dependent photoactivity of BiVO₄, remain poorly understood. Preparation of dual-faceted BiVO₄ crystals with varying exposure extent of the {010} and {110} redox functional facets but of comparable size and surface area will be beneficial for better understanding of the crystal-facet-dependent charge transfer properties.

2.5.2. Compositing with Graphene

Coupling of semiconductor with a conductor (i.e., carbon materials) is a promising approach shown to be effective in enhancing the charge separation and transport properties of the semiconductor. Owing to the abundance of delocalized electrons from the conjugative π -system, carbon materials such as fullerenes,¹³⁴⁻¹³⁵ carbon nanotubes,¹³⁶⁻¹³⁷ and graphene¹³⁸ are good in accepting and shuttling the photogenerated electrons from semiconductor photocatalysts and hence effectively separating the electron-hole pairs. However, graphene has attracted more immense research interest than the other two carbon allotropes because of its unique two-dimensionality, contributing to its exceptionally high specific surface area ($\sim 2600 \text{ m}^2 \text{ g}^{-1}$)¹³⁹ that is readily accessible for surface adsorption of chemical molecules (i.e., organic reactants). The single-atom-thick nature of the graphene sheet also allows it to be optically transparent, which is a highly desirable characteristic to minimize the light-shielding-effect when it is being coupled with a semiconductor that works as the main photon absorber.

Among the numerous preparation methods of graphene reported to date (i.e., mechanical cleavage,¹⁴⁰ epitaxial growth,¹⁴¹ and chemical vapor deposition¹⁴²), chemical exfoliation of graphite to graphene oxide (GO) followed by reduction via

chemical, thermal, electrochemical, photocatalytic, sonochemical, photothermal or microwave-reduction method is the most widely employed approach due to the simplicity, reliability, low cost, and large scalability of the process.¹³⁸ In fact, the wide-ranging synthesis methods of graphene-based semiconductor photocatalysts have shown GO as the chief precursor of graphene.¹³⁸ While the presence of various oxygen functional groups (i.e., hydroxyl, epoxy, carboxyl, and carbonyl) on the surface of GO offers potential for functionalization and provides reactive sites for the nucleation and growth of nanoparticles, partial restoration of the conjugated sp^2 network via reduction to obtain reduced graphene oxide (RGO) is essential to resurrect the conductivity of GO.

The pioneering work on the synthesis of graphene-based semiconductor photocatalyst was reported by Williams et al. in 2008.¹⁴³ Apart from showing the practicability of in-situ photocatalytic reduction of GO by TiO_2 (under UV light) to obtain RGO- TiO_2 nanocomposite, the work also elucidated the mechanism of electron transfer pathway from photoexcited TiO_2 to GO, showcasing the electron-accepting attribute of graphene or graphene derivative. A subsequent work by Lightcap et al. demonstrated the stepwise transfer of photogenerated electrons from TiO_2 to GO for RGO formation and then from RGO to Ag^+ ions, resulting in the production of RGO-Ag- TiO_2 composite. The observation of the distinct Ag nanoparticle anchored site from that of the TiO_2 proved the electron-shuttling capability of RGO.¹⁴⁴ Such excellent electron-accepting and shuttling properties of RGO are generally associated with the longer carrier lifetime, lower charge recombination and improved photoactivities of various RGO-based oxide semiconductors, including TiO_2 ,¹⁴⁵⁻¹⁴⁶ WO_3 ,¹⁴⁷ ZnO ,¹⁴⁸ and SnO_2 ¹⁴⁹ to name a few.

The study on RGO- $BiVO_4$ composite was first conducted by Ng et al. via photocatalytic reduction of GO by $BiVO_4$ under visible light.¹⁵⁰ The resulting RGO- $BiVO_4$ exhibited

tenfold enhancement in PEC photocurrent compared to BiVO₄, as displayed in Figure 2.27a. Interestingly, the photocurrent generated by RGO-BiVO₄ under visible light was higher than that produced by UV-excited TiO₂. IPCE action spectra of BiVO₄ and RGO-BiVO₄ (Figure 2.27b) were examined to confirm that the photocurrent generation only occurs upon photoexcitation of BiVO₄ and therefore eliminates the possibilities of improved photocurrent of RGO-BiVO₄ attributing to enhanced light absorption ensuing from RGO addition and contribution of extra electrons from the excited RGO. On the contrary, the considerably increased photoconversion efficiency of RGO-BiVO₄ was proven due to slower charge recombination rate, as evidenced by the longer transient time constant (the time at which $\ln D = -1$, where $D = (I(t) - I_{(st)})/(I_{(in)} - I_{(st)})$, $I(t)$ is the photocurrent at a time t , $I_{(in)}$ the photocurrent at $t = 0$, and $I_{(st)}$ the steady-state photocurrent) of RGO-BiVO₄ in comparison to BiVO₄ (Figure 2.27c). This study thus suggests that the incorporation of RGO primarily provides a low-resistant electron pathway to facilitate electron transport from the photoexcited BiVO₄ to the conductive electrode (schematically illustrated in Figure 2.27d), enhancing charge separation and PEC photocurrent of RGO-BiVO₄. Following this report, the superior performance of RGO-BiVO₄ over bare BiVO₄ in different photocatalytic applications such as organic degradations,¹⁵¹⁻¹⁵² water oxidation,¹⁵³ and reduction of CO₂ and Cr(VI)¹⁵⁴ were also reported.

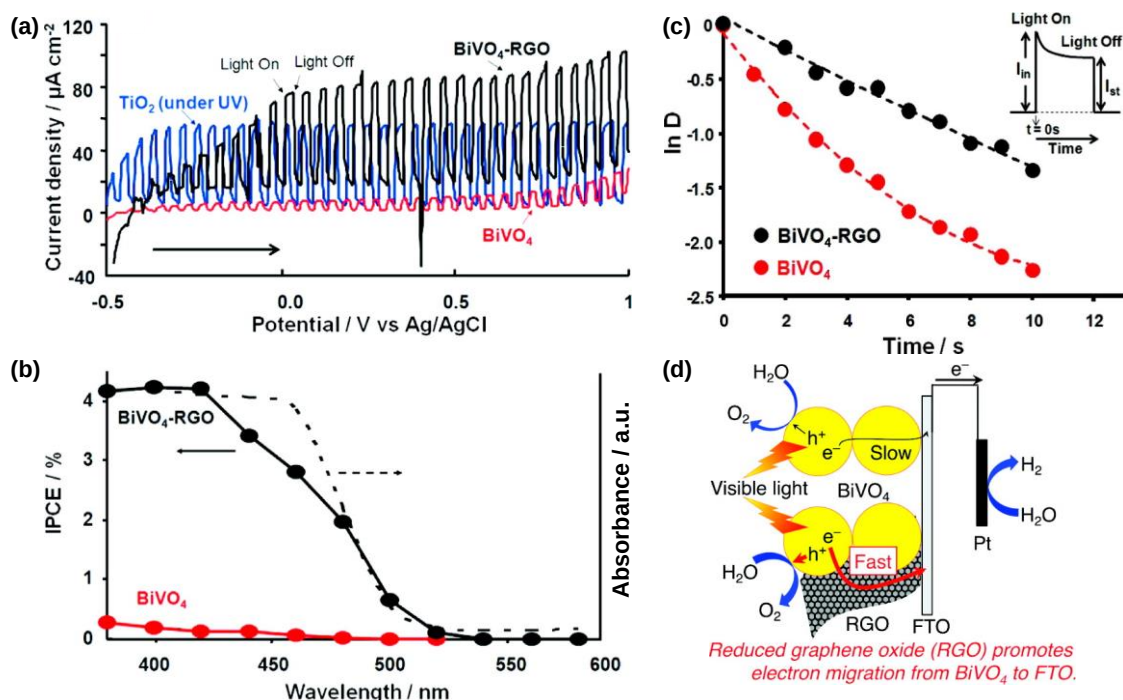


Figure 2.27. (a) Current-potential curves of BiVO_4 , RGO-BiVO_4 , and TiO_2 . Both BiVO_4 and RGO-BiVO_4 were illuminated by visible light, whereas TiO_2 by UV light. (b) IPCE and UV-vis diffuse reflectance spectra of BiVO_4 and RGO-BiVO_4 . (c) Plots of normalized transient photocurrent of BiVO_4 and RGO-BiVO_4 as a function of time. Inset shows the schematic representation of a typical photocurrent transient response curve. (d) Schematic illustration of the role of RGO in facilitating electron transport in RGO-BiVO_4 material. Adapted from Ng et al.¹⁵⁰

Notably, research available in respect of graphene-based semiconductors predominantly focuses on highlighting graphene-mediated enhanced photoactivity and streamlining their preparation methods. Given that the improved charge separation of graphene-semiconductor composite fundamentally relies on the charge transfer at the interface, a few studies have been devoted on maximizing the interfacial contact between graphene and semiconductor via the construction of a graphene-wrapped semiconductor structure.¹⁵⁵⁻¹⁵⁶ For instance, Wang et al. reported the production of RGO-BiVO_4 composites with the BiVO_4 polyhedrons fully covered with RGO sheets, resulting in enhanced charge separation and high activity of the material for methylene blue

photodegradation,¹⁵⁶ as schematically depicted in Figure 2.28a. Despite of this, the influences of the semiconductor morphology changes (i.e., size, shape, and exposed crystal facets) on its charge interactions with graphene are scarcely studied. The photocatalytic activities of various semiconductors have been extensively shown to be affected by their morphology properties. Understanding of the relationships between graphene-semiconductor charge interactions and the semiconductor's morphology properties is indispensable to rationalize the design of highly functionalized graphene-semiconductor materials.

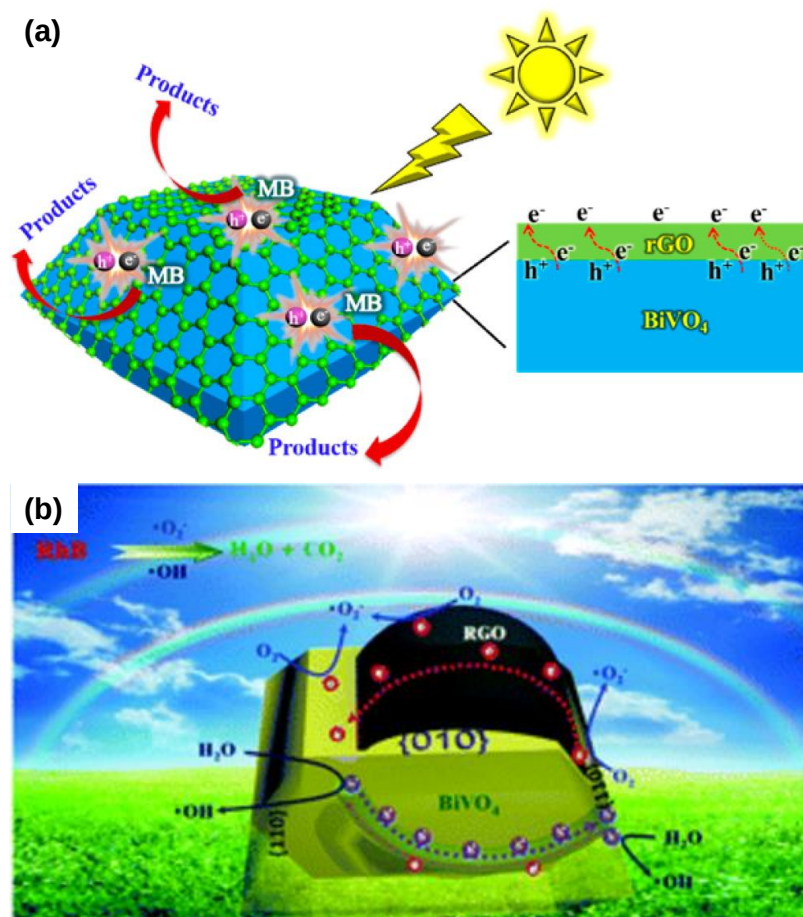


Figure 2.28. Schematic illustrations of (a) RGO-wrapped BiVO₄ for enhanced charge separation efficiency and improved activity for photocatalytic degradation of methylene blue (MB)¹⁵⁶ and (b) efficient electron and hole separation via electron transfer through RGO and hole migration through the internal structure of BiVO₄ for improved photodegradation of rhodamine B (RhB).¹⁵⁷

As previously described in Section 2.5.1., BiVO₄ with well-defined {010} and {110} facets have been extensively suggested to have efficient charge separation since photogenerated electrons from the {110} facets with relatively higher (i.e., more negative) conduction band potential are preferentially transferred to the {010} facets of lower conduction band potential, while holes move in the opposite direction. However, recombination between electrons and holes is inevitable during their transition between the two facets via a single channel in the BiVO₄ particle. To further optimize the charge separation efficiency of the dual-faceted BiVO₄, Feng et al. proposed to incorporate RGO into the faceted BiVO₄ as an additional channel that only allows transport of electron, realizing dual-channel charge separation with high selectivity.¹⁵⁷ As portrayed in Figure 2.28b, the RGO sheet was suggested to serve as an external channel for electron migration from the {110} surface to electron-accumulating {010} surface, whereas hole transfer in the opposite direction happens in the internal structure of BiVO₄. The existence of such thermodynamically feasible distinctive migration channels of electron and hole was supported by the emergence of a new photoluminescence emission peak in the RGO-BiVO₄ sample, which energy corresponds to the difference of the energy levels between the conduction band of {110} facets and the valence band of the {010} facets. Although this study suggests preferential electron transfer from the {110} facets of BiVO₄ to RGO, the differences in charge interactions between graphene and the {110} and {010} facets of BiVO₄ as well as the impacts of the relative exposure extent of the two facets on graphene-BiVO₄ interfacial charge interactions remain unclear. Deeper insights into these aspects may extend the application of crystal facet engineering in the fabrication of graphene-semiconductor materials.

2.5.3. Annealing Treatment

Annealing has generally been employed as a post-synthesis treatment, which is useful to promote crystal grain growth and to tailor the phase composition of metal oxide photocatalysts. The increase of grain size results in the improve of crystallinity,¹⁵⁸⁻¹⁶¹ whereas the temperature dependence phase transformation allows such heat treatment to expedite formation of the more thermodynamically stable structure of the materials.^{36, 162-163} Apart from that, annealing-mediated morphological changes such as particle size and shape are also commonly observed due to the minimization of surface free energy in response to the provision of thermal energy.^{159, 161, 164} These changes in the physicochemical properties affects the charge generation, separation, and transport behaviors of the metal oxide photocatalysts, indicating that the intrinsic poor charge properties of the materials can be addressed in part by annealing treatment.

Although earlier works on thermal annealing were predominantly performed in an oxygen-rich atmosphere (e.g., air and O₂ gases), more recent studies have extended the heat treatment to oxygen-deficient environment such as nitrogen (N₂), argon (Ar), and H₂ gases.^{42, 165-167} Annealing in both oxygen-rich and deficient conditions was demonstrated capable to tailor the physicochemical properties of the treated metal oxides as aforementioned. However, heat treatment in oxygen-deficient atmosphere was revealed to induce the formation of oxygen defects known as oxygen vacancies, which on the other hand are inhibited in oxygen-rich atmosphere. For instance, thermal treatment of N-doped TiO₂ particles in N₂ and air atmospheres was demonstrated by Yamada et al. to have opposite effects on oxygen vacancy formation in the material: increased after N₂-treatment but decreased after air-treatment.¹⁶⁵ Likewise, Mtangi et al. reported that a new defect possibly related to oxygen vacancy was exhibited by ZnO

after H₂ and Ar annealing, but absent after O₂ annealing.¹⁶⁷ The formation of oxygen vacancies contributes to self-doping effect, which can tune the optical and electronic properties of metal oxides.¹⁶⁸

Among the oxygen-deficient gases, tremendous efforts have been focused on H₂ annealing (i.e., hydrogenation) because of its strong reducing ability shown to be highly efficient to instigate oxygen vacancy formation in various metal oxides. Black TiO₂ nanocrystals with a highly disordered surface covering the TiO₂ core obtained via hydrogenation of TiO₂, was first reported by Chen et al.¹⁶⁹ Midgap electronic states were revealed to be created in the black TiO₂, as supported by the significant reduced band gap from 3.30 eV of the untreated, white TiO₂ to ~ 1.54 eV for the treated TiO₂. On the other hand, subjection of TiO₂,¹⁷⁰ ZnO¹⁷¹, and WO₃¹⁷² to hydrogen treatment (based on the separate studies conducted by Li and coworkers) consistently showed an increase of oxygen vacancies in the respective treated metal oxides.⁴² The introduction of oxygen vacancies, which are known as the shallow donors of metal oxides, was demonstrated to result in improved donor density, charge transport properties, and photoactivity of all the hydrogenated samples.

A more recent work of Li and co-workers has also validated the beneficial role of hydrogenation on the PEC performance of BiVO₄,²⁴ similar to that reported for other metal oxides. The visible light absorption ability of BiVO₄ was enhanced upon hydrogenation, suggesting the presence of midgap states in the hydrogenated BiVO₄ (H-BiVO₄) samples. The creation of oxygen vacancies in H-BiVO₄ was confirmed by the increased of surface adsorbed oxygen species O_{ads} (represented by the peak located at a higher binding energy relative to the O 1s peak corresponds to the surface lattice oxygen O_{latt} of BiVO₄), evolution of V⁴⁺ species and negative shift of the Bi 4f peaks

(indicative of the reduction of Bi^{3+} in BiVO_4 to lower oxidation states), as depicted in Figure 2.29a-c, respectively. Surface oxygen vacancies are positively charged and therefore incline to adsorb negatively charged species such as OH^- , O^- , O^{2-} , and O_2^{2-} .¹⁷³ Increased adsorption of these negative species would lead to the formation of V^{4+} species due to electron transfer to the cation V^{5+} to maintain the electroneutrality of the oxide material.¹⁷⁴ As such, the O_{ads} and V^{4+} species are associated with oxygen vacancies in BiVO_4 .¹⁷⁵⁻¹⁷⁶ In addition, partial reduction of Bi^{3+} has also been correlated with oxygen vacancies.¹⁷⁷ The oxygen vacancy formation was proved to increase the donor density of the hydrogenated BiVO_4 (H-BiVO_4) by one order of magnitude, as evidenced by the considerably smaller slope of its Mott-Schottky plot in comparison to that of BiVO_4 (Figure 2.29d). Such increase of donor density was in consistent with the DFT calculations, which predicted oxygen vacancy as shallow donor for BiVO_4 .^{24, 178} Electrochemical impedance spectroscopic measurements manifested that the Nyquist plot arc radius of H-BiVO_4 (Figure 2.29e) was greatly reduced, signifying a smaller charge transfer resistance at the semiconductor-electrolyte interface. The enhanced charge transport ability attributable to the increased donor density of H-BiVO_4 thus explained its improved PEC photocurrent with respect to BiVO_4 .

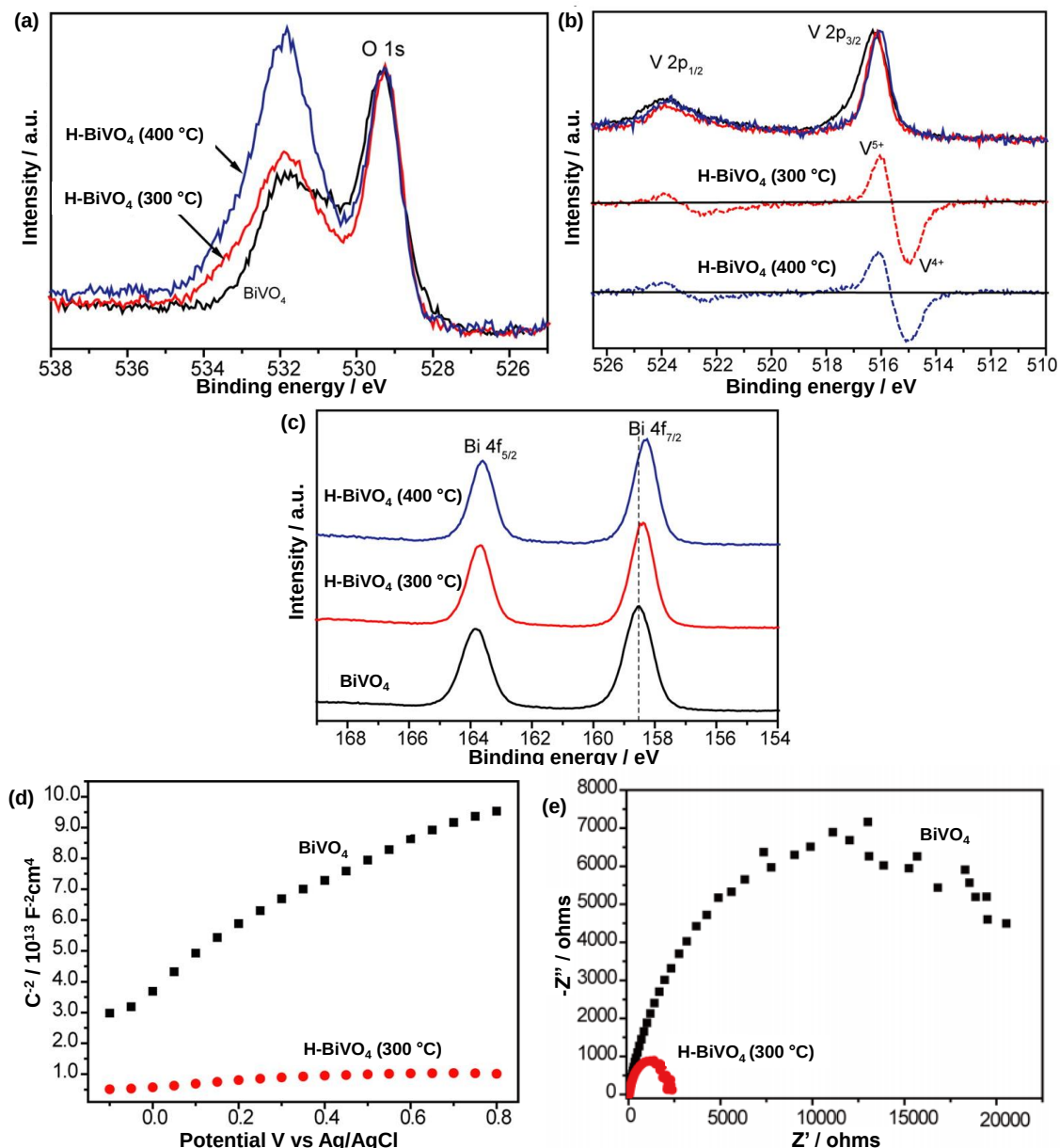


Figure 2.29. (a) O 1s, (b) V 2p, and (c) Bi 4f XPS spectra of BiVO₄ (black) and H-BiVO₄ samples heated at 300 (red) and 400 °C (blue). (d) Mott-Schottky and (e) Nyquist plots of BiVO₄ and H-BiVO₄ (300 °C) obtained under dark condition. Adapted from Wang et al.²⁴

A later study on the effects of hydrogen treatment on the structural, optical, electronic, and PEC properties of BiVO₄ conducted by Singh et al. also presented findings similar to that reported by Li and co-workers (as detailed above).¹⁷⁴ In light of hydrogen treatment as a straightforward approach to improve the charge transport properties of

metal oxides, it has also been combined with the deposition of different oxygen evolution cocatalysts as a synergistic approach to develop highly efficient BiVO₄ photoanodes.¹⁷⁹⁻¹⁸⁰

H₂, which is a flammable gas, has to be handled with extra care during the experimental setup for hydrogenation treatment. Furthermore, the strong reducing ability of H₂ limits the temperature range applicable for hydrogenation treatment to avoid undesirable reduction effects. For instance, unfavourable reduction of the SnO₂ layer on the fluorine-doped tin oxide (FTO) substrate to metallic Sn was observed for TiO₂/FTO photoelectrode hydrogenated at temperatures higher than 450 °C.¹⁷⁰ This then restrains the extent of improvement achievable for the physicochemical properties (e.g., crystallinity) for the treated material, which are generally in proportion to the annealing temperature. Hence, N₂ or Ar gases may be a safer substitute for H₂ to provide oxygen-deficient atmosphere for the annealing process.

However, studies on annealing treatment of metal oxides in N₂ and Ar atmospheres with clear elucidation of the effects on the structural, optical and electronic properties of the treated materials have been scarce. Very recently, annealing of nanoporous BiVO₄ photoanode in N₂ flow was demonstrated to result in enhanced photon absorption, carrier density and mobility because of the combined effects of N-doping and oxygen vacancy formation.¹⁸¹ Although this is the only study available for N₂-treated BiVO₄, it provides experimental and computational evidences showing the practicability of N₂ annealing to induce oxygen vacancy formation in BiVO₄, which on the other hand still remains unknown in the case of Ar annealing. Given that Ar gas is the other oxygen-deficient gas prevalently used in various experimental setups operated at elevated

temperature due to its inertness, exploration of the impacts of Ar annealing on the properties of oxide materials, particularly oxygen vacancy formation, is imperative.

2.5.4. Nanoscaling

Upon photoexcitation, the photoinduced electrons and holes have to migrate from the bulk of the semiconductor photocatalyst to the surface to take part in redox reactions. In the absence of an external field, the charge carriers move by diffusion. The average distance a carrier moves from the point of generation and before recombination is defined as the diffusion length (L) which relies on the lifetime τ and mobility μ of the carrier.⁹⁰

$$L = \sqrt{D\tau} \quad (2.6)$$

where D is the carrier diffusion coefficient that is related to μ by the Einstein relation:¹⁸²

$$D = \mu \frac{kT}{q} \quad (2.7)$$

In order to optimize the collection of both electrons and holes at the semiconductor surface, a semiconductor film thickness and the dimensions of suspended semiconductor have to be in the same range as the diffusion lengths of the charge carriers,⁸⁵ as illustrated in Figure 2.30. Clearly, this can be achieved by nanostructuring the surface of the film (Figure 2.30b) and downsizing the suspended particle to nanoscale (Figure 2.30c).

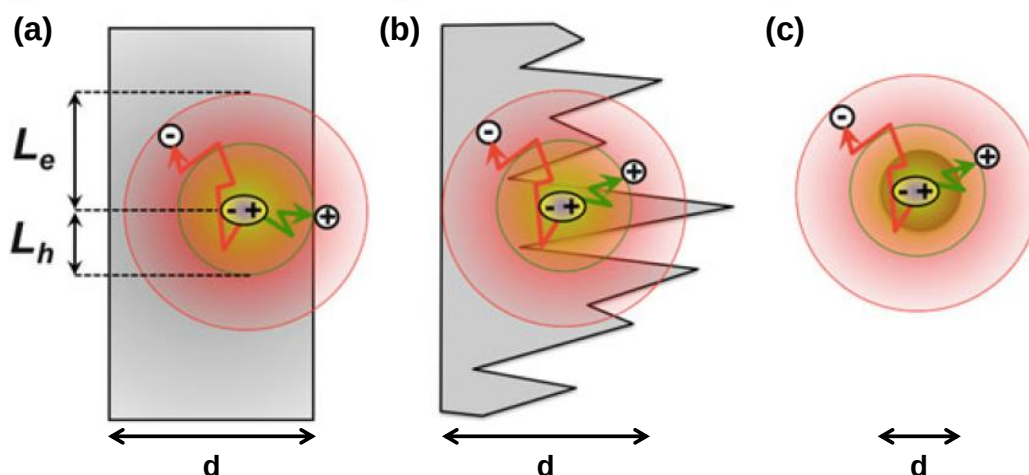


Figure 2.30. Charge collection in (a) flat films, (b) nanostructured films, and (c) suspended particles. L_e and L_h denote the respective diffusion lengths of electron and hole, whereas d represents the film or particle thickness. Adapted from Osterloh.⁸⁵

The nanostructuring/nanoscaling approach is useful to overcome the limitations of oxide photocatalysts such as short carrier lifetimes and low mobility.⁸⁵ In view of this, nanostructured morphologies are extensively adopted in studies related to BiVO_4 photoanode,^{83, 95, 109-110, 183} which has been shown to suffer from poor carrier mobility. For instance, Kim and Choi fabricated a nanostructured BiVO_4 electrode composed of particles (mean size 76 ± 5 nm) smaller than its hole diffusion length (~ 100 nm).¹¹⁰ The resulting electrode was demonstrated to have a remarkably high charge separation efficiency of 90 % at 1.23 V vs. RHE in comparison to the typical value of < 30 % reported for BiVO_4 photoanode, attributing to the short charge transport pathways. Additionally, the porous structure ensuing from the nanoparticle network also allows the electrolyte to easily penetrate into the semiconductor film, increasing the contact area between the semiconductor and the electrolyte and promoting interfacial charge transfer to suppress charge recombination.^{83, 95, 109-110, 183}

On the other hand, nanowire/nanorod arrays are another type of nanostructure potent for enhanced charge separation and transport properties of semiconductor electrodes. While both nanoparticle and nanowire/nanorod provide high surface area per electrode volume, the one-dimensional nanowire/nanorod enables vectorial charge transport (i.e., the majority carriers move along the wire/rod to the electron collector back substrate, while the minority carriers travel radially outward to the semiconductor-electrolyte interface) which is a more effective mechanism of charge separation compared to the non-directional carrier movement in nanoparticle-based electrode.¹⁸⁴ To this end, Su et al. prepared WO₃-BiVO₄ heterojunction films with conformal deposition of nanoporous BiVO₄ particles on the WO₃ nanorod arrays, which were shown to have better IPCE than the planar WO₃-BiVO₄ heterojunction films accrediting to the higher surface area and faster charge separation at the WO₃-BiVO₄ interface of the nanorod structure.¹⁸⁵ Such WO₃-BiVO₄ nanostructure was further refined by Rao et al. into a core-shell nanowire structure, which was demonstrated to be one of the best-performing BiVO₄-based photoanodes, generating an AM1.5 photocurrent of 3.1 mA/cm² at 1.23 V vs. RHE.¹⁸⁶

It is obvious that contemporary research on nanoscale photocatalyst is stimulated by the prospects of efficient charge carrier extraction and enlarged active surface area. However, the large specific surface area of nanomaterials commonly results in the increase of grain boundaries, surface states, and defects, which are reflected by the decrease of crystallinity.⁴⁵ The presence of these defect sites promotes charge recombination on the surface of photocatalyst. Moreover, separation of electrons and holes in small particles is harder to achieve because of the smaller or the absence of SCL, which is essential to generate a built-in electric field as the internal mechanism of

charge separation (previously explained in Section 2.4.2.3.).⁸⁵ As a result, the effects of particle size on the activity of semiconductor photocatalyst are a complicated issue, particularly in different configurations for water splitting (i.e., PS and particulate PEC systems).

In fact, there has been contradiction in the literature regarding the size effects of WO_3 particles on its water oxidation performance in the PS and PEC systems. For example, using three WO_3 samples with different morphologies and particle sizes (namely, nanodots, nanoplates, and microcrystals with average diameters of 32 ± 16 nm, 475 ± 98 nm by 58 ± 16 nm, and $2 \mu\text{m}$, respectively), Newton and Osterloh observed that both the photocatalytic O_2 evolution activity (Figure 2.31a) and the PEC photocurrent (Figure 2.31b) of the WO_3 concordantly increased with decrease of particle size.¹⁸⁷ The plots of O_2 evolution rate and photocurrent magnitude against the inverse particle diameter (displayed in Figure 2.31c,d, respectively) indicate a linear relationship in both cases, suggesting that the two systems are governed by minority carrier transport which is facilitated by the decrease of particle size. Conversely, Hong et al. reported the opposite behaviors of PS and PEC systems with respect to the particle size of WO_3 .⁸⁷ Four WO_3 samples with different particle sizes in the range of 30 – 500 nm were obtained via calcination at different temperatures. As shown in Figure 2.32, larger particle size generates higher amount of O_2 but lower photocurrent. Such contrary effects of particle size on the water oxidation performance of WO_3 in the PS and PEC systems were ascribed to the different charge separation mechanisms (refer to Section 2.4.2.3.), whereby efficient charge separation in the PS system is provided by large particle with high crystallinity and well-developed SCL, while the PEC system relies on the reduced hole diffusion length by small particle.

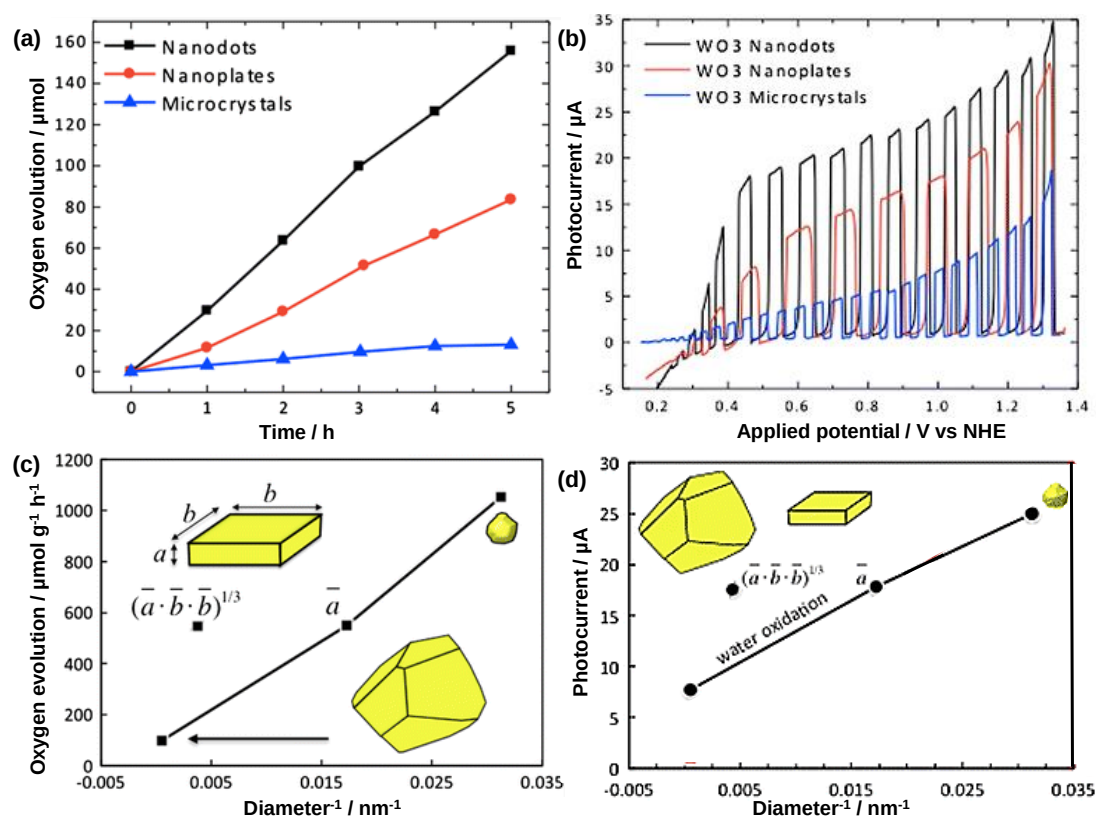


Figure 2.31. (a) Time profile of O₂ evolution and (b) current-potential curves of WO₃ with different particle sizes. The corresponding photocatalytic rates of process (a) and (b) as a function of inverse particle diameter are displayed in (c) and (d), respectively. Adapted from Newton and Osterloh.¹⁸⁷

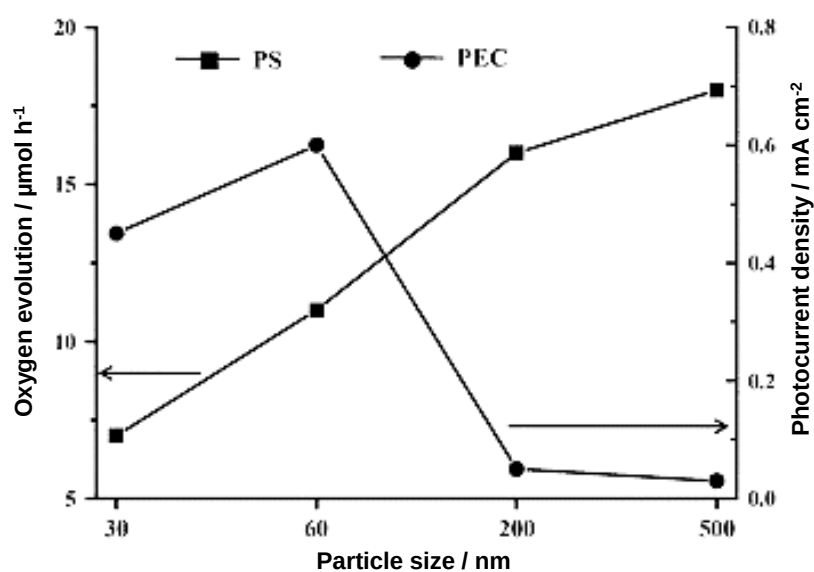


Figure 2.32. Photoactivities of WO₃ in PS and PEC systems as a function of particle size.⁸⁷

While it is relatively recent that BiVO_4 is recognized as an auspicious visible-light-active photocatalyst highly active for water oxidation, which is viable through both the PS and PEC systems, the nanoscaling effect on its activity in the PS system is scarcely studied relative to the PEC system. A very few studies associated with the preparation of nanosized BiVO_4 particles suggested that the suspended nanoparticles have poor activity for photocatalytic O_2 evolution from aqueous AgNO_3 solution.^{88, 188} These results may suggest that nanoscaling is detrimental to the performance of BiVO_4 in PS system, which is in contrast with that observed in the PEC system as aforementioned. However, direct comparison of the particle size dependence of BiVO_4 water oxidation photocactivities in the PS and PEC systems based on the separate studies is inexpedient due to the variant properties of the photocatalyst materials being investigated. Instead, a systematic comparison should be executed using materials of the same properties in the two systems to understand the fundamental differences of the two in order to propel further advancement of BiVO_4 -based materials in the respective systems.

2.6. Summary

The overview of the crystal structure, optical, and electronic properties of BiVO_4 , in particular that of monoclinic scheelite structure has shown the promises of BiVO_4 as a visible-light-active photocatalyst with high oxidizing potential. In fact, the abilities of BiVO_4 for photocatalytic organic degradations, photocatalytic water oxidation, Z-scheme overall water splitting, and PEC water splitting under visible light have been widely demonstrated. However, the solar conversion efficiencies of BiVO_4 -based materials reported to date are far below the theoretical values, mainly due to rapid charge recombination arising from the intrinsic poor electron transport, slow kinetics for oxygen evolution and low carrier mobility of BiVO_4 . Numerous strategies such as

crystal facet engineering, coupling with graphene, annealing treatment, and nanoscaling have been employed to effectively circumvent part of these limitations.

Nevertheless, knowledge gaps still exist in these strategies where more in-depth investigations are required to attain the full potential of such promising material. Crystal-facet-engineered BiVO₄ with exposed {010} and {110} surfaces was revealed to facilitate charge separation, in which photogenerated electrons are preferentially driven to the {010} facets and holes to the {110}. While further understanding of the crystal-facet-dependent charge transfer between BiVO₄ and reactants (i.e., electron donor/acceptor) is required, considerable room of improvement for the dual-faceted BiVO₄ material in the aspects of charge transport and separation is still available (potentially through introduction of graphene as a conductor and subsection of the BiVO₄ to annealing post-synthesis treatment). Therefore, the focuses of this thesis are to provide understanding on the {010}/{110} relative exposure extent on the charge transfer efficiency of BiVO₄ as well as to elucidate efficacies of a combination of strategies to improve the charge kinetics and photoactivity of BiVO₄.

Firstly, the photooxidation performances of BiVO₄ with distinctly different relative exposure extents of {010} and {110} are investigated with respect to the surface available electron and hole populations. The influences of the {010}/{110} relative exposure extent on the interfacial charge interactions between BiVO₄ and an electron conductor – graphene are then studied in the following results chapter. Next, the feasibility of Ar annealing to improve the charge transport and separation properties of the faceted BiVO₄ is examined. Lastly, the water oxidation activity of the faceted BiVO₄ microcrystals is compared to other smaller BiVO₄ particles in different systems: powder suspension and photoelectrochemical.

2.7. References

1. Carp, O.; Huisman, C. L.; Reller, A., Photoinduced Reactivity of Titanium Dioxide. *Prog. Solid State Chem.* **2004**, 32 (1), 33-177.
2. Zhang, Q.; Dandeneau, C. S.; Zhou, X.; Cao, G., ZnO Nanostructures for Dye - Sensitized Solar Cells. *Adv. Mater.* **2009**, 21 (41), 4087-4108.
3. Sayama, K.; Nomura, A.; Arai, T.; Sugita, T.; Abe, R.; Yanagida, M.; Oi, T.; Iwasaki, Y.; Abe, Y.; Sugihara, H., Photoelectrochemical Decomposition of Water into H₂ and O₂ on Porous BiVO₄ Thin-Film Electrodes under Visible Light and Significant Effect of Ag Ion Treatment. *J. Phys. Chem. B* **2006**, 110 (23), 11352-11360.
4. Bott, A. W., Electrochemistry of Semiconductors. *Curr. Sep.* **1998**, 17, 87-92.
5. Linsebigler, A. L.; Lu, G.; Yates, J. T., Photocatalysis on TiO₂ Surfaces: Principles, Mechanisms, and Selected Results. *Chem. Rev.* **1995**, 95 (3), 735-758.
6. Zayat, M.; Garcia-Parejo, P.; Levy, D., Preventing UV-Light Damage of Light Sensitive Materials using a Highly Protective UV-Absorbing Coating. *Chem. Soc. Rev.* **2007**, 36 (8), 1270-1281.
7. Abe, R., Recent Progress on Photocatalytic and Photoelectrochemical Water Splitting under Visible Light Irradiation. *J. Photochem. Photobiol., C* **2010**, 11 (4), 179-209.
8. Viswanathan, B.; Subramanian, V.; Lee, J. S., *Materials and Processes for Solar Fuel Production*. Springer: **2014**.
9. Kudo, A., Photocatalyst Materials for Water Splitting. *Catal. Surv. Asia* **2003**, 7 (1), 31-38.
10. Gerischer, H., Electrochemical Behavior of Semiconductors under Illumination. *J. Electrochem. Soc.* **1966**, 113 (11), 1174-1182.

11. Behnajady, M.; Modirshahla, N.; Hamzavi, R., Kinetic Study on Photocatalytic Degradation of CI Acid Yellow 23 by ZnO Photocatalyst. *J. Hazard. Mater.* **2006**, *133* (1), 226-232.
12. Georgekutty, R.; Seery, M. K.; Pillai, S. C., A Highly Efficient Ag-ZnO Photocatalyst: Synthesis, Properties, and Mechanism. *J. Phys. Chem. C* **2008**, *112* (35), 13563-13570.
13. Choi, W.; Termin, A.; Hoffmann, M. R., The Role of Metal Ion Dopants in Quantum-Sized TiO₂: Correlation between Photoreactivity and Charge Carrier Recombination Dynamics. *J. Phys. Chem.* **1994**, *98* (51), 13669-13679.
14. Kamat, P. V., Photochemistry on Nonreactive and Reactive (Semiconductor) Surfaces. *Chem. Rev.* **1993**, *93* (1), 267-300.
15. Santato, C.; Odziemkowski, M.; Ulmann, M.; Augustynski, J., Crystallographically Oriented Mesoporous WO₃ Films: Synthesis, Characterization, and Applications. *J. Am. Chem. Soc.* **2001**, *123* (43), 10639-10649.
16. Chen, D.; Ye, J., Hierarchical WO₃ Hollow Shells: Dendrite, Sphere, Dumbbell, and Their Photocatalytic Properties. *Adv. Funct. Mater.* **2008**, *18* (13), 1922-1928.
17. Ng, C.; Ye, C.; Ng, Y. H.; Amal, R., Flower-Shaped Tungsten Oxide with Inorganic Fullerene-Like Structure: Synthesis and Characterization. *Cryst. Growth Des.* **2010**, *10* (8), 3794-3801.
18. Wen, X.; Wang, S.; Ding, Y.; Wang, Z. L.; Yang, S., Controlled Growth of Large-Area, Uniform, Vertically Aligned Arrays of α -Fe₂O₃ Nanobelts and Nanowires. *J. Phys. Chem. B* **2005**, *109* (1), 215-220.

19. Kay, A.; Cesar, I.; Grätzel, M., New Benchmark for Water Photooxidation by Nanostructured α -Fe₂O₃ Films. *J. Am. Chem. Soc.* **2006**, *128* (49), 15714-15721.
20. Sivula, K.; Le Formal, F.; Grätzel, M., Solar Water Splitting: Progress using Hematite (α - Fe₂O₃) Photoelectrodes. *ChemSusChem* **2011**, *4* (4), 432-449.
21. Scaife, D., Oxide Semiconductors in Photoelectrochemical Conversion of Solar Energy. *Solar Energy* **1980**, *25* (1), 41-54.
22. Teoh, W. Y.; Scott, J. A.; Amal, R., Progress in Heterogeneous Photocatalysis: From Classical Radical Chemistry to Engineering Nanomaterials and Solar Reactors. *J. Phys. Chem. Lett.* **2012**, *3* (5), 629-639.
23. Kudo, A.; Miseki, Y., Heterogeneous Photocatalyst Materials for Water Splitting. *Chem. Soc. Rev.* **2009**, *38* (1), 253-278.
24. Wang, G.; Ling, Y.; Lu, X.; Qian, F.; Tong, Y.; Zhang, J. Z.; Lordi, V.; Rocha Leao, C.; Li, Y., Computational and Photoelectrochemical Study of Hydrogenated Bismuth Vanadate. *J. Phys. Chem. C* **2013**, *117* (21), 10957-10964.
25. Kudo, A.; Omori, K.; Kato, H., A Novel Aqueous Process for Preparation of Crystal Form-Controlled and Highly Crystalline BiVO₄ Powder from Layered Vanadates at Room Temperature and Its Photocatalytic and Photophysical Properties. *J. Am. Chem. Soc.* **1999**, *121* (49), 11459-11467.
26. Fu, H.; Pan, C.; Yao, W.; Zhu, Y., Visible-Light-Induced Degradation of Rhodamine B by Nanosized Bi₂WO₆. *J. Phys. Chem. B* **2005**, *109* (47), 22432-22439.
27. Li, G.; Yang, N.; Wang, W.; Zhang, W., Band Structure and Photoelectrochemical Behavior of AgNbO₃-NaNbO₃ Solid Solution Photoelectrodes. *Electrochim. Acta* **2010**, *55* (24), 7235-7239.

28. Errandonea, D.; Muñoz, A.; Rodriguez-Hernandez, P.; Proctor, J. E.; Sapiña, F.; Bettinelli, M., Theoretical and Experimental Study of the Crystal Structures, Lattice Vibrations, and Band Structures of Monazite-Type PbCrO_4 , PbSeO_4 , SrCrO_4 , and SrSeO_4 . *Inorg. Chem.* **2015**, *54* (15), 7524-7535.
29. Hosogi, Y.; Shimodaira, Y.; Kato, H.; Kobayashi, H.; Kudo, A., Role of Sn^{2+} in the Band Structure of SnM_2O_6 and $\text{Sn}_2\text{M}_2\text{O}_7$ (M=Nb and Ta) and Their Photocatalytic Properties. *Chem. Mater.* **2008**, *20* (4), 1299-1307.
30. Endriss, H., Bismuth Vanadates. In *High Performance Pigments*, Wiley-VCH Verlag GmbH & Co. KGaA: **2003**, pp 7-12.
31. Bierlein, J. D.; Sleight, A. W., Ferroelasticity in BiVO_4 . *Solid State Commun.* **1975**, *16* (1), 69-70.
32. Pinczuk, A.; Welber, B.; Dacol, F., Mechanism of the Ferroelastic Transition of BiVO_4 . *Solid State Commun.* **1979**, *29* (7), 515-518.
33. Manolikas, C.; Amelinckx, S., Ferroelastic domains in BiVO_4 . *Phys. Status Solidi A* **1980**, *60* (1), 167-172.
34. David, W.; Wood, I., Ferroelastic Phase Transition in BiVO_4 : VI. Some Comments on the Relationship between Spontaneous Deformation and Domain Walls in Ferroelastics. *J. Phys. C: Solid State Phys.* **1983**, *16* (26), 5149.
35. Lim, A.; Choh, S.; Jang, M., Ferroelastic Phase Transition of BiVO_4 Studied by ^{51}V NMR. *Ferroelectrics* **1989**, *94* (1), 389-394.
36. Bhattacharya, A. K.; Mallick, K. K.; Hartridge, A., Phase Transition in BiVO_4 . *Mater. Lett.* **1997**, *30* (1), 7-13.
37. Hirota, K.; Komatsu, G.; Yamashita, M.; Takemura, H.; Yamaguchi, O., Formation, Characterization and Sintering of Alkoxy-Derived Bismuth Vanadate. *Mater. Res. Bull.* **1992**, *27* (7), 823-830.

38. Tokunaga, S.; Kato, H.; Kudo, A., Selective Preparation of Monoclinic and Tetragonal BiVO_4 with Scheelite Structure and Their Photocatalytic Properties. *Chem. Mater.* **2001**, *13* (12), 4624-4628.
39. Liang, Y.; Tsubota, T.; Mooij, L. P.; van de Krol, R., Highly Improved Quantum Efficiencies for Thin Film BiVO_4 Photoanodes. *J. Phys. Chem. C* **2011**, *115* (35), 17594-17598.
40. Abdi, F. F.; Firet, N.; van de Krol, R., Efficient BiVO_4 Thin Film Photoanodes Modified With Cobalt Phosphate Catalyst and W - Doping. *ChemCatChem* **2013**, *5* (2), 490-496.
41. Prévot, M. S.; Sivula, K., Photoelectrochemical Tandem Cells for Solar Water Splitting. *J. Phys. Chem. C* **2013**, *117* (35), 17879-17893.
42. Wang, G.; Ling, Y.; Li, Y., Oxygen-Deficient Metal Oxide Nanostructures for Photoelectrochemical Water Oxidation and Other Applications. *Nanoscale* **2012**, *4* (21), 6682-6691.
43. Hong, S. J.; Lee, S.; Jang, J. S.; Lee, J. S., Heterojunction $\text{BiVO}_4/\text{WO}_3$ Electrodes for Enhanced Photoactivity of Water Oxidation. *Energy Environ. Sci.* **2011**, *4* (5), 1781-1787.
44. Lim, A. R.; Choh, S. H.; Jang, M. S., Prominent Ferroelastic Domain Walls in BiVO_4 Crystal. *J. Phys.: Condens. Matter* **1995**, *7* (37), 7309.
45. Park, Y.; McDonald, K. J.; Choi, K.-S., Progress in Bismuth Vanadate Photoanodes for Use in Solar Water Oxidation. *Chem. Soc. Rev.* **2013**, *42* (6), 2321-2337.
46. Yu, J.; Kudo, A., Effects of Structural Variation on the Photocatalytic Performance of Hydrothermally Synthesized BiVO_4 . *Adv. Funct. Mater.* **2006**, *16* (16), 2163-2169.

47. Walsh, A.; Yan, Y.; Huda, M. N.; Al-Jassim, M. M.; Wei, S.-H., Band Edge Electronic Structure of BiVO₄: Elucidating the Role of the Bi s and V d Orbitals. *Chem. Mater.* **2009**, *21* (3), 547-551.
48. Payne, D.; Robinson, M.; Egdell, R.; Walsh, A.; McNulty, J.; Smith, K.; Piper, L., The Nature of Electron Lone Pairs in BiVO₄. *Appl. Phys. Lett.* **2011**, *98* (21), 212110.
49. Zhao, Z.; Li, Z.; Zou, Z., Electronic Structure and Optical Properties of Monoclinic Clinobisvanite BiVO₄. *Phys. Chem. Chem. Phys.* **2011**, *13* (10), 4746-4753.
50. Cooper, J. K.; Gul, S.; Toma, F. M.; Chen, L.; Glans, P.-A.; Guo, J.; Ager, J. W.; Yano, J.; Sharp, I. D., Electronic Structure of Monoclinic BiVO₄. *Chem. Mater.* **2014**, *26* (18), 5365-5373.
51. Yang, J.; Wang, D.; Zhou, X.; Li, C., A Theoretical Study on the Mechanism of Photocatalytic Oxygen Evolution on BiVO₄ in Aqueous Solution. *Chem. Eur. J.* **2013**, *19* (4), 1320-1326.
52. Fujishima, A.; Rao, T. N.; Tryk, D. A., Titanium Dioxide Photocatalysis. *J. Photochem. Photobiol., C* **2000**, *1* (1), 1-21.
53. Martinez-de La Cruz, A.; Pérez, U. G., Photocatalytic Properties of BiVO₄ Prepared by the Co-Precipitation Method: Degradation of Rhodamine B and Possible Reaction Mechanisms under Visible Irradiation. *Mater. Res. Bull.* **2010**, *45* (2), 135-141.
54. Zhou, L.; Wang, W.; Zhang, L.; Xu, H.; Zhu, W., Single-Crystalline BiVO₄ Microtubes with Square Cross-Sections: Microstructure, Growth Mechanism, and Photocatalytic Property. *J. Phys. Chem. C* **2007**, *111* (37), 13659-13664.

55. Zheng, Y.; Wu, J.; Duan, F.; Xie, Y., Gemini Surfactant Directed Preparation and Photocatalysis of m-BiVO₄ Hierarchical Frameworks. *Chem. Lett.* **2007**, 36 (4), 520-521.
56. Zhang, X.; Ai, Z.; Jia, F.; Zhang, L.; Fan, X.; Zou, Z., Selective Synthesis and Visible-Light Photocatalytic Activities of BiVO₄ with Different Crystalline Phases. *Mater. Chem. Phys.* **2007**, 103 (1), 162-167.
57. Iwase, A.; Kato, H.; Kudo, A., A Simple Preparation Method of Visible-Light-Driven BiVO₄ Photocatalysts from Oxide Starting Materials (Bi₂O₃ and V₂O₅) and Their Photocatalytic Activities. *J. Sol. Energy Eng.* **2010**, 132 (2), 021106.
58. Zhou, L.; Wang, W.; Liu, S.; Zhang, L.; Xu, H.; Zhu, W., A Sonochemical Route to Visible-Light-Driven High-Activity BiVO₄ Photocatalyst. *J. Mol. Catal. A: Chem.* **2006**, 252 (1), 120-124.
59. Ge, L., Novel Pd/BiVO₄ Composite Photocatalysts for Efficient Degradation of Methyl Orange under Visible Light Irradiation. *Mater. Chem. Phys.* **2008**, 107 (2), 465-470.
60. Kohtani, S.; Makino, S.; Kudo, A.; Tokumura, K.; Ishigaki, Y.; Matsunaga, T.; Nikaido, O.; Hayakawa, K.; Nakagaki, R., Photocatalytic Degradation of 4-n-Nonylphenol under Irradiation from Solar Simulator: Comparison between BiVO₄ and TiO₂ Photocatalysts. *Chem. Lett.* **2002**, (7), 660-661.
61. Kohtani, S.; Koshiko, M.; Kudo, A.; Tokumura, K.; Ishigaki, Y.; Toriba, A.; Hayakawa, K.; Nakagaki, R., Photodegradation of 4-Alkylphenols using BiVO₄ Photocatalyst under Irradiation with Visible Light from a Solar Simulator. *Appl. Catal., B* **2003**, 46 (3), 573-586.
62. Kohtani, S.; Hiro, J.; Yamamoto, N.; Kudo, A.; Tokumura, K.; Nakagaki, R., Adsorptive and Photocatalytic Properties of Ag-loaded BiVO₄ on the

- Degradation of 4-n-Alkylphenols under Visible Light Irradiation. *Catal. Commun.* **2005**, 6 (3), 185-189.
63. Thalluri, S. M.; Hussain, M.; Saracco, G.; Barber, J.; Russo, N., Green-Synthesized BiVO₄ Oriented along {040} Facets for Visible-Light-Driven Ethylene Degradation. *Ind. Eng. Chem. Res.* **2014**, 53 (7), 2640-2646.
64. Kohtani, S.; Tomohiro, M.; Tokumura, K.; Nakagaki, R., Photooxidation Reactions of Polycyclic Aromatic Hydrocarbons over pure and Ag-Loaded BiVO₄ Photocatalysts. *Appl. Catal., B* **2005**, 58 (3), 265-272.
65. Kohtani, S.; Yoshida, K.; Maekawa, T.; Iwase, A.; Kudo, A.; Miyabe, H.; Nakagaki, R., Loading Effects of Silver Oxides upon Generation of Reactive Oxygen Species in Semiconductor Photocatalysis. *Phys. Chem. Chem. Phys.* **2008**, 10 (20), 2986-2992.
66. Fujishima, A., Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature* **1972**, 238, 37-38.
67. Bard, A. J.; Wrighton, M. S., Thermodynamic Potential for the Anodic Dissolution of n - Type Semiconductors A Crucial Factor Controlling Durability and Efficiency in Photoelectrochemical Cells and an Important Criterion in the Selection of New Electrode/Electrolyte Systems. *J. Electrochem. Soc.* **1977**, 124 (11), 1706-1710.
68. Gerischer, H., On the Stability of Semiconductor Electrodes against Photodecomposition. *J. Electroanal. Chem. Interfacial Electrochem.* **1977**, 82 (1), 133-143.
69. Yang, L.; Zhou, H.; Fan, T.; Zhang, D., Semiconductor Photocatalysts for Water Oxidation: Current Status and Challenges. *Phys. Chem. Chem. Phys.* **2014**, 16 (15), 6810-6826.

70. Maeda, K.; Takata, T.; Hara, M.; Saito, N.; Inoue, Y.; Kobayashi, H.; Domen, K., GaN: ZnO Solid Solution as a Photocatalyst for Visible-Light-Driven Overall Water Splitting. *J. Am. Chem. Soc.* **2005**, *127* (23), 8286-8287.
71. Sasaki, Y.; Nemoto, H.; Saito, K.; Kudo, A., Solar Water Splitting using Powdered Photocatalysts Driven by Z-Schematic Interparticle Electron Transfer without an Electron Mediator. *J. Phys. Chem. C* **2009**, *113* (40), 17536-17542.
72. Bard, A. J., Photoelectrochemistry and Heterogeneous Photo-catalysis at Semiconductors. *J. Photochem.* **1979**, *10* (1), 59-75.
73. Iwase, A.; Ng, Y. H.; Ishiguro, Y.; Kudo, A.; Amal, R., Reduced Graphene Oxide as a Solid-State Electron Mediator in Z-Scheme Photocatalytic Water Splitting under Visible Light. *J. Am. Chem. Soc.* **2011**, *133* (29), 11054-11057.
74. Iwase, A.; Yoshino, S.; Takayama, T.; Ng, Y. H.; Amal, R.; Kudo, A., Water Splitting and CO₂ Reduction under Visible Light Irradiation Using Z-Scheme Systems Consisting of Metal Sulfides, CoOx-Loaded BiVO₄, and a Reduced Graphene Oxide Electron Mediator. *J. Am. Chem. Soc.* **2016**, *138* (32), 10260-10264.
75. Darwent, J. R.; Mills, A., Photo-Oxidation of Water Sensitized by WO₃ Powder. *J. Chem. Soc., Faraday Trans. 2* **1982**, *78* (2), 359-367.
76. Kudo, A.; Ueda, K.; Kato, H.; Mikami, I., Photocatalytic O₂ Evolution under Visible Light Irradiation on BiVO₄ in Aqueous AgNO₃ Solution. *Catal. Lett.* **1998**, *53* (3-4), 229-230.
77. Liu, H.; Nakamura, R.; Nakato, Y., Promoted Photo-Oxidation Reactivity of Particulate BiVO₄ Photocatalyst Prepared by a Photoassisted Sol-Gel Method. *J. Electrochem. Soc.* **2005**, *152* (11), G856-G861.

78. Kato, H.; Hori, M.; Kato, R.; Shimodaira, Y.; Kudo, A., Construction of Z-Scheme Type Heterogeneous Photocatalysis Systems for Water Splitting into H₂ and O₂ under Visible Light Irradiation. *Chem. Lett.* **2004**, 33 (10), 1348-1349.
79. Sasaki, Y.; Iwase, A.; Kato, H.; Kudo, A., The Effect of Co-Catalyst for Z-Scheme Photocatalysis Systems with an Fe³⁺/Fe²⁺ Electron Mediator on Overall Water Splitting under Visible Light Irradiation. *J. Catal.* **2008**, 259 (1), 133-137.
80. Sasaki, Y.; Kato, H.; Kudo, A., [Co(bpy)₃]^{3+/2+} and [Co(phen)₃]^{3+/2+} Electron Mediators for Overall Water Splitting under Sunlight Irradiation using Z-Scheme Photocatalyst System. *J. Am. Chem. Soc.* **2013**, 135 (14), 5441-5449.
81. Walter, M. G.; Warren, E. L.; McKone, J. R.; Boettcher, S. W.; Mi, Q.; Santori, E. A.; Lewis, N. S., Solar Water Splitting Cells. *Chem. Rev.* **2010**, 110 (11), 6446-6473.
82. Zhang, K.; Ma, M.; Li, P.; Wang, D. H.; Park, J. H., Water Splitting Progress in Tandem Devices: Moving Photolysis beyond Electrolysis. *Adv. Energy Mater.* **2016**.
83. Sayama, K.; Nomura, A.; Zou, Z.; Abe, R.; Abe, Y.; Arakawa, H., Photoelectrochemical Decomposition of Water on Nanocrystalline BiVO₄ Film Electrodes under Visible Light. *Chem. Commun.* **2003**, (23), 2908-2909.
84. Rajeshwar, K., Fundamentals of Semiconductor Electrochemistry and Photoelectrochemistry. *Encycl. Electrochem.* **2007**.
85. Osterloh, F. E., Nanoscale Effects in Water Splitting Photocatalysis. In *Solar Energy for Fuels*, Springer International Publishing: **2015**, pp 105-142.
86. Memming, R., Photoinduced Charge Transfer Processes at Semiconductor Electrodes and Particles. In *Electron Transfer I*, Springer: **1994**, pp 105-181.

87. Hong, S. J.; Jun, H.; Borse, P. H.; Lee, J. S., Size Effects of WO₃ Nanocrystals for Photooxidation of Water in Particulate Suspension and Photoelectrochemical Film Systems. *Int. J. Hydrogen Energy* **2009**, *34* (8), 3234-3242.
88. Iwase, A.; Kudo, A., Photoelectrochemical Water Splitting using Visible-Light-Responsive BiVO₄ Fine Particles Prepared in an Aqueous Acetic Acid Solution. *J. Mater. Chem.* **2010**, *20* (35), 7536-7542.
89. Abdi, F. F.; van de Krol, R., Nature and Light Dependence of Bulk Recombination in Co-Pi-Catalyzed BiVO₄ Photoanodes. *J. Phys. Chem. C* **2012**, *116* (17), 9398-9404.
90. Abdi, F. F.; Savenije, T. J.; May, M. M.; Dam, B.; van de Krol, R., The Origin of Slow Carrier Transport in BiVO₄ Thin Film Photoanodes: A Time-Resolved Microwave Conductivity Study. *J. Phys. Chem. Lett.* **2013**, *4* (16), 2752-2757.
91. Zhong, D. K.; Choi, S.; Gamelin, D. R., Near-Complete Suppression of Surface Recombination in Solar Photoelectrolysis by “Co-Pi” Catalyst-Modified W: BiVO₄. *J. Am. Chem. Soc.* **2011**, *133* (45), 18370-18377.
92. Rettie, A. J.; Lee, H. C.; Marshall, L. G.; Lin, J.-F.; Capan, C.; Lindemuth, J.; McCloy, J. S.; Zhou, J.; Bard, A. J.; Mullins, C. B., Combined charge carrier transport and photoelectrochemical characterization of BiVO₄ single crystals: Intrinsic behavior of a complex metal oxide. *J. Am. Chem. Soc.* **2013**, *135* (30), 11389-11396.
93. Kweon, K. E.; Hwang, G. S., Structural Phase-Dependent Hole Localization and Transport in Bismuth Vanadate. *Phys. Rev. B* **2013**, *87* (20), 205202.
94. Ye, H.; Lee, J.; Jang, J. S.; Bard, A. J., Rapid Screening of BiVO₄-Based Photocatalysts by Scanning Electrochemical Microscopy (SECM) and Studies of

- Their Photoelectrochemical Properties. *J. Phys. Chem. C* **2010**, *114* (31), 13322-13328.
95. Luo, W.; Yang, Z.; Li, Z.; Zhang, J.; Liu, J.; Zhao, Z.; Wang, Z.; Yan, S.; Yu, T.; Zou, Z., Solar Hydrogen Generation from Seawater with a Modified BiVO₄ Photoanode. *Energy Environ. Sci.* **2011**, *4* (10), 4046-4051.
96. Parmar, K. P. S.; Kang, H. J.; Bist, A.; Dua, P.; Jang, J. S.; Lee, J. S., Photocatalytic and Photoelectrochemical Water Oxidation over Metal - Doped Monoclinic BiVO₄ Photoanodes. *ChemSusChem* **2012**, *5* (10), 1926-1934.
97. Park, H. S.; Kweon, K. E.; Ye, H.; Paek, E.; Hwang, G. S.; Bard, A. J., Factors in the Metal Doping of BiVO₄ for Improved Photoelectrocatalytic Activity as Studied by Scanning Electrochemical Microscopy and First-Principles Density-Functional Calculation. *J. Phys. Chem. C* **2011**, *115* (36), 17870-17879.
98. Berglund, S. P.; Rettie, A. J.; Hoang, S.; Mullins, C. B., Incorporation of Mo and W into Nanostructured BiVO₄ Films for Efficient Photoelectrochemical Water Oxidation. *Phys. Chem. Chem. Phys.* **2012**, *14* (19), 7065-7075.
99. Beni, G.; Schiavone, L.; Shay, J.; Dautremont-Smith, W.; Schneider, B., Electrocatalytic Oxygen Evolution on Reactively Sputtered Electrochromic Iridium Oxide Films. *Nature* **1979**, *282*, 281-283.
100. Harriman, A.; Pickering, I. J.; Thomas, J. M.; Christensen, P. A., Metal Oxides as Heterogeneous Catalysts for Oxygen Evolution under Photochemical Conditions. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84* (8), 2795-2806.
101. Wang, D.; Li, R.; Zhu, J.; Shi, J.; Han, J.; Zong, X.; Li, C., Photocatalytic Water Oxidation on BiVO₄ with the Electrocatalyst as an Oxidation Cocatalyst: Essential Relations between Electrocatalyst and Photocatalyst. *J. Phys. Chem. C* **2012**, *116* (8), 5082-5089.

102. Jeon, T. H.; Choi, W.; Park, H., Cobalt–Phosphate Complexes Catalyze the Photoelectrochemical Water Oxidation of BiVO₄ Electrodes. *Phys. Chem. Chem. Phys.* **2011**, *13* (48), 21392-21401.
103. Zhou, M.; Bao, J.; Bi, W.; Zeng, Y.; Zhu, R.; Tao, M.; Xie, Y., Efficient Water Splitting via a Heteroepitaxial BiVO₄ Photoelectrode Decorated with Co - Pi Catalysts. *ChemSusChem* **2012**, *5* (8), 1420-1425.
104. Pilli, S. K.; Deutsch, T. G.; Furtak, T. E.; Turner, J. A.; Brown, L. D.; Herring, A. M., Light Induced Water Oxidation on Cobalt-Phosphate (Co–Pi) Catalyst Modified Semi-Transparent, Porous SiO₂–BiVO₄ Electrodes. *Phys. Chem. Chem. Phys.* **2012**, *14* (19), 7032-7039.
105. Ye, H.; Park, H. S.; Bard, A. J., Screening of Electrocatalysts for Photoelectrochemical Water Oxidation on W-Doped BiVO₄ Photocatalysts by Scanning Electrochemical Microscopy. *J. Phys. Chem. C* **2011**, *115* (25), 12464-12470.
106. Li, R.; Han, H.; Zhang, F.; Wang, D.; Li, C., Highly Efficient Photocatalysts Constructed by Rational Assembly of Dual-Cocatalysts Separately on Different Facets of BiVO₄. *Energy Environ. Sci.* **2014**, *7* (4), 1369-1376.
107. Jia, Q.; Iwashina, K.; Kudo, A., Facile Fabrication of an Efficient BiVO₄ Thin Film Electrode for Water Splitting under Visible Light Irradiation. *Proceedings of the National Academy of Sciences* **2012**, *109* (29), 11564-11569.
108. Seabold, J. A.; Choi, K.-S., Efficient and Stable Photo-Oxidation of Water by a Bismuth Vanadate Photoanode Coupled with an Iron Oxyhydroxide Oxygen Evolution Catalyst. *J. Am. Chem. Soc.* **2012**, *134* (4), 2186-2192.
109. McDonald, K. J.; Choi, K.-S., A New Electrochemical Synthesis Route for a BiOI Electrode and its Conversion to a Highly Efficient Porous BiVO₄

- Photoanode for Solar Water Oxidation. *Energy Environ. Sci.* **2012**, 5 (9), 8553-8557.
110. Kim, T. W.; Choi, K.-S., Nanoporous BiVO₄ Photoanodes with Dual-Layer Oxygen Evolution Catalysts for Solar Water Splitting. *Science* **2014**, 343 (6174), 990-994.
111. Morris Hotsenpiller, P.; Bolt, J.; Farneth, W.; Lowekamp, J.; Rohrer, G., Orientation Dependence of Photochemical Reactions on TiO₂ Surfaces. *J. Phys. Chem. B* **1998**, 102 (17), 3216-3226.
112. Pan, J.; Liu, G.; Lu, G. Q. M.; Cheng, H. M., On the True Photoreactivity Order of {001},{010}, and {101} Facets of Anatase TiO₂ Crystals. *Angew. Chem. Int. Ed.* **2011**, 50 (9), 2133-2137.
113. Read, C. G.; Steinmiller, E. M.; Choi, K.-S., Atomic Plane-Selective Deposition of Gold Nanoparticles on Metal Oxide Crystals Exploiting Preferential Adsorption of Additives. *J. Am. Chem. Soc.* **2009**, 131 (34), 12040-12041.
114. Martin, D. J.; Umezawa, N.; Chen, X.; Ye, J.; Tang, J., Facet Engineered Ag₃PO₄ for Efficient Water Photooxidation. *Energy Environ. Sci.* **2013**, 6 (11), 3380-3386.
115. Zhou, X.; Lan, J.; Liu, G.; Deng, K.; Yang, Y.; Nie, G.; Yu, J.; Zhi, L., Facet - Mediated Photodegradation of Organic Dye over Hematite Architectures by Visible Light. *Angew. Chem.* **2012**, 124 (1), 182-186.
116. Xie, Y. P.; Liu, G.; Yin, L.; Cheng, H.-M., Crystal Facet-Dependent Photocatalytic Oxidation and Reduction Reactivity of Monoclinic WO₃ for Solar Energy Conversion. *J. Mater. Chem.* **2012**, 22 (14), 6746-6751.

117. Yang, H. G.; Sun, C. H.; Qiao, S. Z.; Zou, J.; Liu, G.; Smith, S. C.; Cheng, H. M.; Lu, G. Q., Anatase TiO₂ Single Crystals with a Large Percentage of Reactive Facets. *Nature* **2008**, 453 (7195), 638-641.
118. Gong, X.-Q.; Selloni, A., Reactivity of Anatase TiO₂ Nanoparticles: The Role of the Minority (001) Surface. *J. Phys. Chem. B* **2005**, 109 (42), 19560-19562.
119. Zhang, D.; Li, G.; Yang, X.; Jimmy, C. Y., A Micrometer-Size TiO₂ Single-Crystal Photocatalyst with Remarkable 80% Level of Reactive Facets. *Chem. Commun.* **2009**, (29), 4381-4383.
120. Liu, G.; Sun, C.; Yang, H. G.; Smith, S. C.; Wang, L.; Lu, G. Q. M.; Cheng, H.-M., Nanosized Anatase TiO₂ Single Crystals for Enhanced Photocatalytic Activity. *Chem. Commun.* **2010**, 46 (5), 755-757.
121. Han, X.; Kuang, Q.; Jin, M.; Xie, Z.; Zheng, L., Synthesis of Titania Nanosheets with a High Percentage of Exposed (001) Facets and Related Photocatalytic Properties. *J. Am. Chem. Soc.* **2009**, 131 (9), 3152-3153.
122. Selloni, A., Crystal Growth: Anatase Shows Its Reactive Side. *Nat. Mater.* **2008**, 7 (8), 613-615.
123. Zhang, L.; Chen, D.; Jiao, X., Monoclinic Structured BiVO₄ Nanosheets: Hydrothermal Preparation, Formation Mechanism, and Coloristic and Photocatalytic Properties. *J. Phys. Chem. B* **2006**, 110 (6), 2668-2673.
124. Xi, G.; Ye, J., Synthesis of Bismuth Vanadate Nanoplates with Exposed {001} Facets and Enhanced Visible-Light Photocatalytic Properties. *Chem. Commun.* **2010**, 46 (11), 1893-1895.
125. Wang, D.; Jiang, H.; Zong, X.; Xu, Q.; Ma, Y.; Li, G.; Li, C., Crystal Facet Dependence of Water Oxidation on BiVO₄ Sheets under Visible Light Irradiation. *Chem. Eur. J.* **2011**, 17 (4), 1275-1282.

126. Ohno, T.; Sarukawa, K.; Matsumura, M., Crystal Faces of Rutile and Anatase TiO₂ Particles and Their Roles in Photocatalytic Reactions. *New J. Chem.* **2002**, 26 (9), 1167-1170.
127. Li, R.; Zhang, F.; Wang, D.; Yang, J.; Li, M.; Zhu, J.; Zhou, X.; Han, H.; Li, C., Spatial Separation of Photogenerated Electrons and Holes Among {010} and {110} Crystal Facets of BiVO₄. *Nat. Commun.* **2013**, 4, 1432.
128. Tachikawa, T.; Yamashita, S.; Majima, T., Evidence for Crystal-Face-Dependent TiO₂ Photocatalysis from Single-Molecule Imaging and Kinetic Analysis. *J. Am. Chem. Soc.* **2011**, 133 (18), 7197-7204.
129. Zhang, L.; Wang, W.; Sun, S.; Jiang, D.; Gao, E., Selective Transport of Electron and Hole among {001} and {110} Facets of BiOCl for Pure Water Splitting. *Appl. Catal., B* **2015**, 162, 470-474.
130. Li, H.; Yu, H.; Quan, X.; Chen, S.; Zhao, H., Improved Photocatalytic Performance of Heterojunction by Controlling the Contact Facet: High Electron Transfer Capacity between TiO₂ and the {110} Facet of BiVO₄ Caused by Suitable Energy Band Alignment. *Adv. Funct. Mater.* **2015**, 25 (20), 3074-3080.
131. Kim, Y.; Shin, D.; Chang, W. J.; Jang, H. L.; Lee, C. W.; Lee, H. E.; Nam, K. T., Hybrid Z - Scheme Using Photosystem I and BiVO₄ for Hydrogen Production. *Adv. Funct. Mater.* **2015**, 25 (16), 2369-2377.
132. Zhu, J.; Fan, F.; Chen, R.; An, H.; Feng, Z.; Li, C., Direct Imaging of Highly Anisotropic Photogenerated Charge Separations on Different Facets of a Single BiVO₄ Photocatalyst. *Angew. Chem.* **2015**, 127 (31), 9239-9242.
133. Tachikawa, T.; Ochi, T.; Kobori, Y., Crystal-Face-Dependent Charge Dynamics on a BiVO₄ Photocatalyst Revealed by Single-Particle Spectroelectrochemistry. *ACS Catal.* **2016**, 6 (4), 2250-2256.

134. Zhu, S.; Xu, T.; Fu, H.; Zhao, J.; Zhu, Y., Synergetic Effect of Bi₂WO₆ Photocatalyst with C₆₀ and Enhanced Photoactivity under Visible Irradiation. *Environ. Sci. Technol.* **2007**, *41* (17), 6234-6239.
135. Fu, H.; Xu, T.; Zhu, S.; Zhu, Y., Photocorrosion Inhibition and Enhancement of Photocatalytic Activity for ZnO via Hybridization with C₆₀. *Environ. Sci. Technol.* **2008**, *42* (21), 8064-8069.
136. Jiang, L.; Gao, L., Fabrication and Characterization of ZnO-Coated Multi-Walled Carbon Nanotubes with Enhanced Photocatalytic Activity. *Mater. Chem. Phys.* **2005**, *91* (2), 313-316.
137. Kongkanand, A.; Martínez Domínguez, R.; Kamat, P. V., Single Wall Carbon Nanotube Scaffolds for Photoelectrochemical Solar Cells. Capture and Transport of Photogenerated Electrons. *Nano Lett.* **2007**, *7* (3), 676-680.
138. Xiang, Q.; Yu, J.; Jaroniec, M., Graphene-Based Semiconductor Photocatalysts. *Chem. Soc. Rev.* **2012**, *41* (2), 782-796.
139. Stankovich, S.; Dikin, D. A.; Dommett, G. H.; Kohlhaas, K. M.; Zimney, E. J.; Stach, E. A.; Piner, R. D.; Nguyen, S. T.; Ruoff, R. S., Graphene-Based Composite Materials. *Nature* **2006**, *442* (7100), 282-286.
140. Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A., Electric Field Effect in Atomically Thin Carbon Films. *Science* **2004**, *306* (5696), 666-669.
141. Li, X., *Epitaxial Graphene Films on Silicon Carbide: Growth, Characterization, and Devices*. ProQuest: **2008**.
142. Sun, Z.; Yan, Z.; Yao, J.; Beitler, E.; Zhu, Y.; Tour, J. M., Growth of Graphene from Solid Carbon Sources. *Nature* **2010**, *468* (7323), 549-552.

143. Williams, G.; Seger, B.; Kamat, P. V., TiO₂-Graphene Nanocomposites. UV-Assisted Photocatalytic Reduction of Graphene Oxide. *ACS Nano* **2008**, 2 (7), 1487-1491.
144. Lightcap, I. V.; Kosel, T. H.; Kamat, P. V., Anchoring Semiconductor and Metal Nanoparticles on a Two-Dimensional Catalyst Mat. Storing and Shuttling Electrons with Reduced Graphene Oxide. *Nano Lett.* **2010**, 10 (2), 577-583.
145. Zhang, H.; Lv, X.; Li, Y.; Wang, Y.; Li, J., P25-Graphene Composite as a High Performance Photocatalyst. *ACS Nano* **2009**, 4 (1), 380-386.
146. Bell, N. J.; Ng, Y. H.; Du, A.; Coster, H.; Smith, S. C.; Amal, R., Understanding the Enhancement in Photoelectrochemical Properties of Photocatalytically Prepared TiO₂-Reduced Graphene Oxide Composite. *J. Phys. Chem. C* **2011**, 115 (13), 6004-6009.
147. An, X.; Jimmy, C. Y.; Wang, Y.; Hu, Y.; Yu, X.; Zhang, G., WO₃ Nanorods/Graphene Nanocomposites for High-Efficiency Visible-Light-Driven Photocatalysis and NO₂ Gas Sensing. *J. Mater. Chem.* **2012**, 22 (17), 8525-8531.
148. Li, B.; Cao, H., ZnO@ Graphene Composite with Enhanced Performance for the Removal of Dye from Water. *J. Mater. Chem.* **2011**, 21 (10), 3346-3349.
149. Zhang, J.; Xiong, Z.; Zhao, X., Graphene-Metal-Oxide Composites for the Degradation of Dyes under Visible Light Irradiation. *J. Mater. Chem.* **2011**, 21 (11), 3634-3640.
150. Ng, Y. H.; Iwase, A.; Kudo, A.; Amal, R., Reducing Graphene Oxide on a Visible-Light BiVO₄ Photocatalyst for an Enhanced Photoelectrochemical Water Splitting. *J. Phys. Chem. Lett* **2010**, 1 (17), 2607-2612.

151. Gawande, S. B.; Thakare, S. R., Graphene Wrapped BiVO₄ Photocatalyst and Its Enhanced Performance under Visible Light Irradiation. *Int. Nano Lett.* **2012**, 2 (1), 1-7.
152. Yan, Y.; Sun, S.; Song, Y.; Yan, X.; Guan, W.; Liu, X.; Shi, W., Microwave-Assisted In Situ Synthesis of Reduced Graphene Oxide-BiVO₄ Composite Photocatalysts and Their Enhanced Photocatalytic Performance for the Degradation of Ciprofloxacin. *J. Hazard. Mater.* **2013**, 250–251 (0), 106-114.
153. Wang, Y.; Li, F.; Li, H.; Bai, L.; Sun, L., Photocatalytic Water Oxidation via Combination of BiVO₄-RGO and Molecular Cobalt Catalysts. *Chem. Commun.* **2016**, 52 (14), 3050-3053.
154. Wang, A.; Shen, S.; Zhao, Y.; Wu, W., Preparation and Characterizations of BiVO₄/Reduced Graphene Oxide Nanocomposites with Higher Visible Light Reduction Activities. *J. Colloid Interface Sci.* **2015**, 445, 330-336.
155. Wang, C.; Meng, D.; Sun, J.; Memon, J.; Huang, Y.; Geng, J., Graphene Wrapped TiO₂ Based Catalysts with Enhanced Photocatalytic Activity. *Adv. Mater. Interfaces* **2014**, 1 (4).
156. Wang, T.; Li, C.; Ji, J.; Wei, Y.; Zhang, P.; Wang, S.; Fan, X.; Gong, J., Reduced Graphene Oxide (rGO)/BiVO₄ Composites with Maximized Interfacial Coupling for Visible Light Photocatalysis. *ACS Sustainable Chem. Eng.* **2014**, 2 (10), 2253-2258.
157. Feng, W.; Weng, S.; Zheng, Z.; Fang, Z.; Liu, P., 1 Rational Design of a Charge Shunt: Modification upon Crystal Facet Engineering of Semiconductor Photocatalysts. *Chem. Commun.* **2015**, 51 (56), 11186-11189.
158. Reddy, B. M.; Khan, A.; Yamada, Y.; Kobayashi, T.; Lorient, S.; Volta, J.-C., Structural Characterization of CeO₂-MO₂ (M=Si⁴⁺, Ti⁴⁺, and Zr⁴⁺) Mixed Oxides

- p>by Raman Spectroscopy, X-Ray Photoelectron Spectroscopy, and Other Techniques.
- J. Phys. Chem. B*
- 2003**
- ,
- 107*
- (41), 11475-11484.
159. Kang, H. S.; Kang, J. S.; Kim, J. W.; Lee, S. Y., Annealing Effect on the Property of Ultraviolet and Green Emissions of ZnO Thin Films. *J. Appl. Phys.* **2004**, *95* (3), 1246-1250.
 160. Oh, S. W.; Bang, H. J.; Bae, Y. C.; Sun, Y.-K., Effect of Calcination Temperature on Morphology, Crystallinity and Electrochemical Properties of Nano-Crystalline Metal Oxides (Co₃O₄, CuO, and NiO) Prepared via Ultrasonic Spray Pyrolysis. *J. Power Sources* **2007**, *173* (1), 502-509.
 161. Yu, J.; Wang, B., Effect of Calcination Temperature on Morphology and Photoelectrochemical Properties of Anodized Titanium Dioxide Nanotube Arrays. *Appl. Catal., B* **2010**, *94* (3), 295-302.
 162. Hanaor, D.; Sorrell, C., Review of the Anatase to Rutile Phase Transformation. *J. Mater. Sci.* **2011**, *46* (4), 855-874.
 163. Yu, J.-G.; Yu, H.-G.; Cheng, B.; Zhao, X.-J.; Yu, J. C.; Ho, W.-K., The Effect of Calcination Temperature on the Surface Microstructure and Photocatalytic Activity of TiO₂ Thin Films Prepared by Liquid Phase Deposition. *J. Phys. Chem. B* **2003**, *107* (50), 13871-13879.
 164. Ng, C.; Ng, Y. H.; Iwase, A.; Amal, R., Influence of Annealing Temperature of WO₃ in Photoelectrochemical Conversion and Energy Storage for Water Splitting. *ACS Appl. Mater. Interfaces* **2013**, *5* (11), 5269-5275.
 165. Yamada, K.; Yamane, H.; Matsushima, S.; Nakamura, H.; Ohira, K.; Kouya, M.; Kumada, K., Effect of Thermal Treatment on Photocatalytic Activity of N-Doped TiO₂ Particles under Visible Light. *Thin Solid Films* **2008**, *516* (21), 7482-7487.

166. Chae, Y.; Mori, S.; Suzuki, M., Visible-Light Photocatalytic Activity of Anatase TiO₂ Treated with Argon Plasma. *Thin Solid Films* **2009**, 517 (14), 4260-4263.
167. Mtangi, W.; Auret, F. D.; Meyer, W.; Legodi, M.; van Rensburg, P. J.; Coelho, S.; Diale, M.; Nel, J., Effects of Hydrogen, Oxygen, and Argon Annealing on the Electrical Properties of ZnO and ZnO Devices Studied by Current-Voltage, Deep Level Transient Spectroscopy, and Laplace DLTS. *J. Appl. Phys.* **2012**, 111 (9), 094504.
168. Zuo, F.; Wang, L.; Wu, T.; Zhang, Z.; Borchardt, D.; Feng, P., Self-Doped Ti³⁺ Enhanced Photocatalyst for Hydrogen Production under Visible Light. *J. Am. Chem. Soc.* **2010**, 132 (34), 11856-11857.
169. Chen, X.; Liu, L.; Peter, Y. Y.; Mao, S. S., Increasing Solar Absorption for Photocatalysis with Black Hydrogenated Titanium Dioxide Nanocrystals. *Science* **2011**, 331 (6018), 746-750.
170. Wang, G.; Wang, H.; Ling, Y.; Tang, Y.; Yang, X.; Fitzmorris, R. C.; Wang, C.; Zhang, J. Z.; Li, Y., Hydrogen-Treated TiO₂ Nanowire Arrays for Photoelectrochemical Water Splitting. *Nano Lett.* **2011**, 11 (7), 3026-3033.
171. Lu, X.; Wang, G.; Xie, S.; Shi, J.; Li, W.; Tong, Y.; Li, Y., Efficient Photocatalytic Hydrogen Evolution over Hydrogenated ZnO Nanorod Arrays. *Chem. Commun.* **2012**, 48 (62), 7717-7719.
172. Wang, G.; Ling, Y.; Wang, H.; Yang, X.; Wang, C.; Zhang, J. Z.; Li, Y., Hydrogen-Treated WO₃ Nanoflakes Show Enhanced Photostability. *Energy Environ. Sci.* **2012**, 5 (3), 6180-6187.
173. Zhang, Y.; Guo, Y.; Duan, H.; Li, H.; Sun, C.; Liu, H., Facile Synthesis of V⁴⁺ Self-Doped,[010] Oriented BiVO₄ Nanorods with Highly Efficient Visible

- Light-Induced Photocatalytic Activity. *Phys. Chem. Chem. Phys.* **2014**, 16 (44), 24519-24526.
174. Singh, A. P.; Kodan, N.; Dey, A.; Krishnamurthy, S.; Mehta, B. R., Improvement in the Structural, Optical, Electronic and Photoelectrochemical Properties of Hydrogen Treated Bismuth Vanadate Thin Films. *Int. J. Hydrogen Energy* **2015**, 40 (12), 4311-4319.
 175. Jiang, H.; Dai, H.; Meng, X.; Ji, K.; Zhang, L.; Deng, J., Porous Olive-Like BiVO₄: Alchoho-Hydrothermal Preparation and Excellent Visible-Light-Driven Photocatalytic Performance for the Degradation of Phenol. *Appl. Catal., B* **2011**, 105 (3), 326-334.
 176. Liu, Y.; Dai, H.; Deng, J.; Zhang, L.; Au, C. T., Three-Dimensional Ordered Macroporous Bismuth Vanadates: PMMA-Templating Fabrication and Excellent Visible Light-Driven Photocatalytic Performance for Phenol Degradation. *Nanoscale* **2012**, 4 (7), 2317-2325.
 177. Huang, Y.; Li, H.; Balogun, M.-S.; Liu, W.; Tong, Y.; Lu, X.; Ji, H., Oxygen Vacancy Induced Bismuth Oxyiodide with Remarkably Increased Visible-Light Absorption and Superior Photocatalytic Performance. *ACS Appl. Mater. Interfaces* **2014**, 6 (24), 22920-22927.
 178. Yin, W.-J.; Wei, S.-H.; Al-Jassim, M. M.; Turner, J.; Yan, Y., Doping Properties of Monoclinic BiVO₄ Studied by First-Principles Density-Functional Theory. *Phys. Rev. B* **2011**, 83 (15), 155102.
 179. Gan, J.; Lu, X.; Rajeeva, B. B.; Menz, R.; Tong, Y.; Zheng, Y., Efficient Photoelectrochemical Water Oxidation over Hydrogen - Reduced Nanoporous BiVO₄ with Ni - Bi Electrocatalyst. *ChemElectroChem* **2015**, 2 (9), 1385-1395.

180. Zhang, Y.; Wang, D.; Zhang, X.; Chen, Y.; Kong, L.; Chen, P.; Wang, Y.; Wang, C.; Wang, L.; Liu, Y., Enhanced Photoelectrochemical Performance of Nanoporous BiVO₄ Photoanode by Combining Surface Deposited Cobalt-Phosphate with Hydrogenation Treatment. *Electrochim. Acta* **2016**, *195*, 51-58.
181. Kim, T. W.; Ping, Y.; Galli, G. A.; Choi, K.-S., Simultaneous Enhancements in Photon Absorption and Charge Transport of Bismuth Vanadate Photoanodes for Solar Water Splitting. *Nat. Commun.* **2015**, *6*, 8769.
182. Hodes, G.; Kamat, P. V., Understanding the Implication of Carrier Diffusion Length in Photovoltaic Cells. *J. Phys. Chem. Lett.* **2015**, *6* (20), 4090-4092.
183. Seabold, J. A.; Zhu, K.; Neale, N. R., Efficient Solar Photoelectrolysis by Nanoporous Mo: BiVO₄ through Controlled Electron Transport. *Phys. Chem. Chem. Phys.* **2014**, *16* (3), 1121-1131.
184. Jiang, Z.; Tang, Y.; Tay, Q.; Zhang, Y.; Malyi, O. I.; Wang, D.; Deng, J.; Lai, Y.; Zhou, H.; Chen, X., Understanding the Role of Nanostructures for Efficient Hydrogen Generation on Immobilized Photocatalysts. *Adv. Energy Mater.* **2013**, *3* (10), 1368-1380.
185. Su, J.; Guo, L.; Bao, N.; Grimes, C. A., Nanostructured WO₃/BiVO₄ Heterojunction Films for Efficient Photoelectrochemical Water Splitting. *Nano Lett.* **2011**, *11* (5), 1928-1933.
186. Rao, P. M.; Cai, L.; Liu, C.; Cho, I. S.; Lee, C. H.; Weisse, J. M.; Yang, P.; Zheng, X., Simultaneously Efficient Light Absorption and Charge Separation in WO₃/BiVO₄ Core/Shell Nanowire Photoanode for Photoelectrochemical Water Oxidation. *Nano Lett.* **2014**, *14* (2), 1099-1105.

187. Newton, K. A.; Osterloh, F. E., Size and Morphology of Suspended WO_3 Particles Control Photochemical Charge Carrier Extraction and Photocatalytic Water Oxidation Activity. *Top. Catal.* **2016**, 1-7.
188. Kho, Y. K.; Teoh, W. Y.; Iwase, A.; Madler, L.; Kudo, A.; Amal, R., Flame Preparation of Visible-Light-Responsive BiVO_4 Oxygen Evolution Photocatalysts with Subsequent Activation via Aqueous Route. *ACS Appl. Mater. Interfaces* **2011**, 3 (6), 1997-2004.

Chapter 3

BiVO₄ {010} and {110} Relative Exposure Extent: Governing Factor of Surface Charge Population and Photoactivity

3.1. Introduction

Different photoreactivities of different crystal facets on a photocatalyst have commonly been associated with surface reactivity¹⁻² and selective reactant adsorption.³ Nevertheless, recent observations of facet-selective photooxidation and photoreduction processes on a photocatalyst suggest that photogenerated electrons and holes are spatially driven to different facets, which function distinctively as active reduction or oxidation site. Such phenomenon was first demonstrated by Ohno et al. with titanium dioxide (TiO₂),⁴ a benchmark photocatalyst. Interestingly, Li et al. also proved the presence of similar redox functional facets on the visible-light-responsive monoclinic bismuth vanadate (BiVO₄), in which {010} facets provided the reduction sites and {110} facets functioned as the oxidation sites.⁵ BiVO₄, with a relatively small band gap of 2.4 – 2.5 eV, has been widely shown to be active for visible-light-triggered organic degradations⁶⁻⁷ and oxygen evolution from water,⁸⁻¹⁰ attributing to its deep valence band energy level. Understanding the intrinsic charge properties of BiVO₄ in relation to its crystal facets is therefore of great interest to allow advanced design of high-performing BiVO₄.

Despite {110} being proven as the oxidation functional facets, photooxidation performance of BiVO₄ has been suggested to correlate with its {010} facets. For instance, BiVO₄ materials with exposed {010} facets exhibited enhanced photooxidation of water¹¹⁻¹² and organic molecules.^{11, 13} One might argue that the two-dimensional BiVO₄ nanoplates and nanosheets prepared by Xi et al.¹¹ and Zhang et al.,¹³ respectively, do not justify the advantage of {010} for photooxidation compared to other facets. However, using dual-faceted BiVO₄ with exposed {010} and {110}, a similar correlation was also reported by Wang et al.¹² It is unclear why photooxidation performs better on {010} dominant BiVO₄ although {010} facet is the reduction functional surface. Are the beneficial roles of {010} facets in water photooxidation mainly attributed to its higher charge mobility, preferential water adsorption and lower energy barrier than that of {110} facets as proposed by Yang et al.,¹⁴ or could the underlying reasons be due to manipulation of surface charge population and charge transfer efficiency from varying the relative exposure extent of {010} and {110} facets on BiVO₄?

It is known that efficient transfer of photogenerated electrons and holes to the respective electron acceptors and donors is a key aspect that determines the activity of a photocatalyst.¹⁵⁻¹⁶ Accumulation of either charge species is deleterious due to increased charge recombination and lower quantum yield.¹⁷ Liu et al. proposed that improved photooxidation can result from the concurrently effective photoreduction,¹⁸ indicative of efficient electrons removal being imperative for photooxidation reactions. Congruously, Gerischer and Heller claimed that the rate of electron transfer was the rate- or yield-controlling factor in photooxidation activity of TiO₂.¹⁷ Given the importance of efficient charge transfer in photocatalysis,¹⁹⁻²⁰ there still have been no studies on redox functional

facets' relative exposure extent dependence of the charge transfer kinetics of a photocatalyst.

In this chapter, we show that the population of photoinduced electrons and holes available on BiVO₄ surface are dependent on the relative exposure extent of {010} and {110} facets. The difference in electron transfer efficiency is shown to play a governing role in the photocatalytic activity of BiVO₄, including water oxidation and 2,4-dichlorophenoxyacetic acid (2,4-D) degradation.

3.2. Experimental

3.2.1. Synthesis of BiVO₄

BiVO₄ was synthesized using solid-liquid state reaction by mixing equimolar amounts (2.5 mmol) of bismuth (III) oxide (Bi₂O₃) and vanadium (V) oxide (V₂O₅) in 25 mL of nitric acid (HNO₃) with two different concentrations: 0.50 M and 1.00 M. The mixture was stirred for 4 days at room temperature. The vivid yellow BiVO₄ product was collected by suction filtration, washed with distilled water and dried at 110 °C.

3.2.2. Photocatalytic Reactions

3.2.2.1. Photocatalytic O₂ Evolution

Photocatalytic O₂ evolution from aqueous silver nitrate (AgNO₃) solution was executed in an enclosed top-irradiation cell with a Pyrex window via visible light irradiation of 100 mg of BiVO₄ suspended in 100 mL of 0.05 M AgNO₃ solution (pH 4.5). A 300 W Xe lamp (Oriel) installed with a 420 nm cut-off filter was used as the light source. Prior to illumination, the suspension was purged with argon (Ar) gas for 30 min. The amount

of O₂ generated was quantified by gas chromatography (TCD, Shimadzu GC-8A, Ar carrier gas).

For quantification of the amount of Ag deposited on BiVO₄ during water photooxidation, a separate reaction with similar conditions as above was carried out with continuous deaeration of the suspension using Ar gas. The suspension was sampled intermittently and the photoreduced product (Ag-loaded BiVO₄) was retrieved using centrifugation and dried at 60 °C. Loading of Ag on the obtained Ag-loaded BiVO₄ powder was determined using inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis, in which digestion of Ag was carried out using nitric acid heated at 60 °C.

The apparent quantum yield (AQY) for photocatalytic O₂ evolution from aqueous AgNO₃ solution was determined at 400 nm by using a band pass filter and calculated according to the equation 3.1:²¹

$$\text{AQY} / \% = \frac{\text{The number of reacted holes}}{\text{The number of incident photons}} \times 100 \quad (3.1)$$

The number of incident photons was measured using a solar simulator calibrated reference cell and meter (Newport; 91150V).

3.2.2.2. 2,4-Dichlorophenoxyacetic Acid Degradation

100 mg of BiVO₄ was dispersed in 100 mL solution containing 0.065 mM of 2,4-D. The suspension was constantly stirred and purged with air throughout the experiment. The BiVO₄ particles were allowed to equilibrate with the analyte for 30 min in dark conditions prior to irradiation with visible light (same light source as that in Section

3.2.2.1.) Degradation of 2,4-D was examined using a UV-vis-NIR spectrometer (liquid state, Shimadzu UV-3600).

3.2.3. Material Characterization

Scanning electron microscopy (SEM) images of BiVO₄ and Ag-loaded BiVO₄ powder were obtained with a FEI Nova NanoSEM 230 FESEM microscope operated at 5 kV. The elemental analysis of Ag-loaded BiVO₄ particles was measured by energy-dispersive X-ray spectroscopy (EDS) coupled with the SEM microscope.

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images of BiVO₄ were obtained with a Phillips CM200 microscope.

X-Ray diffraction (XRD) measurements were conducted on a Phillips Xpert Multipurpose X-ray Diffraction System (MPD) at room temperature using Cu K α radiation ($\lambda = 1.54\text{\AA}$) with a potential of 45 kV and a current of 40 mA.

Diffuse reflectance spectra of powder samples were analyzed using a Shimadzu UV-3600 UV-vis-NIR spectrophotometer and were converted from reflectance to absorbance using the Kubelka-Munk method.

Brunauer-Emmett-Teller (BET) surface area of BiVO₄ particles was measured using a Micromeritics Tristar 3030 nitrogen adsorption apparatus at 77 K. Prior to the surface area analysis, the particles were degassed in a Micromeritics Smart VacPrep unit at 110 °C for 3 h under vacuum.

Steady-state fluorescence spectra were obtained on Horiba Fluoromax-4 spectrofluorometer with an excitation wavelength of 405 nm. Typically, 3 mL of 0.8

mM BiVO₄ was filled into a cuvette and purged with Ar gas prior to excitation. In the presence of electron or hole scavenger, different concentrations of AgNO₃ or CH₃OH were added, namely molar concentrations of 0.06, 0.12 and 0.17 M.

The time-resolved photoluminescence (PL) was measured by the time-correlated single-photon-counting (TCSPC) technique (Microtime-200 system, Picoquant) with the excitation of a 470 nm laser. The time resolution of the system was determined as 200 ps.

3.2.4. Electrochemical Impedance Spectroscopy Measurements

The Mott-Schottky plots were measured using an Autolab instrument (potentiostat model PGSTAT12/ frequency response analyzer FRA2 modules). The impedance spectroscopy was carried out in light condition using 0.5 M sodium sulfate (Na₂SO₄, pH 6) as the electrolyte in a three-electrode electrochemical system. The working electrode was made by dropcasting suspension of BiVO₄-ethanol on a conductive fluoride-doped tin oxide (FTO) substrate. A platinum wire and Ag/AgCl electrode were used as the counter and the reference electrodes, respectively. The measurements were done using a frequency of 500 Hz and an AC amplitude of 5 mV at each potential. A 300 W Xe lamp (Oriel) with a 420 nm cutoff filter was used as the irradiation source. The flat band potential (V_{fb}) of BiVO₄ is represented by the x-intercept of a plot of $1/C^2$ against V according to the Mott-Schottky equation 3.2:²²

$$\frac{1}{C^2} = \frac{2}{\epsilon_0 A^2 e N_D} \left(V - V_{fb} - \frac{k_B T}{e} \right) \quad (3.2)$$

where C is the space-charge capacitance, ϵ is the relative permittivity of the material, ϵ_0 is the vacuum permittivity, A is the illuminated area, e is the electronic charge, N_D is the

donor density, V is the applied potential, k_B is the Boltzmann constant and T is the temperature.

3.3. Results and Discussion

3.3.1. Morphological, Structural and Optical Properties

Large BiVO₄ particles with clear edges and well-developed crystal facets were produced using a template- and surfactant-free method reported by Iwase et al.⁹ Scanning electron microscopy (SEM) images (Figure 3.1) show that the as-synthesized BiVO₄ particles are decahedron shaped, consisting of truncated tetragonal bipyramid with the top and bottom flat surfaces geometrically defined as {010} facets, while the isosceles trapezoidal sides are assigned as {110} facets. The facet assignments were supported by the high-resolution transmission electron microscopy (HRTEM) images (Figure 3.2) showing lattice spacings of 5.85 and 4.75 Å corresponding to the (020) and (110) planes of monoclinic BiVO₄. The thickness of BiVO₄ particles was altered using two nitric acid concentrations during the synthesis process. Evidently, lower acid concentration produces markedly thinner BiVO₄ particles. Herein, the sample is denoted as BiVO₄_x, where x represents the concentration of nitric acid being used during synthesis. BiVO₄_1.00M indicates the thick BiVO₄ (Figure 3.1a), whereas BiVO₄_0.50M corresponds to the thin one (Figure 3.1b). The apparent decrease in thickness indicates that BiVO₄_0.50M has a much greater exposure extent of {010} facets relative to that of {110}. Conversely, {110} are the dominating facets in the BiVO₄_1.00M.

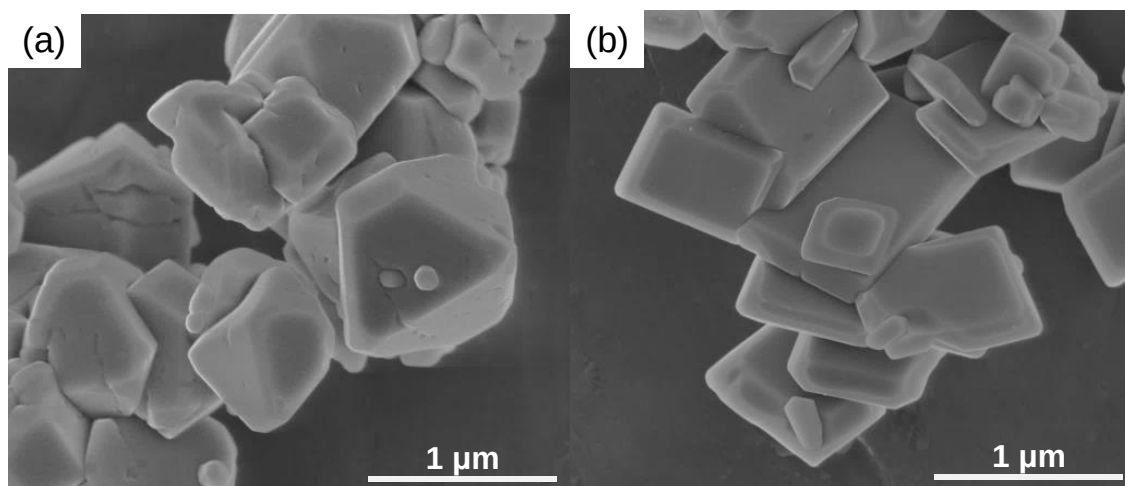


Figure 3.1. Scanning electron microscopy (SEM) images of (a) $\text{BiVO}_4_{1.00\text{M}}$ and (b) $\text{BiVO}_4_{0.50\text{M}}$.

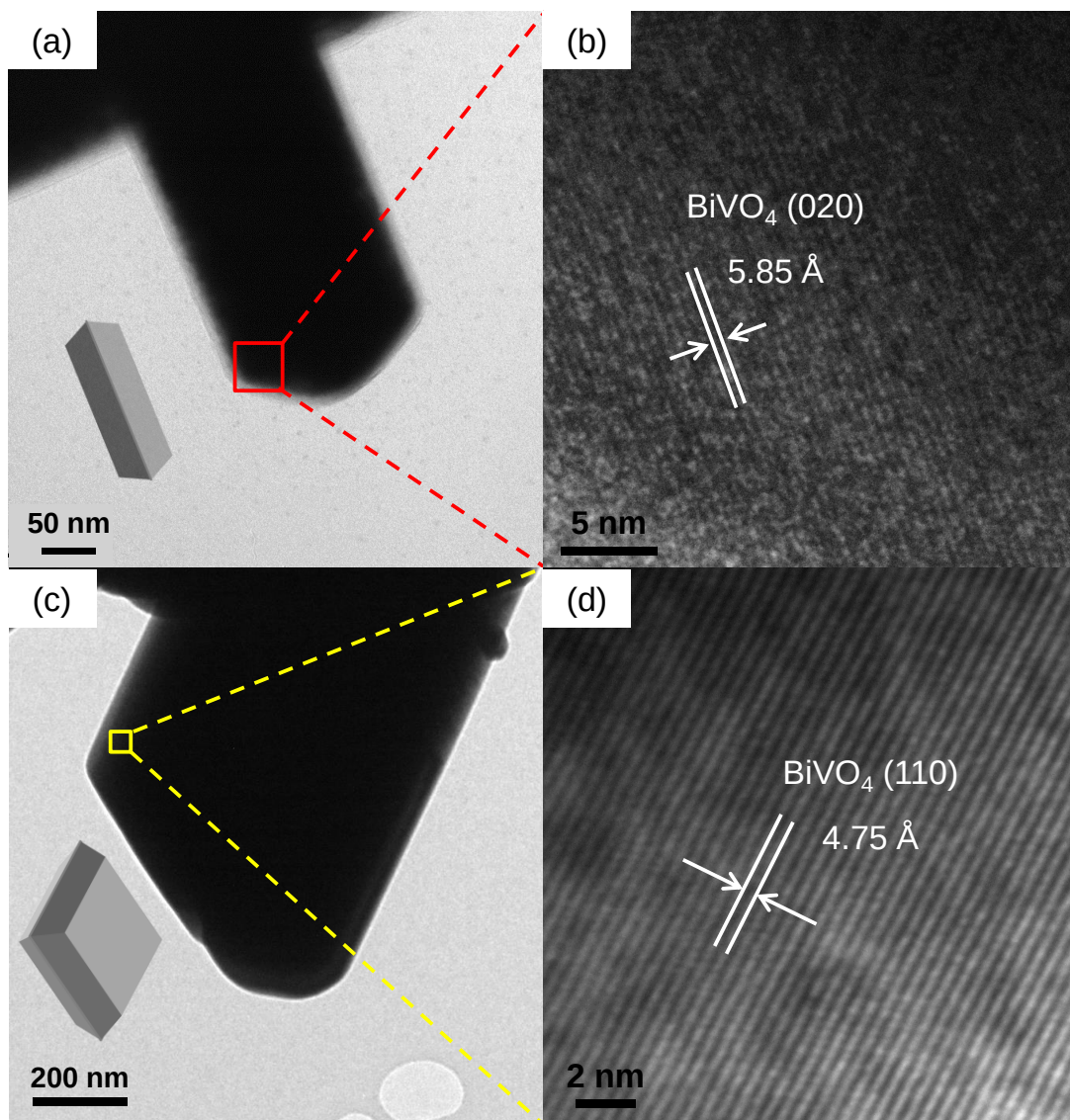


Figure 3.2. (a,c) Transmission electron microscopy (TEM) images of BiVO₄_0.50M with the corresponding particle orientation schematically shown as the inset. (b) and (d) depict the high-resolution TEM (HRTEM) images of the area highlighted in (a) and (c), respectively. The lattice spacings of 5.85 and 4.75 Å correspond to the (020) and (110) planes of monoclinic BiVO₄.

X-ray diffraction (XRD) patterns of the obtained BiVO₄ (Figure 3.3a) exhibit characteristic diffraction peaks of single phase monoclinic scheelite structure of BiVO₄, which is the most active phase for visible light O₂ evolution.²³ The narrow diffraction peaks suggest high crystallinity, consistent with that reflected in the SEM images. A few studies related to anisotropic crystal growth such as ZnO nanorods²⁴ and BiVO₄

crystals with highly exposed (040) facet¹² have observed apparent changes in the relative intensity of their XRD peaks. In this study, despite the discernible difference in {010}/{110} relative exposure extent on BiVO_4 _1.00M and BiVO_4 _0.50M (as observed from SEM), the XRD patterns of the two samples are comparable with no noteworthy change in the relative intensity of the XRD peaks corresponding to {010} and {110} planes. This may be attributed to the random orientation of our BiVO_4 particles during packing of the powder samples for XRD measurement, which is a bulk analysis. The crystallite sizes and BET specific surface areas of the two BiVO_4 were also analyzed whereby both these attributes of the two samples are shown to be comparable (Table 3.1). The ultraviolet-visible (UV-vis) diffuse reflectance spectra in Figure 3.3b show that both BiVO_4 samples illustrate similar onset of absorption edge at wavelength of ca. 500 nm, corresponding to a band gap energy of 2.5 eV, attesting them as visible-light-active.

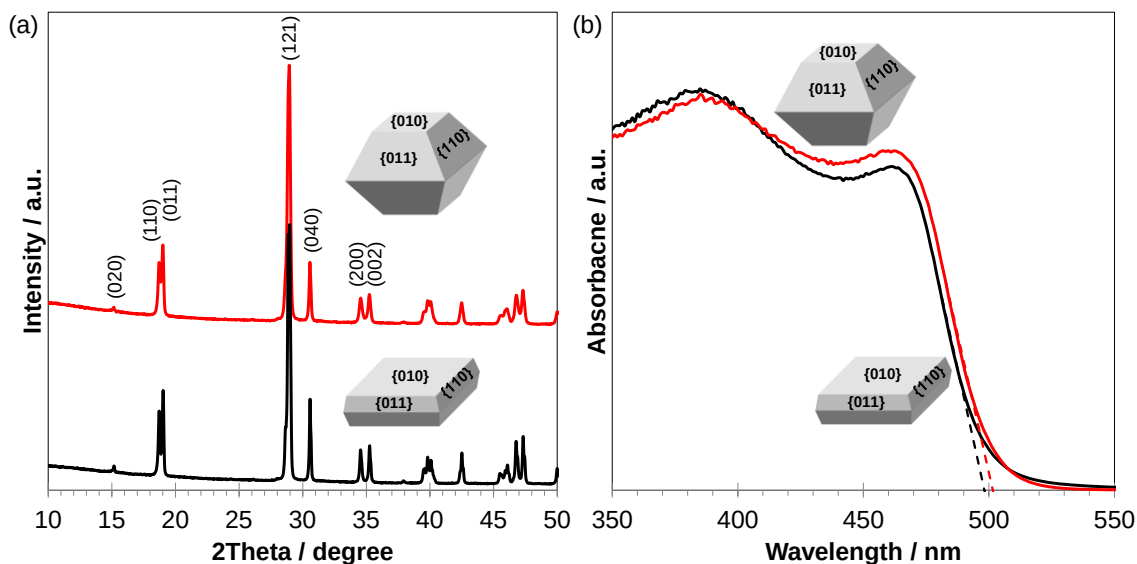


Figure 3.3. (a) XRD diffractograms and (b) UV-vis diffuse reflectance spectra of BiVO_4 _1.00M (red line) and BiVO_4 _0.50M (black line).

Table 3.1. Crystallite sizes and specific surface areas of the BiVO₄ samples, in which the former were estimated by Scherrer equation using the full width of half-maximum of the dominant XRD peak located at 30.6 °, while the latter were analyzed using BET measurement.

BiVO ₄ sample	Crystallite size [nm]	Specific surface area [m ² g ⁻¹]
BiVO ₄ _1.00M	81	2.3
BiVO ₄ _0.50M	91	2.1

3.3.2. {010} as the Active Reduction Functional Facet of BiVO₄

SEM imaging of silver (Ag)-loaded BiVO₄ particles (BiVO₄_1.00M in Figure 3.4a and BiVO₄_0.50M in Figure 3.4b) produced from visible-light-induced O₂ evolution using BiVO₄ in aqueous silver nitrate (AgNO₃) solution, reveals agglutinated particles being selectively photodeposited on {010} facets. Energy-dispersive X-ray spectroscopy (EDS) (Figure 3.5) confirms that these particles are primarily composed of Ag metal. This observation is in accordance with the findings of Li et. al.,⁵ in which photoreduction of metal ions selectively proceeded on BiVO₄ {010} facets, whereas the deposition of photooxidized metal ions was mainly seen on the {110} facets of BiVO₄. The facet-selective deposition of Ag by photoreduction of Ag⁺ ions discerned in this work confirms that the active reduction sites on the as-produced BiVO₄ are the {010} facets, where photogenerated electrons are preferentially driven. Meanwhile, photogenerated holes are accumulated on the {110} facets.⁵

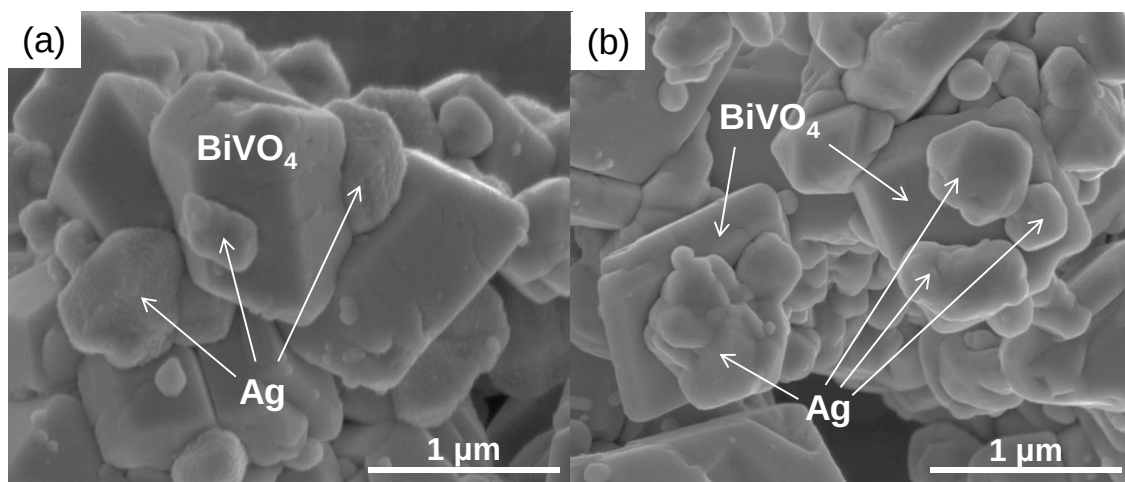


Figure 3.4. SEM images of Ag-deposited (a) $\text{BiVO}_4_{1.00\text{M}}$ and (b) $\text{BiVO}_4_{0.50\text{M}}$. EDS mapping confirms that the clusters found on {010} surfaces in panels a and b are mainly Ag, as shown in Figure 3.5.

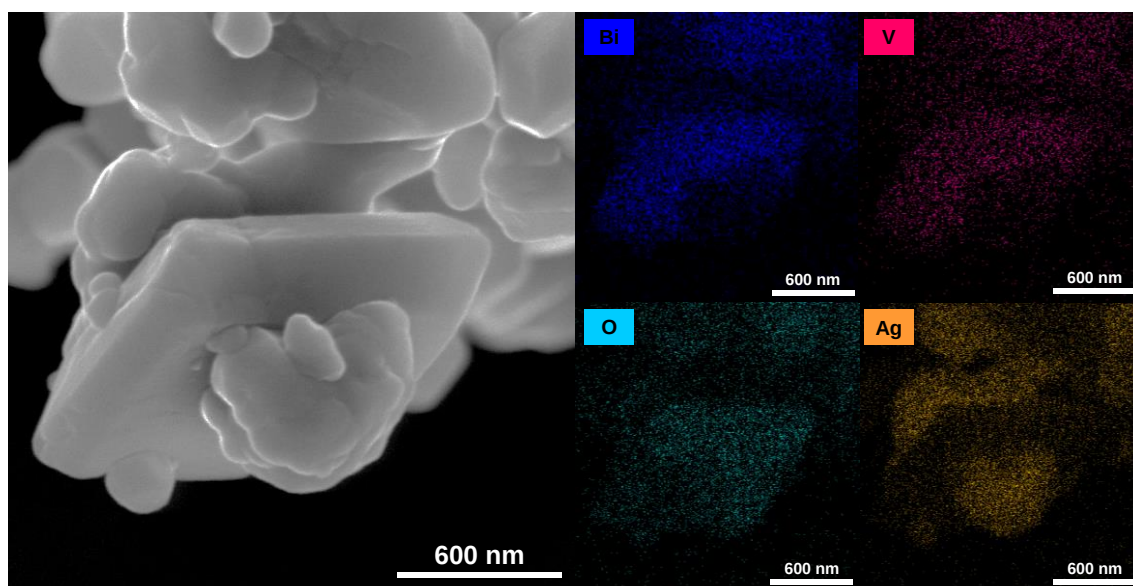


Figure 3.5. SEM image of Ag-loaded $\text{BiVO}_4_{0.50\text{M}}$ and the corresponding EDS mapping of Bi, V, O and Ag elements. Note the clumped particles deposited on the {010} facets of the well-faceted $\text{BiVO}_4_{0.50\text{M}}$ are primarily composed of Ag, confirming photoreduction of Ag^+ ions to metallic Ag selectively proceeded on {010} facets and therefore {010} was identified as the active reduction functional facet.

3.3.3. Photocatalytic O₂ Evolution and 2,4-D Degradation

The photocatalytic activity of the as-synthesized BiVO₄ with distinct morphology was investigated using two model reactions: water photooxidation using aqueous AgNO₃ solution and 2,4-D degradation in an aerated solution. In water photooxidation, electrons are scavenged by Ag⁺ ions, and holes are involved in oxidation of water molecules into oxygen. Figure 3.6a clearly shows that a greater amount of O₂ was generated by BiVO₄_0.50M compared to BiVO₄_1.00M, signifying photooxidation of water occurring at a quicker rate on the former BiVO₄. Similarly, better photooxidation performance of BiVO₄_0.50M was also exhibited in 2,4-D decomposition (Figure 3.6b), in which electrons and holes participate in the reduction of dissolved oxygen and 2,4-D oxidation, respectively. 2,4-D exhibits two main absorption bands at wavelengths of 230 nm and 285 nm.²⁵ The degradation of 2,4-D was validated by the decrease of the main absorption band at 230 nm over the illumination period (Figure 3.7a). As shown in Figure 3.6b, the initial 30 minutes of the decay curves (Figure 3.7b) was fitted with pseudo-first-order kinetics. This indicates that BiVO₄_0.50M has a higher degradation rate constant than BiVO₄_1.00M (-0.021 min⁻¹ and -0.016 min⁻¹, respectively). These results unambiguously infer the beneficial role of having enlarged {010} facets in promoting the photooxidation reaction on the surface of BiVO₄.

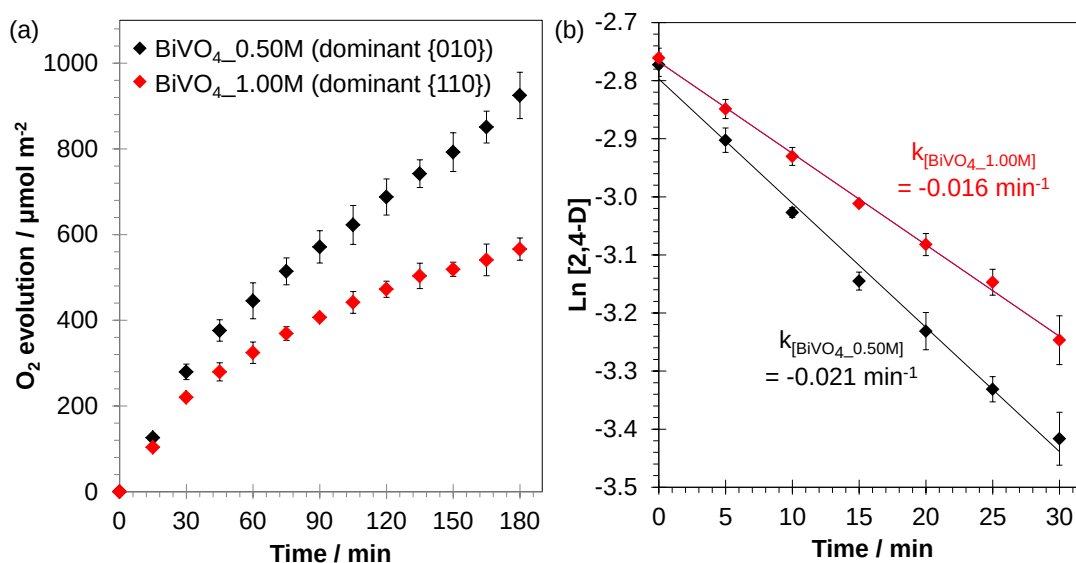


Figure 3.6. (a) Photocatalytic O_2 evolution from aqueous AgNO_3 solution (normalized in relation to per m^2 of surface) and (b) pseudo-first-order-fitted 2,4-D decay curves of the initial 30 min illumination of BiVO_4 1.00M (red) and BiVO_4 0.50M (black) under visible light ($\lambda > 420 \text{ nm}$). The value given for each experiment was an average over three runs with the error bars corresponding to standard deviation.

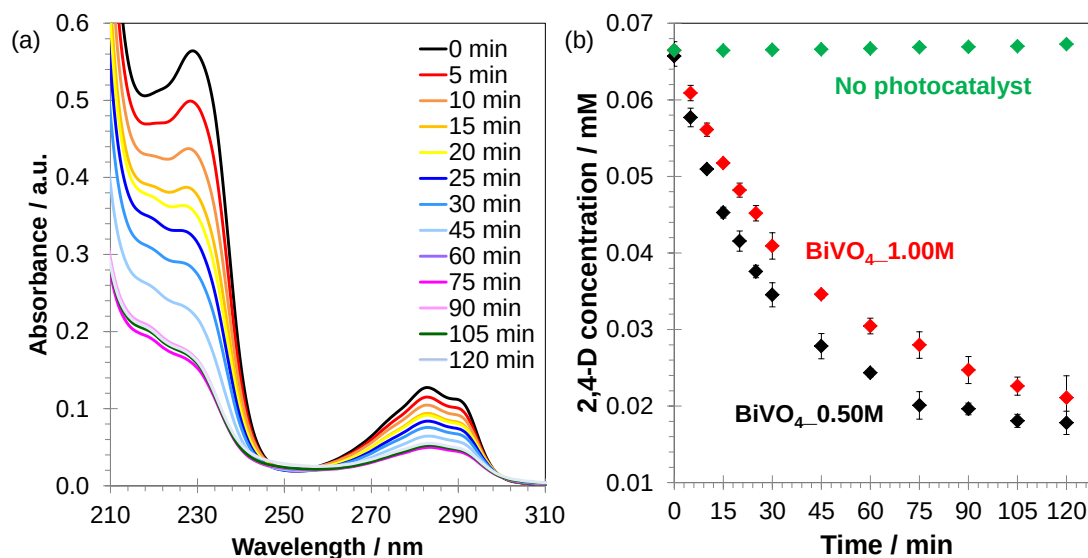


Figure 3.7. (a) Evolution of the absorption spectra of 0.065 mM aqueous 2,4-D in the presence of visible-light-excited BiVO_4 0.50M. (b) Time profile of 2,4-D degradation by BiVO_4 1.00M and BiVO_4 0.50M under visible light (of wavelength, $\lambda > 420 \text{ nm}$) illumination. The control experiment executed in the absence of photocatalyst confirms the degradation of 2,4-D in our experimental conditions did not originate from the photolysis of 2,4-D.

3.3.4. Photoluminescence and Electrochemical Impedance Measurements

Photoluminescence (PL) spectroscopy is a powerful technique to gain insights into the dynamics of the photogenerated electron-hole pairs, including their recombination, transfer and defect/surface trapping processes. Steady-state fluorescence spectra of both BiVO₄_1.00M and BiVO₄_0.50M exhibit a prominent band located at 500 nm and a low-energy tail band that is broadly extended to 650 nm, as displayed in Figure 3.8. These emission bands originate from radiative recombination of electron-hole pairs via several major pathways upon above band gap photoexcitation, as schematically presented in the inset. The primary step involves effective relaxation of charge carriers to the bottom of the conduction band (in the case of electrons) or the top of the valence band (in the case of holes) and to the shallow surface trap states.²⁶⁻²⁷ Subsequently, the electron-hole pairs can recombine radiatively or non-radiatively. The former contributes to band edge emission while the latter involves charge trapping at defect states that lie within the band gap. Radiative recombination of these trapped charges (commonly known as donor-acceptor pair recombination²⁸) produces additional emission band that is of lower energy than the band edge emission.^{27, 29} As the main emission band at 500 nm corresponds to the onset of absorption edge shown in Figure 3.3b, it is ascribed to the band edge emission. Meanwhile, the low-energy tail band is attributed to recombination of donor-acceptor pairs.

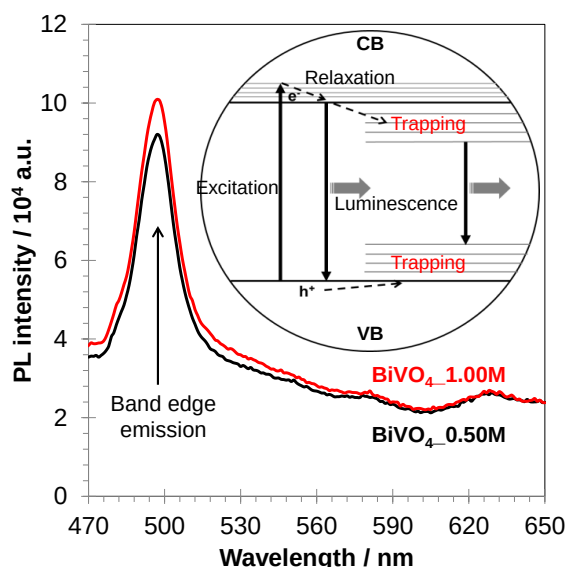


Figure 3.8. Steady-state fluorescence spectra of $\text{BiVO}_4_{1.00\text{M}}$ and $\text{BiVO}_4_{0.50\text{M}}$. Inset displays the mechanism of photoluminescence, where CB represents the conduction band while VB denotes the valence band.

The steady-state fluorescence spectra in Figure 3.8 reflect the overall dynamics of both photogenerated electrons and holes, particularly the extent of electron-hole pair recombination that happens within the bulk and on the surface of the as-produced BiVO_4 , but do not relay information on the relative number of free electrons and holes available on the surface. Given that the as-produced BiVO_4 has the salient feature of uneven exposure extent of {010} and {110} facets, the surface areas accessible for the respective photogenerated electrons and holes migrating from the bulk are unequal. As the $\text{BiVO}_4_{1.00\text{M}}$ has a considerably smaller absolute area of the {010} facets than that of the {110} facets, the {010} surface area available to accommodate the photogenerated electrons is thus restricted in comparison to that of the {110} surface for photogenerated holes. Therefore, the number of free electrons available on the surface of photoexcited $\text{BiVO}_4_{1.00\text{M}}$ should be lesser than holes. Analogous but opposite phenomenon could be applied to $\text{BiVO}_4_{0.50\text{M}}$, where the much larger {010} facets in relative to {110} facets render larger population of photogenerated electrons on the

surface. Since PL originates from radiative recombination of free electrons and holes, its intensity is therefore governed by the free charge species of smaller population. When the population of said free charge species is further reduced by the introduction of its corresponding charge scavenger, surface electron-hole pair recombination will be diminished, as schematically depicted in Figure 3.9a. Consequently, substantial quenching of PL intensity will be observed. By contrast, in the presence of a scavenger targeted at the more populous free charge species, the decrease in charge recombination will not be as severe. In this case, a lesser extent of PL quenching will be obtained.

In order to identify the difference in surface relative population of photogenerated electrons and holes on each BiVO₄, electron and hole scavengers were added separately in PL measurements to selectively consume the photogenerated electrons or holes from the surface of BiVO₄. Methanol (CH₃OH) and Ag⁺ ion are the widely reported efficient hole and electron scavengers, respectively.^{15, 30-31} The perceptible PL quenching effect exhibited by BiVO₄_1.00M (Figure 3.9b inset) and BiVO₄_0.50M (Figure 3.9c inset) in the presence of either electron or hole scavenger is in agreement with that reported in literature,³²⁻³⁴ where photocatalysts other than BiVO₄ were examined. Interestingly, in this study using BiVO₄, different PL quenching extents were observed for the different scavengers. While addition of electron-scavenging AgNO₃ significantly quenches the PL intensity of BiVO₄_1.00M, the extent of quenching was limited in the presence of hole-scavenging CH₃OH. Reverse scenario was demonstrated by BiVO₄_0.50M. These trends were further confirmed using different concentrations of CH₃OH or AgNO₃, as shown in Figure 3.9b,c. These results suggest that while BiVO₄_1.00M has a relatively smaller population of photogenerated electrons on its surface, the opposite is true for BiVO₄_0.50M, affirming our postulation of the difference in relative amount of

photogenerated electrons and holes available on the surface of the two BiVO₄ with different dominant facets.

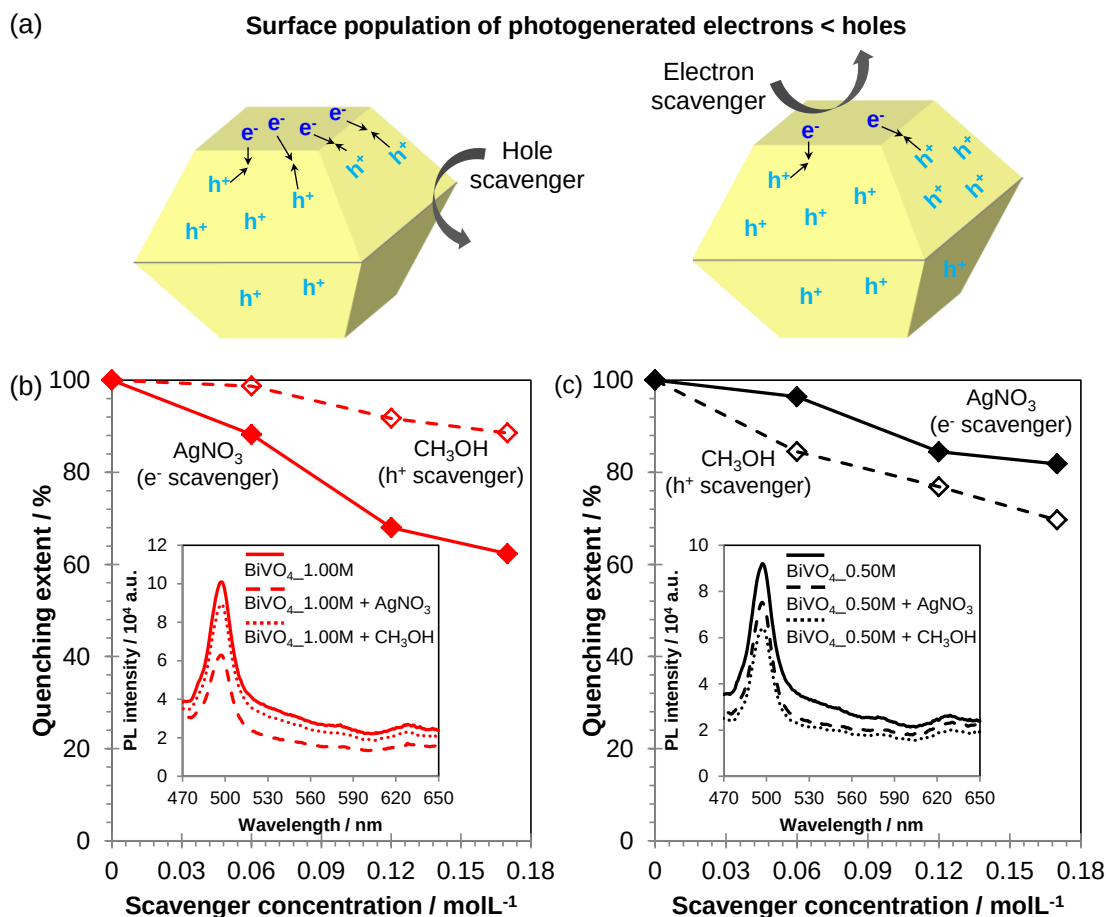


Figure 3.9. (a) Schematic illustration of the likelihood of surface electron-hole pair recombination in the presence of hole or electron scavenger, represented by a photocatalyst containing relative larger population of photogenerated holes on its surface. Different quenching extents of the band edge emission of (b) BiVO₄_1.00M and (c) BiVO₄_0.50M in the presence of hole and electron scavengers (CH₃OH and AgNO₃, respectively) using varying scavenger concentrations. Insets shown in panels b and c are the respective steady-state fluorescence spectra of BiVO₄_1.00M and BiVO₄_0.50M with the addition of 0.17 molL⁻¹ CH₃OH and AgNO₃.

The band edge fluorescence lifetime of BiVO₄_1.00M and BiVO₄_0.50M was determined using time correlated single photon counting (TCSPC) technique. As shown in Figure 3.10a, each decay curve displays a sharp decay that is beyond the time

resolution (200 ps) of the system³⁵ used in this study, which can be ascribed to ultrafast hole trapping in BiVO₄ reported to happen in 5 ps.³⁶ The PL decay curve can be fitted with a biexponential function indicating two decay mechanisms: the fast component is most likely attributed to electron trapping and the slow component is due to electron-hole recombination, as reported by Ravensbergen et al.³⁶ BiVO₄_0.50M has lifetimes of 1.0 ns and 9.5 ns for the fast (τ_1) and slow (τ_2) components, respectively. Note that BiVO₄_1.00M has shorter lifetimes for both components, with 0.8 ns fitted for τ_1 and 6.8 ns for τ_2 , suggesting that it has a greater extent of electron trapping and faster charge recombination as compared to BiVO₄_0.50M.

The greater extent of electron trapping in BiVO₄_1.00M indicates that a comparatively larger number of photogenerated electrons are accumulated in this BiVO₄ relative to that of BiVO₄_0.50M. An increased number of accumulated electrons can result in negative shifting of the Fermi level (E_F) of a semiconductor according to equation 3.3:³⁷

$$E_F = E_{CB} + kT \ln n_c / N_c \quad (3.3)$$

where E_{CB} is the energy level of conduction band versus NHE, n_c is the density of accumulated electrons and N_c is the charge carrier density. Such negative shift of E_F arising from a higher degree of electron accumulation has been observed for metal-semiconductor composites.³⁷⁻³⁸ In general, the flat band potential (V_{fb}) of a semiconductor corresponds to its E_F .³⁹ Therefore, the change in the E_F of BiVO₄ can be reflected by its V_{fb} , which is represented by the x-intercept of the Mott-Schottky plot shown in Figure 3.10b. The positive slopes indicate that both BiVO₄ are n-type semiconductors. The flat band potential of -0.53 V vs. Ag/AgCl (+0.02 V vs. NHE at pH = 0) measured for BiVO₄_0.50M agrees well with literature values.^{30, 40} However,

the V_{fb} of BiVO₄_1.00M is negatively shifted to -0.57 V vs. Ag/AgCl, allowing us to further ascertain the occurrence of greater extent of electron trapping in this sample. Such phenomenon can be attributed to the greater thickness of BiVO₄_1.00M (ca. 850 nm in comparison to ca. 320 nm for BiVO₄_0.50M, estimated from the SEM images), at which photogenerated electrons have to diffuse a longer distance of about 265 nm from bulk to the {010} surface. The longer distance of diffusion increases the probability of photogenerated electrons encountering and being trapped by crystal defects.

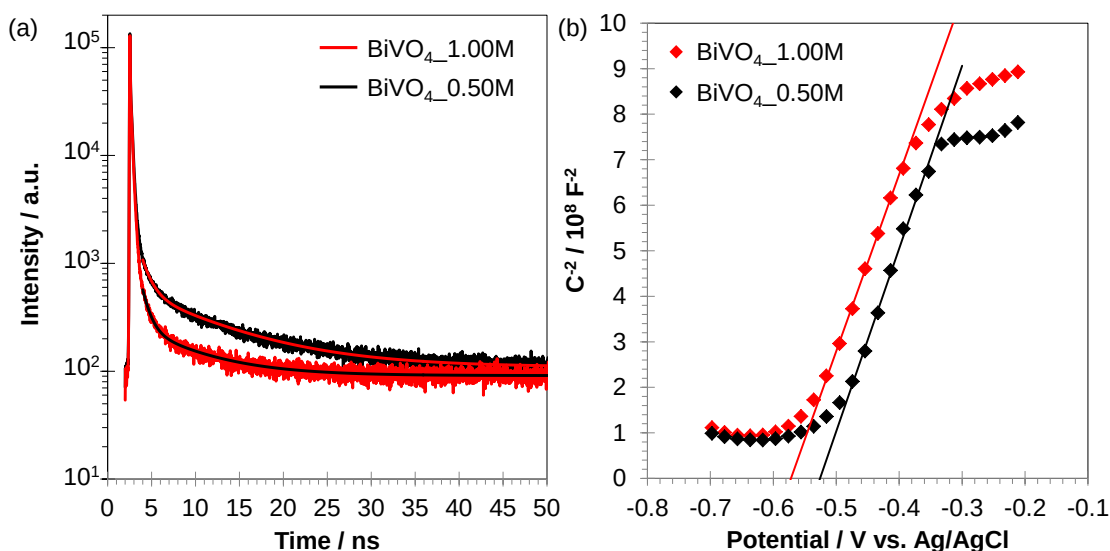


Figure 3.10. (a) Time-resolved PL spectra of the band edge emission of BiVO₄_1.00M and BiVO₄_0.50M. The solid lines are fitted lines using biexponential functions. (b) Mott-Schottky plots measured under visible light (of wavelength, $\lambda > 420$ nm) illumination with a frequency of 500 Hz.

3.3.5. Proposed Crystal-Facet-Dependent Charge Transfer Kinetics

The activity of a photocatalyst is highly dependent on its physicochemical properties such as specific surface area, particle size, crystal structure, and crystallinity.^{8, 41-42} XRD analysis has confirmed the two BiVO₄'s in this work have similar scheelite-monoclinic

structure with high crystallinity. Additionally, according to Table 3.1, both BiVO₄'s also have comparable crystallite sizes and specific surface areas. These experimental facts reinforce the difference of photocatalytic activities between BiVO₄_1.00M and BiVO₄_0.50M originating primarily from their distinct relative exposure extent of {010} and {110} facets, validated through SEM micrographs. Evidently, the photocatalytic performances of BiVO₄_0.50M with dominant reduction functional {010} facets surpass that of BiVO₄_1.00M.

On the basis of the difference in surface available charge population and charge trapping, the charge transfer kinetics contributing to the difference in photocatalytic activities of BiVO₄_1.00M and BiVO₄_0.50M are postulated and depicted in Figure 3.11. Owing to the extended {010} facets exposed on BiVO₄_0.50M, the greater population of photogenerated electrons available on its surface (as substantiated by the steady-state PL measurements in the presence of charge scavengers) can facilitate electron transfer to electron acceptor. This is supported by the greater amount of metallic Ag being loaded on BiVO₄_0.50M in comparison to that of BiVO₄_1.00M during water photooxidation in aqueous AgNO₃ solution (Figure 3.12). This improved rate of electron extraction simultaneously minimizes charge recombination and promotes the photooxidation activities of BiVO₄_0.50M.

On the contrary, in addition to the impeded electron transfer due to the limited photogenerated electrons available on the smaller {010} surface, the greater extent of electron trapping signifies that photogenerated electrons are preferentially accumulated within BiVO₄_1.00M. These trapped electrons can recombine with holes and thus diminishes the holes available for oxidation reactions. Studies related to charge recombination reported that electrons and holes recombine on a nanosecond time

scale.⁴³⁻⁴⁵ On the other hand, Tang et al. suggested that the oxidation process, in particular the oxygen evolution reaction only occurs in ca. 1s.¹⁵ It can thus be inferred that electron-hole recombination occurs much faster than holes' reaction with electron donors (water). As such, the inferior performance of BiVO₄_1.00M in photooxidation reactions is ascribed to holes loss due to increased charge recombination induced by trapped electrons. The better charge separation of BiVO₄_0.50M in comparison to that of BiVO₄_1.00M is also corroborated by the higher apparent quantum yield of the former (1.04 % and 0.90 %, respectively), measured for O₂ generation from aqueous AgNO₃ solution at 400 nm.

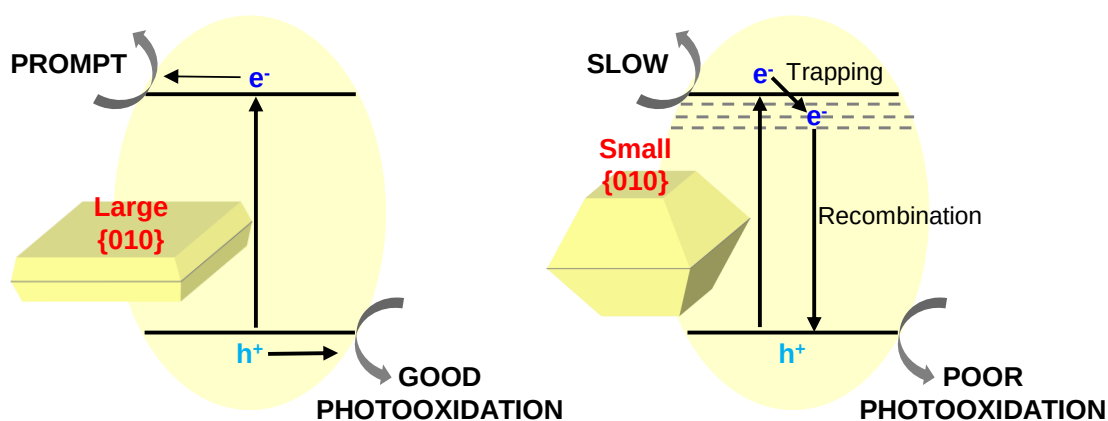


Figure 3.11. Schematic illustration of the different photoactivity of (left) BiVO₄_0.50M and (right) BiVO₄_1.00M due to their difference in electron transfer efficiency and greater extent of electron trapping in the latter BiVO₄.

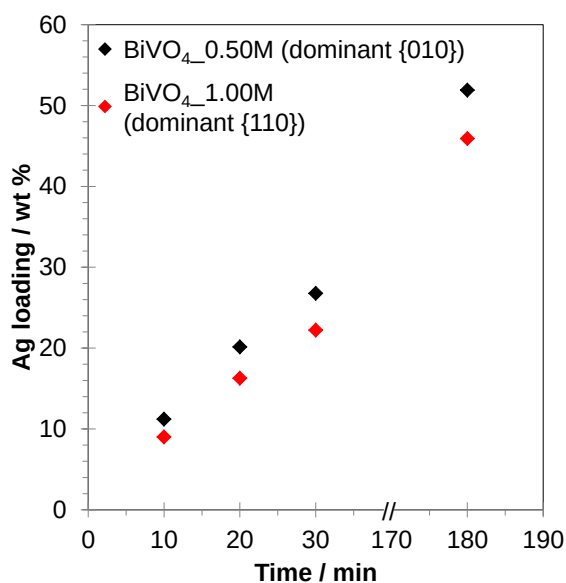


Figure 3.12. Time profile of the amount of Ag being loaded on $\text{BiVO}_4_{0.50\text{M}}$ and $\text{BiVO}_4_{1.00\text{M}}$, resulting from photoreduction of Ag^+ ions which is the reaction happens concurrently with water photooxidation during illumination of the BiVO_4 particles in aqueous AgNO_3 solution under visible light (of wavelength, $\lambda > 420$ nm).

3.4. Summary

Given that photogenerated electrons and holes are spatially driven to the {010} and {110} facets of BiVO₄ upon excitation, manipulation of the relative exposure extent of the two facets was revealed to affect the surface charge population, charge transfer efficiency, and photoactivity of the dual-faceted BiVO₄. Although BiVO₄_0.50M has considerably larger reduction functional {010} facets, it was shown to have superior photooxidation activities than BiVO₄_1.00M with dominating oxidation functional {110} facets. The difference in photocatalytic activity was ascribed to different electron transfer efficiency, which relies on the number of surface available photogenerated electrons that is proportional to the exposure extent of BiVO₄ {010} facets. Steady-state PL measurements in the presence of electron or hole scavenger manifested that BiVO₄_0.50M with dominant {010} facets has larger population of electrons in relative to holes available on the surface, whereas the surface of BiVO₄_1.00M with dominant {110} facets has more holes than electrons. Additionally, greater extent of electron trapping was found to present in BiVO₄_1.00M, as evidenced by the shorter lifetime of the fast component of time-resolved PL and negative shift of V_{fb} in comparison to those of BiVO₄_0.50M. The limited number of electrons available on the small {010} surface and the greater degree of electron trapping thus hamper efficient electron extraction from BiVO₄_1.00M and results in its poor photoactivity due to augmented holes loss through electron-hole pair recombination. It is hereby shown that enlargement of {010} facets relative to {110} in BiVO₄ is indispensable for better suppression of electron trapping not only to improve photoreduction efficiency, but also for effective photooxidation reactions.

3.5. References

1. Gong, X.-Q.; Selloni, A., Reactivity of Anatase TiO₂ Nanoparticles: The Role of the Minority (001) Surface. *J. Phys. Chem. B* **2005**, *109* (42), 19560-19562.
2. Pan, J.; Liu, G.; Lu, G. Q. M.; Cheng, H. M., On the True Photoreactivity Order of {001},{010}, and {101} Facets of Anatase TiO₂ Crystals. *Angew. Chem. Int. Ed.* **2011**, *50* (9), 2133-2137.
3. Read, C. G.; Steinmiller, E. M.; Choi, K.-S., Atomic Plane-Selective Deposition of Gold Nanoparticles on Metal Oxide Crystals Exploiting Preferential Adsorption of Additives. *J. Am. Chem. Soc.* **2009**, *131* (34), 12040-12041.
4. Ohno, T.; Sarukawa, K.; Matsumura, M., Crystal Faces of Rutile and Anatase TiO₂ Particles and Their Roles in Photocatalytic Reactions. *New J. Chem.* **2002**, *26* (9), 1167-1170.
5. Li, R.; Zhang, F.; Wang, D.; Yang, J.; Li, M.; Zhu, J.; Zhou, X.; Han, H.; Li, C., Spatial Separation of Photogenerated Electrons and Holes Among {010} and {110} Crystal Facets of BiVO₄. *Nat. Commun.* **2013**, *4*, 1432.
6. Zhou, L.; Wang, W.; Liu, S.; Zhang, L.; Xu, H.; Zhu, W., A Sonochemical Route to Visible-Light-Driven High-Activity BiVO₄ Photocatalyst. *J. Mol. Catal. A: Chem.* **2006**, *252* (1), 120-124.
7. Li, G.; Zhang, D.; Yu, J. C., Ordered Mesoporous BiVO₄ through Nanocasting: A Superior Visible Light-Driven Photocatalyst. *Chem. Mater.* **2008**, *20* (12), 3983-3992.
8. Kudo, A.; Omori, K.; Kato, H., A Novel Aqueous Process for Preparation of Crystal Form-Controlled and Highly Crystalline BiVO₄ Powder from Layered Vanadates at Room Temperature and Its Photocatalytic and Photophysical Properties. *J. Am. Chem. Soc.* **1999**, *121* (49), 11459-11467.

9. Iwase, A.; Kato, H.; Kudo, A., A Simple Preparation Method of Visible-Light-Driven BiVO₄ Photocatalysts from Oxide Starting Materials (Bi₂O₃ and V₂O₅) and Their Photocatalytic Activities. *J. Sol. Energy Eng.* **2010**, *132* (2), 021106.
10. Liu, H.; Nakamura, R.; Nakato, Y., Promoted Photo-Oxidation Reactivity of Particulate BiVO₄ Photocatalyst Prepared by a Photoassisted Sol-Gel Method. *J. Electrochem. Soc.* **2005**, *152* (11), G856-G861.
11. Xi, G.; Ye, J., Synthesis of Bismuth Vanadate Nanoplates with Exposed {001} Facets and Enhanced Visible-Light Photocatalytic Properties. *Chem. Commun.* **2010**, *46* (11), 1893-1895.
12. Wang, D.; Jiang, H.; Zong, X.; Xu, Q.; Ma, Y.; Li, G.; Li, C., Crystal Facet Dependence of Water Oxidation on BiVO₄ Sheets under Visible Light Irradiation. *Chem. Eur. J.* **2011**, *17* (4), 1275-1282.
13. Zhang, L.; Chen, D.; Jiao, X., Monoclinic Structured BiVO₄ Nanosheets: Hydrothermal Preparation, Formation Mechanism, and Coloristic and Photocatalytic Properties. *J. Phys. Chem. B* **2006**, *110* (6), 2668-2673.
14. Yang, J.; Wang, D.; Zhou, X.; Li, C., A Theoretical Study on the Mechanism of Photocatalytic Oxygen Evolution on BiVO₄ in Aqueous Solution. *Chem. Eur. J.* **2013**, *19* (4), 1320-1326.
15. Tang, J.; Durrant, J. R.; Klug, D. R., Mechanism of Photocatalytic Water Splitting in TiO₂. Reaction of Water with Photoholes, Importance of Charge Carrier Dynamics, and Evidence for Four-Hole Chemistry. *J. Am. Chem. Soc.* **2008**, *130* (42), 13885-13891.
16. Wang, M.; Iocozia, J.; Sun, L.; Lin, C.; Lin, Z., Inorganic-Modified Semiconductor TiO₂ Nanotube Arrays for Photocatalysis. *Energy Environ. Sci.* **2014**, *7* (7), 2182-2202.

17. Gerischer, H.; Heller, A., The Role of Oxygen in Photooxidation of Organic Molecules on Semiconductor Particles. *J. Phys. Chem.* **1991**, 95 (13), 5261-5267.
18. Liu, G.; Sun, C.; Yang, H. G.; Smith, S. C.; Wang, L.; Lu, G. Q. M.; Cheng, H.-M., Nanosized Anatase TiO₂ Single Crystals for Enhanced Photocatalytic Activity. *Chem. Commun.* **2010**, 46 (5), 755-757.
19. Wang, M.; Zheng, D.; Ye, M.; Zhang, C.; Xu, B.; Lin, C.; Sun, L.; Lin, Z., One - Dimensional Densely Aligned Perovskite - Decorated Semiconductor Heterojunctions with Enhanced Photocatalytic Activity. *small* **2015**, 11 (12), 1436-1442.
20. Liu, X.; Li, Z.; Zhao, W.; Zhao, C.; Wang, Y.; Lin, Z., A Facile Route to the Synthesis of Reduced Graphene Oxide-Wrapped Octahedral Cu₂O with Enhanced Photocatalytic and Photovoltaic Performance. *J. Mater. Chem. A* **2015**, 3 (37), 19148-19154.
21. Jia, Q.; Iwase, A.; Kudo, A., BiVO₄-Ru/SrTiO₃: Rh Composite Z-scheme Photocatalyst for Solar Water Splitting. *Chem. Sci.* **2014**, 5 (4), 1513-1519.
22. Ma, Y.; Pendlebury, S. R.; Reynal, A.; Le Formal, F.; Durrant, J. R., Dynamics of Photogenerated Holes in Undoped BiVO₄ Photoanodes for Solar Water Oxidation. *Chem. Sci.* **2014**, 5 (8), 2964-2973.
23. Tokunaga, S.; Kato, H.; Kudo, A., Selective Preparation of Monoclinic and Tetragonal BiVO₄ with Scheelite Structure and Their Photocatalytic Properties. *Chem. Mater.* **2001**, 13 (12), 4624-4628.
24. Height, M. J.; Mller, L.; Pratsinis, S. E.; Krumeich, F., Nanorods of ZnO Made by Flame Spray Pyrolysis. *Chem. Mater.* **2006**, 18 (2), 572-578.
25. Ng, Y. H.; Lightcap, I. V.; Goodwin, K.; Matsumura, M.; Kamat, P. V., To What Extent do Graphene Scaffolds Improve the Photovoltaic and

- Photocatalytic Response of TiO₂ Nanostructured Films? *J. Phys. Chem. Lett.* **2010**, 1 (15), 2222-2227.
26. Bawendi, M. G.; Wilson, W. L.; Rothberg, L.; Carroll, P. J.; Jedju, T. M.; Steigerwald, M. L.; Brus, L. E., Electronic Structure and Photoexcited-Carrier Dynamics in Nanometer-Size CdSe Clusters. *Phys. Rev. Lett.* **1990**, 65 (13), 1623.
27. Klimov, V.; Bolivar, P. H.; Kurz, H., Ultrafast Carrier Dynamics in Semiconductor Quantum Dots. *Phys. Rev. B* **1996**, 53 (3), 1463.
28. Dingle, R.; Ilegems, M., Donor-Acceptor Pair Recombination in GaN. *Solid State Commun.* **1971**, 9 (3), 175-180.
29. Underwood, D. F.; Kippeny, T.; Rosenthal, S. J., Ultrafast Carrier Dynamics in CdSe Nanocrystals Determined by Femtosecond Fluorescence Upconversion Spectroscopy. *J. Phys. Chem. B* **2001**, 105 (2), 436-443.
30. Sayama, K.; Nomura, A.; Arai, T.; Sugita, T.; Abe, R.; Yanagida, M.; Oi, T.; Iwasaki, Y.; Abe, Y.; Sugihara, H., Photoelectrochemical Decomposition of Water into H₂ and O₂ on Porous BiVO₄ Thin-Film Electrodes under Visible Light and Significant Effect of Ag Ion Treatment. *J. Phys. Chem. B* **2006**, 110 (23), 11352-11360.
31. Santato, C.; Ulmann, M.; Augustynski, J., Photoelectrochemical Properties of Nanostructured Tungsten Trioxide Films. *J. Phys. Chem. B* **2001**, 105 (5), 936-940.
32. Williams, G.; Kamat, P. V., Graphene–Semiconductor Nanocomposites: Excited-State Interactions between ZnO Nanoparticles and Graphene Oxide. *Langmuir* **2009**, 25 (24), 13869-13873.

33. Kamat, P. V.; Huehn, R.; Nicolaescu, R., A “Sense and Shoot” Approach for Photocatalytic Degradation of Organic Contaminants in Water. *J. Phys. Chem. B* **2002**, *106* (4), 788-794.
34. Greenham, N. C.; Peng, X.; Alivisatos, A. P., Charge Separation and Transport in Conjugated-Polymer/Semiconductor-Nanocrystal Composites Studied by Photoluminescence Quenching and Photoconductivity. *Phys. Rev. B* **1996**, *54* (24), 17628.
35. Wen, X.; Yu, P.; Toh, Y. R.; Hao, X.; Tang, J., Intrinsic and Extrinsic Fluorescence in Carbon Nanodots: Ultrafast Time - Resolved Fluorescence and Carrier Dynamics. *Adv. Opt. Mater.* **2013**, *1* (2), 173-178.
36. Ravensbergen, J.; Abdi, F. F.; van Santen, J. H.; Frese, R. N.; Dam, B.; van de Krol, R.; Kennis, J. T., Unraveling the Carrier Dynamics of BiVO₄: A Femtosecond to Microsecond Transient Absorption Study. *J. Phys. Chem. C* **2014**, *118* (48), 27793-27800.
37. Subramanian, V.; Wolf, E. E.; Kamat, P. V., Catalysis with TiO₂/Gold Nanocomposites. Effect of Metal Particle Size on the Fermi Level Equilibration. *J. Am. Chem. Soc.* **2004**, *126* (15), 4943-4950.
38. Wood, A.; Giersig, M.; Mulvaney, P., Fermi Level Equilibration in Quantum Dot-Metal Nanojunctions. *J. Phys. Chem. B* **2001**, *105* (37), 8810-8815.
39. Scaife, D., Oxide Semiconductors in Photoelectrochemical Conversion of Solar Energy. *Solar Energy* **1980**, *25* (1), 41-54.
40. Hong, S. J.; Lee, S.; Jang, J. S.; Lee, J. S., Heterojunction BiVO₄/WO₃ Electrodes for Enhanced Photoactivity of Water Oxidation. *Energy Environ. Sci.* **2011**, *4* (5), 1781-1787.

41. Sun, J.; Gao, L.; Zhang, Q., Synthesizing and Comparing the Photocatalytic Properties of High Surface Area Rutile and Anatase Titania Nanoparticles. *J. Am. Ceram. Soc.* **2003**, 86 (10), 1677-1682.
42. Liao, D.; Liao, B., Shape, Size and Photocatalytic Activity Control of TiO₂ Nanoparticles with Surfactants. *J. Photochem. Photobiol., A* **2007**, 187 (2), 363-369.
43. Serpone, N.; Lawless, D.; Khairutdinov, R.; Pelizzetti, E., Subnanosecond Relaxation Dynamics in TiO₂ Colloidal Sols (Particle Sizes $R_p=1.0-13.4$ nm). Relevance to Heterogeneous Photocatalysis. *J. Phys. Chem.* **1995**, 99 (45), 16655-16661.
44. Bahnemann, D. W.; Hilgendorff, M.; Memming, R., Charge Carrier Dynamics at TiO₂ Particles: Reactivity of Free and Trapped Holes. *J. Phys. Chem. B* **1997**, 101 (21), 4265-4275.
45. Leytner, S.; Hupp, J. T., Evaluation of the Energetics of Electron Trap States at the Nanocrystalline Titanium Dioxide/Aqueous Solution Interface via Time-Resolved Photoacoustic Spectroscopy. *Chem. Phys. Lett.* **2000**, 330 (3), 231-236.

Chapter 4

Interfacing BiVO₄ with Reduced Graphene Oxide for Enhanced Photoactivity: A Tale of Facet Dependence of Electron Shuttling

4.1. Introduction

Graphene-based semiconductor photocatalysts have garnered extensive research interest due to their great potential in energy and environmental applications such as photoelectrochemical water splitting,¹ photocatalytic hydrogen generation,²⁻⁵ and photodegradation of pollutants.⁶⁻⁹ The merit of coupling a semiconductor with graphene is attributed to the latter's renowned unique characteristics. For instance, large specific surface area and hydrophobicity of graphene promote organic adsorption to assist effective photodecontamination of organic pollutants.⁷ Facile surface modification of graphene via chemical approach also allows design and development of graphene-based materials for targeted applications.¹⁰ The main attribute that contributes to the preeminence of graphene-based semiconductor in photocatalysis however, arises from the excellent electron conductivity of graphene which facilitates improved charge transport properties in the composite.

With its π - π conjugation structure, graphene has been widely reported as good electron acceptor and transporter,¹¹ suppressing the undesirable charge recombination in semiconductor that vitiates their photocatalytic efficiency. Using ultraviolet-visible (UV-vis) spectrophotometry, Kamat and co-workers demonstrated the mechanism of electron transfer pathway from photoexcited titanium dioxide (TiO₂) to graphene oxide (GO), resulting in reduction of GO.¹² Following this discovery, the ability of reduced graphene oxide (RGO) in shuttling electrons was substantiated through selective deposition of silver (Ag) nanoparticles on RGO sheets, triggered by Ag⁺ ions reduction by the electrons previously stored in RGO.¹³ Such outstanding electron-accepting and shuttling features of graphene are believed to facilitate slower charge recombination and longer electron lifetime of graphene-BiVO₄ and -TiO₂ composite materials in comparison to their bare semiconductor counterparts.^{1, 14} Addition of graphene has also been shown to improve the charge transfer ability of other semiconductors.⁶⁻⁷

To date, research on graphene-based semiconductor photocatalysts have been mainly dedicated to streamlining their synthesis methods and manifesting their superiority against bare semiconductors in various applications.¹⁵ Given the key role of graphene as an electron mediator, efficient interfacial charge transfer between semiconductor and graphene is essential. Hence, better understanding of the factors, particularly the morphology of semiconductor in dictating the interfacial charge transfer between the two components is indispensable for advanced development of functionalized graphene-semiconductor composites. Morphology control such as shape and size manipulation is emerging as a prominent method to tailor the electronic and optical properties of semiconductors.¹⁶⁻¹⁹ More specifically, different crystal facets on a semiconductor were observed to instigate selective photoreduction and photooxidation reactions.²⁰⁻²¹

Owing to the difference in energy levels of different crystal facets, Li et al. demonstrated that photoreduction and photooxidation of metal ions and oxides occur selectively on the {010} and {110} facets of monoclinic BiVO₄, signifying that photogenerated electrons are spatially driven to the former and holes to the latter.²¹ They also showed water oxidation via photoelectrochemical (PEC) and photocatalytic systems could be greatly improved only when the reduction/oxidation cocatalysts were selectively deposited on the corresponding reduction/oxidation facets. This concept of spatial separation of electrons and holes on {010} and {110} facets were further extended to the other studies related to BiVO₄.²²⁻²⁴ For example, Au or Ag was selectively deposited on {010} facets of BiVO₄ to extract electrons to be transferred to the photosystem I (PSI) protein in a Z-scheme system composed of platinized PSI and BiVO₄ for hydrogen evolution.²² Previously in Chapter 3, we have reported better photooxidation activities of {010}-dominant BiVO₄ in comparison to that of {110}-dominant BiVO₄ due to the presence of more photogenerated electrons on the larger {010} surface, which allows more efficient electron transfer to abate charge recombination. Additionally, BiVO₄-TiO₂ heterojunctions with different interfacial contact facets of TiO₂ with dual-faceted BiVO₄ (namely {010} or {110}) were shown to have different energy band alignments to result in different PEC photocurrent generation and photocatalytic degradation activity.²⁴ These studies collectively indicate crystal facet dependence of the charge transfer and charge separation efficiency of BiVO₄ or BiVO₄-containing composite materials and thus triggered our interest in investigating the role of different facets of BiVO₄ on its interfacial charge interactions with graphene.

By exploiting the redox functional {010} and {110} facets on BiVO₄,²¹ we demonstrate in this chapter that the presence of increased surface area of {010} facets relative to that of {110} facets expedites electron transfer from BiVO₄ to graphene. The more pronounced photocurrent density in conjunction with improved charge transfer ability of RGO incorporated with BiVO₄ of larger {010}/{110} relative exposure extent strongly signify the constructive role of {010} facets in facilitating the interfacial charge transfer in graphene/BiVO₄ composite. Density functional theory (DFT) calculations reveal the difference in the electronic structures of graphene/BiVO₄{010} and graphene/BiVO₄{110} interfaces. Due to the smaller Schottky barrier, higher interface binding energy, and metallic nature at the interface, charge is easier to be transported from {010} facets of BiVO₄ to graphene than from {110} facets.

4.2. Experimental

4.2.1. Synthesis of Graphene Oxide

Graphene oxide (GO) was prepared using Hummers method, in which 1 g of graphite was first reacted with 500 mg of sodium nitrate (NaNO₃) in 23 mL of concentrated sulfuric acid (H₂SO₄) at a temperature of ~ 0 °C by using an ice bath. 3 g of potassium permanganate (KMnO₄) was then added slowly to the mixture to obtain a dark green suspension. Subsequently, the suspension was removed from the ice bath and heated at 35 – 45 °C for an hour, during which the suspension turned into brownish color. The suspension was diluted by first gradually adding 40 mL of distilled water, followed by 10 mL of 10 % hydrogen peroxide (H₂O₂). The as-produced GO was filtered and washed twice using a mixture of 5 % H₂SO₄ and 5 % H₂O₂ and three times with distilled water. The remaining brown solid product was dried in a vacuum desiccator at room temperature and grounded into fine powder.

4.2.2. Synthesis of BiVO₄ and RGO-BiVO₄

In addition to BiVO₄_0.50M and BiVO₄_1.00M as described in Chapter 3, another BiVO₄ prepared using 0.75M of HNO₃ (identified as BiVO₄_0.75M) was used for this chapter of work. The RGO-BiVO₄ composite was obtained by suspending 100 mg of BiVO₄ and 5 mg of GO in 25 mL of solvent-grade ethanol and irradiating the suspension for 3 h. The photoreduction was done under argon (Ar) atmosphere with the suspension being constantly stirred. A color change of the suspension from yellow to dark green was observed, indicating successful reduction of GO to RGO. Upon completion of reaction, the product was dried at 110 °C.

The powder sample (BiVO₄ and RGO-BiVO₄) was thereafter made into thin-film electrode by dropcasting on the FTO slides. Typically, a well-dispersed 0.5 mg cm⁻³ suspension in ethanol was deposited onto 2 x 1.5 cm area of FTO slide dropwise. A side stream of flowing air assisted in quick drying to generate a homogeneous film with surface density of 2 mg cm⁻² on the FTO surface.

4.2.3. Material Characterization

Morphology, band gap energy, crystal structure, and surface area of the BiVO₄ and/or RGO-BiVO₄ were respectively analyzed using SEM and TEM microscopes, UV-vis spectroscopy, X-ray diffraction (XRD), and Brunauer-Emmett-Teller (BET) methods as described in Chapter 3. Likewise, steady-state and time-resolved fluorescence spectra were obtained as previously done without the addition of charge scavengers. For analysis of the distribution of degree of truncation for BiVO₄, 50 particles were randomly selected from the SEM micrographs of BiVO₄.

X-ray photoelectron spectroscopy (XPS) was performed in a vacuum chamber ($< 2 \times 10^{-9}$ mbar) using a Thermo Scientific ESCALAB250Xi probe with monochromated Al K α radiation ($h\nu = 1486.68$ eV) set at 150 W and a pass energy of 20 eV. The binding energy was calibrated using the C 1s peak at 284.8 eV as reference.

Raman spectra of GO, BiVO₄ and RGO-BiVO₄ were recorded using Renishaw inVia Raman microscope with 1800 l/mm grating and 514 nm argon ion laser as the excitation source.

4.2.4. Photoelectrochemical Measurements

4.2.4.1. Photocurrent Measurements

Photoelectrochemical (PEC) characterization was done in a standard three-compartment cell, comprising of a sample electrode as the working electrode, a platinum foil as the counter electrode, and a saturated Ag/AgCl electrode as the reference electrode. 0.1 M sodium sulfate (Na₂SO₄, pH 6) saturated with N₂ was used as the electrolyte. The irradiation source was a 300 W Xe lamp (Oriel) with a light intensity of 390 mW cm⁻² and coupled with a 420 nm cutoff filter. The linear sweep voltammetry (LSV) and chronoamperometry were measured via backside illumination of the working electrode (from the FTO side) under chopped irradiation using an Autolab potentiostat (Model PGSTAT302N) and its GPES software. The voltage scan rate for the LSV was 0.01 Vs⁻¹.

4.2.4.2. Electrochemical Impedance Spectroscopy Studies

Electrochemical impedance spectroscopy (EIS) measurements were conducted on Autolab potentiostat (model PGSTAT12) with its frequency response analyzer FRA2 modules, at similar conditions as described above for PEC analyses and 0.5 M Na₂SO₄

as the electrolyte. The Nyquist plots were acquired at 0 V vs. Ag/AgCl with AC amplitude of 5 mV in the frequency range of 100 kHz to 0.01 Hz.

4.2.5. Theoretical Calculations

All calculations were performed using DFT as implemented in the Vienna ab initio simulation package (VASP)²⁵ using the projector augmented-wave approach²⁶ and a plane-wave energy cutoff of 500 eV. The energy and forces are converged with tolerances of 1×10^{-5} eV and 0.01 eV Å⁻¹. To account for weak van der Waals, we employed the semiempirical DFT-D2 correction due to Grimme.²⁷ To build the graphene/BiVO₄ composites, we transformed the graphene cell into a rectangular cell with lattice vectors 2.46 Å x 4.27 Å. A (2 x 6) graphene sheet was matched with a (1 x 5) and (1 x 2) BiVO₄{010} and BiVO₄{110}, respectively. In each case the lattice mismatch was less than 2.5 %. Solvation effects were taken into account by using an implicit solvation model recently implemented model in VASP.²⁸ This was tested against an explicit treatment of water and with BiVO₄ {010} for which previous work²⁹ showed that the ionization potential was 6.22 eV close to our calculated value of 6.13 eV. All energies were aligned relative to the energy far from the slab surface. The DFT calculations were performed by Dr. Hassan A. Tahini and Prof. Sean C. Smith from the Integrated Materials Design Centre.

4.3. Results and Discussion

4.3.1. Physical and Optical Properties of Bare BiVO₄

The BiVO₄ particles obtained using three concentrations of nitric acid (1.00, 0.75, and 0.50 M) as the reaction medium exhibit sharp edges and well-defined crystal facets, as imaged using scanning electron microscopy (SEM) shown in Figure 4.1a-c, respectively.

While having similar decahedron shape in the form of truncated tetragonal bipyramid, there is an apparent reduction in the particle thickness as the acid concentration decreases. The top and bottom flat surfaces of each particle are assigned to be {010} facets and the isosceles trapezoidal sides are characterized as {110} facets (schematically illustrated in the insets in Figure 4.1a-c), as previously indexed in Chapter 3. With these geometrical assignments, the decrease in thickness of the BiVO₄ particles signifies the increase in the exposure extent of {010} surfaces with respect to {110} that is ascertained by measurement of the degree of truncation (represented by B/A, the length parameters as defined in the insets). The B/A values analyzed for samples BiVO₄_1.00M, BiVO₄_0.75M, and BiVO₄_0.50M are correspondingly displayed in Figure 4.1d-f. Evidently, the average B/A value of the BiVO₄ increases as the concentration of nitric acid decreases, confirming the improved growth extent of {010} facets on BiVO₄ using lower acid concentration.

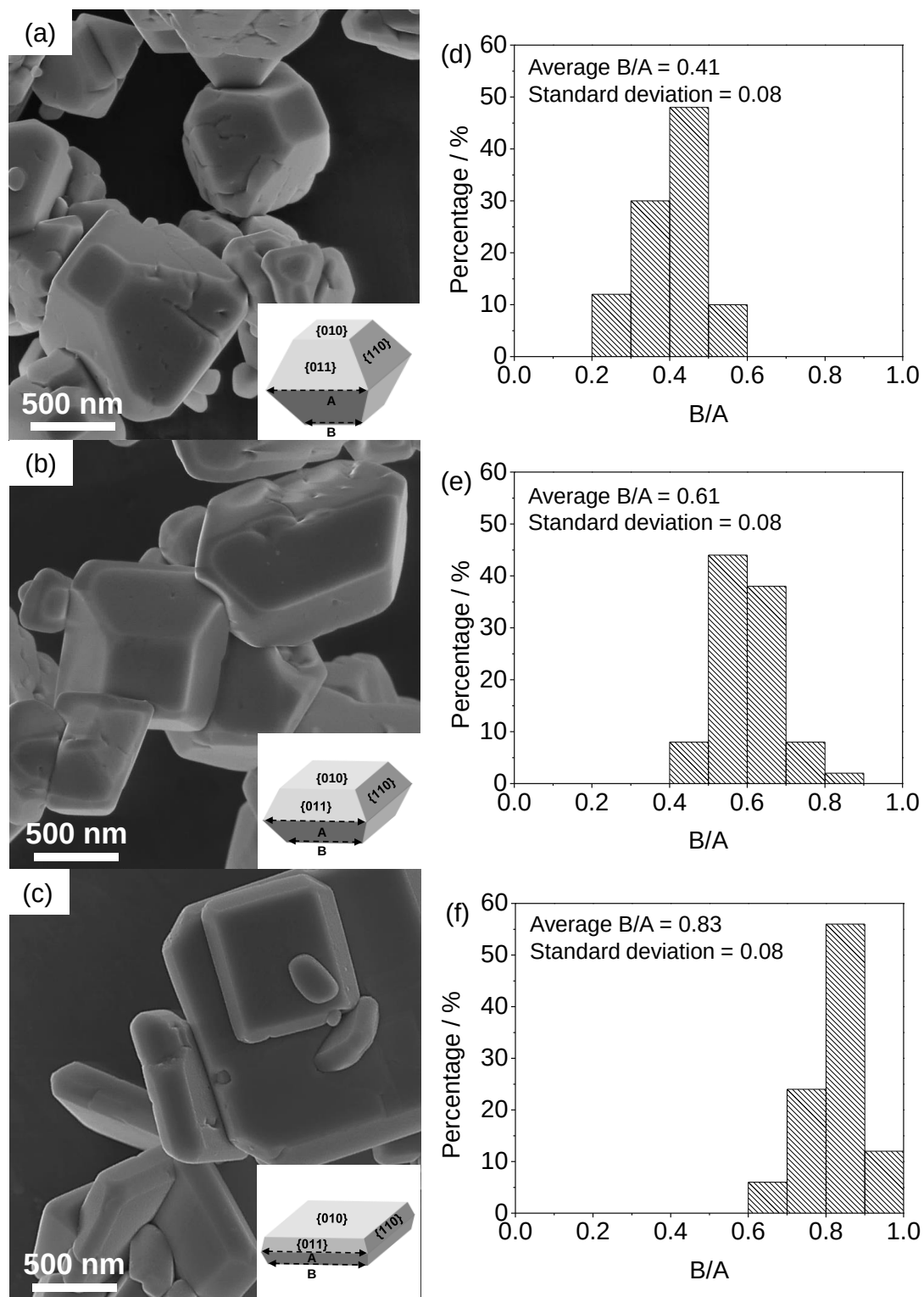


Figure 4.1. Scanning electron microscopy (SEM) micrographs of BiVO₄ prepared using different concentrations of nitric acid as the reaction medium: (a) 1.00 M, (b) 0.75 M, and (c) 0.50 M. The insets present the schematic morphology of each BiVO₄ with the assigned {010} and {110} facets. Histograms (d-f) represent the respective distribution of the degree of truncation (B/A) of the BiVO₄ particles displayed in panels a, b, and c.

Apart from the distinctively different morphologies, other physicochemical and optical properties of these BiVO₄ samples were determined to be comparable. As depicted in Figure 4.2a, all samples exhibit similar X-ray diffraction (XRD) peaks with splitting at around 18.5 °, 35 °, and 46 ° of 2θ, which correspond to the single phase scheelite-monoclinic structure of BiVO₄. Their Raman spectra (Figure 4.2b) display typical vibrational bands of BiVO₄ which are positioned at around 210, 324, 366, 710, and 818 cm⁻¹ ³⁰⁻³¹ without observable shifts, suggesting no change in their local structure. Their BET specific surface areas were also found to be comparable with 2.3 m² g⁻¹ for BiVO₄_1.00M, 2.1 m² g⁻¹ for BiVO₄_0.75M, and 2.1 m² g⁻¹ for BiVO₄_0.50M. On the other hand, the band gap energies of the three BiVO₄ samples were estimated to be similar as 2.5 eV since their optical absorption edges are located closely at wavelength of ca. 500 nm (Figure 4.2c).

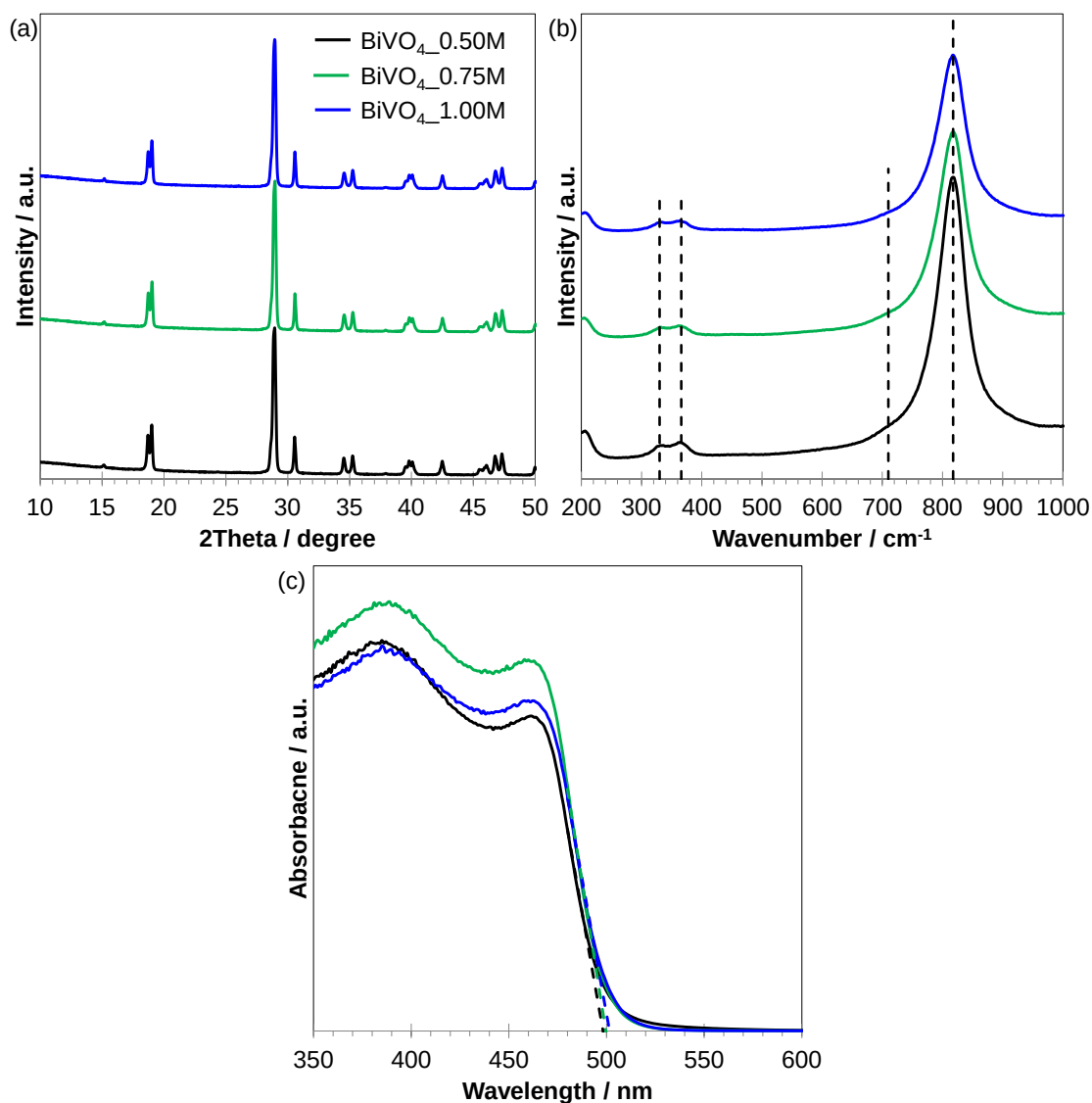


Figure 4.2. (a) XRD diffraction patterns, (b) Raman spectra, and (c) UV-vis diffuse reflectance spectra of the bare BiVO₄s with different relative exposure extents of {010}/{010} facets.

4.3.2. Preparation of RGO-BiVO₄ Composites

The three BiVO₄ samples were separately made into composite with RGO via photocatalytic reduction of GO using BiVO₄, which feasibility was first demonstrated by Ng et al.¹ As GO was introduced into the system containing BiVO₄, attraction of the carboxylic groups on GO towards the surface hydroxyl groups of BiVO₄ intensified, thus enabling attachment of BiVO₄ on GO sheets^{14, 32} and allowing the ensuing electron transfer between the two components during photoreduction process. The higher flat band potential of BiVO₄ at -0.30 V³³ than that of GO around ≈ 0 V vs. NHE at pH 7 is expected to drive efficient electron transfer from the former to the latter. Upon light irradiation, photoinduced electron-hole pairs are generated within BiVO₄ and migrated to the surface. With the presence of ethanol as hole scavenger, excited electrons are injected into GO to partially restore its π - π network to result in the reduction of GO to RGO.

4.3.2.1. Morphological Properties

Figure 4.3a,b displays the representative SEM and TEM images of RGO-BiVO₄ obtained from photoreduction of GO using BiVO₄_0.50M. Clearly, thin and translucent RGO sheets are incorporated into the matrix of BiVO₄ particles. The unique 2D free-standing and highly flexible properties of RGO facilitate adhesion of BiVO₄ particles on both sides of the RGO sheets and allow close interactions of RGO with the different facets exposed on the dual-faceted BiVO₄, namely {010} and {110}. HRTEM image of the contact surface between RGO and BiVO₄, represented by RGO in contact with the (110) plane of BiVO₄ displayed in Figure 4.3c, manifests the tight adhesion of RGO with the exposed facets of BiVO₄. This graphene-scaffold BiVO₄ structure suggests that

effective charge interactions are possible between RGO and the two exposed facets of BiVO_4 .

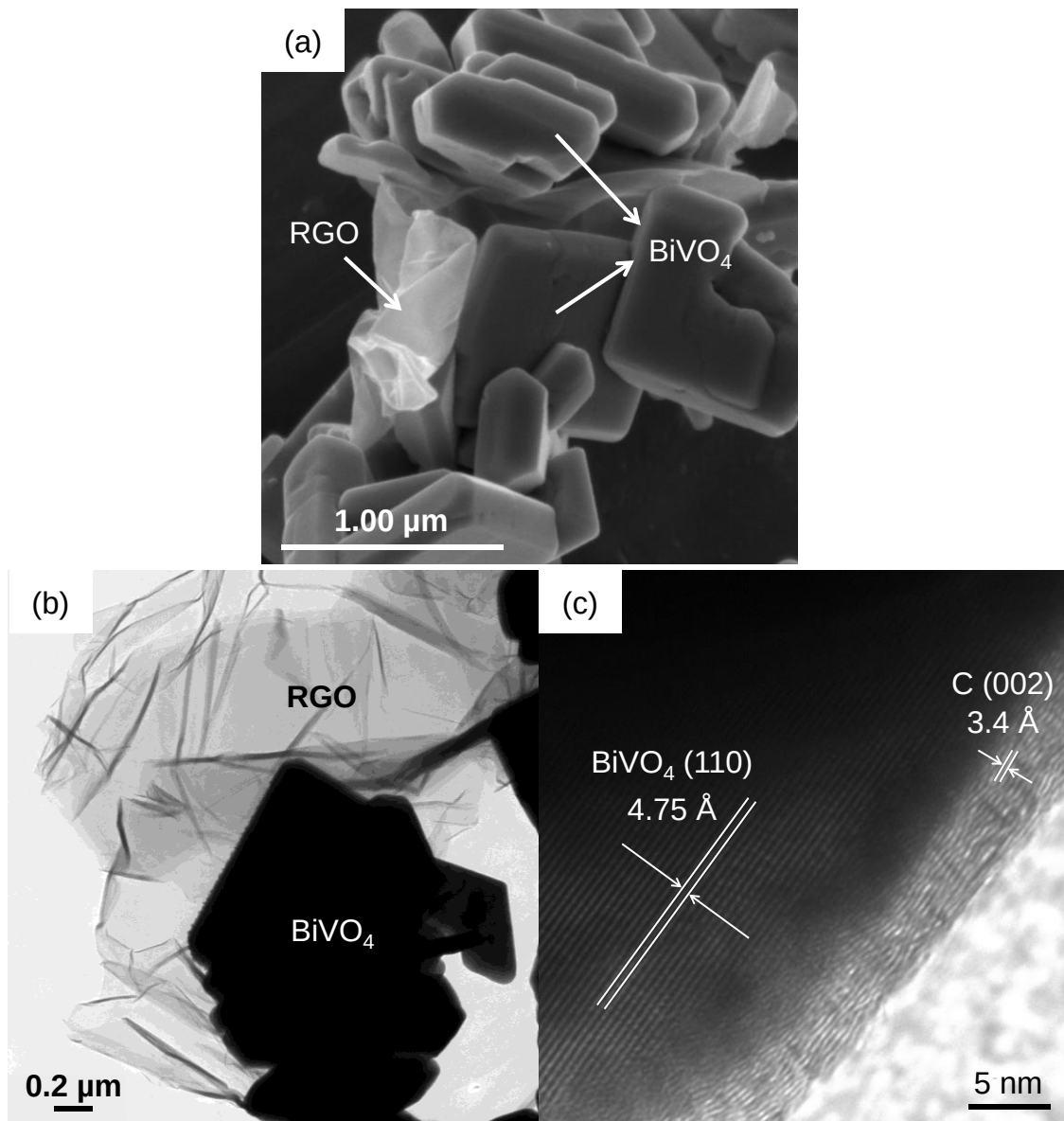


Figure 4.3. (a) SEM and (b) Transmission electron microscopy (TEM) images of RGO- BiVO_4 attained by BiVO_4 -0.50M-induced photoreduction of GO. (c) The corresponding high-resolution TEM (HRTEM) image exhibiting the close contact surface between RGO and BiVO_4 , where the lattice spacings of 3.4 and 4.75 $\text{\AA}$ conform to the (020) plane of carbon and (110) plane of monoclinic BiVO_4 , respectively.

4.3.2.2. Surface Chemical States and Optical Properties

The efficient reduction of GO in the obtained RGO-BiVO₄ composite is verified by the substantial decrease of its C-O bond intensity compared to that of GO, as demonstrated by their respective C1s X-ray photoelectron spectroscopy (XPS) spectrum demonstrated in Figure 4.4a. Generally, each of the C1s spectra of GO and RGO-BiVO₄ shows the presence of non-oxygenated C-C bond at ca. 285 eV and the additional oxygenated-C components at higher binding energies. By comparing the relative area of C-C peak to the total area of all carbon components (C-C and oxygenated-C), the RGO's incorporated with BiVO₄'s of different relative exposure extents of {010}/{110} have reasonably good degree of reduction in the range of 66 – 73 % C-C restoration. Such reduction degree is consistent with that of previously reported GO reduction using other semiconductors such as TiO₂ and WO₃, in addition to that of BiVO₄.^{14, 34} UV-vis diffuse reflectance spectra (Figure 4.4b) indicate that the position of the adsorption edge of RGO-BiVO₄ is similar to that of BiVO₄ at ca. 500 nm. However, the former exhibits stronger absorption in the visible light region at wavelengths longer than 480 nm due to the black color of RGO. This is in agreement with the darker shade of color of RGO-BiVO₄, which appears as dark green in contrast with the vivid yellow of pure BiVO₄.

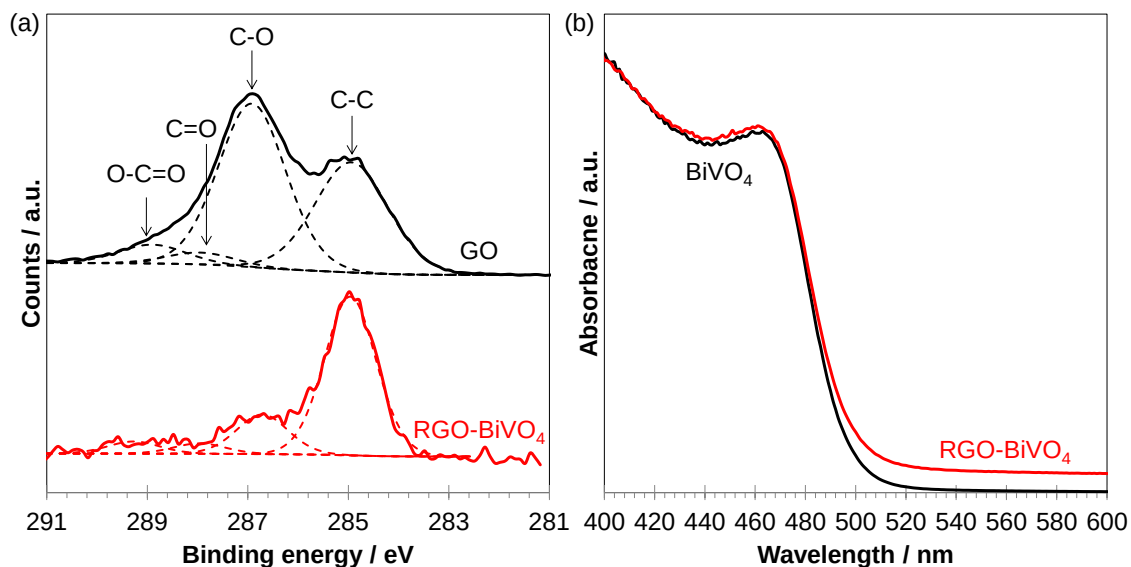


Figure 4.4. (a) C1s XPS spectra of GO and RGO-BiVO₄ and (b) the representative UV-vis diffuse reflectance spectra of BiVO₄ and RGO-BiVO₄ using BiVO₄_0.50M and its corresponding RGO composite.

4.3.2.3. Structural Properties

XRD and Raman spectroscopic analyses were used to further investigate the physicochemical properties of RGO-BiVO₄ in comparison to that of BiVO₄. As displayed in Figure 4.5, the XRD diffraction pattern and Raman bands of RGO-BiVO₄ are akin to that of BiVO₄, in which RGO-related peaks and bands are absent. While a C(002) diffraction peak at region of 25 ° – 26 ° is generally exhibited by the XRD pattern associated with RGO in which the peak position is depending on the RGO's structural quality,³⁵⁻³⁶ only the characteristic diffraction peaks of scheelite-monoclinic BiVO₄ are shown in the diffraction pattern of RGO-BiVO₄ (Figure 4.5a). Despite presence of two distinct D and G bands in the Raman spectrum of GO as illustrated in the inset in Figure 4.5b, these typical peaks of graphene³⁷ also vanished in that of RGO-BiVO₄, which merely depicts BiVO₄-related bands. The untraceable C(002) diffraction peak and D and G Raman bands, albeit successful incorporation of RGO in the sample

as validated by the XPS results discussed earlier, can be attributed to the low loading of RGO (5 wt % with respect to BiVO₄).

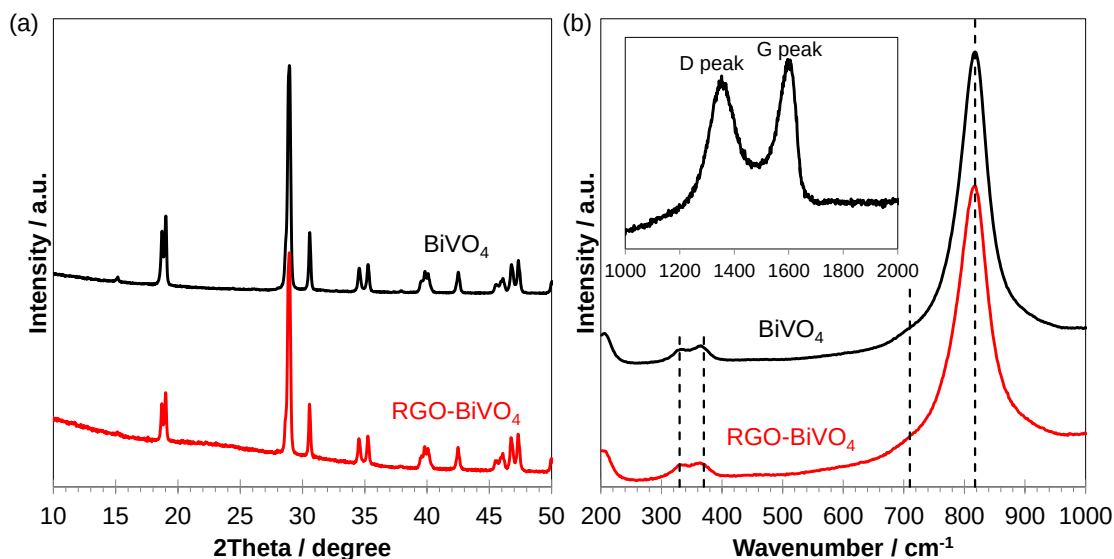


Figure 4.5. (a) XRD diffraction patterns and (b) Raman spectra of BiVO₄ and RGO-BiVO₄. The inset in panel b shows the Raman spectrum of GO.

The UV-vis, XRD, and Raman results collectively suggest that the electronic, crystal phase and local structure of BiVO₄, which can significantly affect its activity,^{30, 38} are maintained in the resultant RGO-BiVO₄ composite after incorporation of RGO. Hence, this allows us to probe the interactions of RGO with BiVO₄ on the basis of physical interfacial charge transfer, particularly the effect of {010}/{110} relative exposure extent of BiVO₄ on its charge interactions with RGO at their interface. For this, PEC method was employed to evaluate the performance of BiVO₄'s with different exposure extents of {010} relative to {110} and to compare with their graphene counterparts. The powder samples (BiVO₄ and RGO-BiVO₄) were therefore made into thin film electrodes via a dropcast method using fluorine-doped tin oxide (FTO) conducting glass as the substrate.

4.3.2.4. Photoelectrochemical Photocurrent

In the PEC system, while holes migrate to the BiVO₄-electrolyte interface to conduct an oxidation reaction at the illuminated photoanode, electrons flow through the external circuit to generate photocurrent. The magnitude of the anodic photocurrent illustrates the rate of electrons transported from BiVO₄ or RGO-BiVO₄ to the FTO collecting electrode, indicative of the photoconversion efficiency and hence the photoactivity of the photocatalyst on the illuminated photoanode. The PEC performance of BiVO₄ has been demonstrated to be restricted by its poor electron transport properties.³⁹ This limiting factor can be overcome by illuminating the BiVO₄/FTO electrode from the FTO side (backside illumination) such that electron-hole pairs are generated closer to the electron collector (FTO substrate), minimizing the travel distance of electrons. Hence, all PEC measurements performed in this work were obtained via backside illumination of the electrode. Figure 4.6a displays the photocurrent-voltage profiles of the representative BiVO₄ and RGO-BiVO₄ during on-off illumination cycle with visible light (of wavelength, $\lambda > 420$ nm). Although both samples portray rapid photoresponse, substantial photocurrent enhancement of RGO-BiVO₄ compared to that of BiVO₄ is readily discernible across the range of biases being applied. Such superior photoresponse of RGO-BiVO₄ was affirmed by the ninefold increase of its photocurrent density relative to its bare BiVO₄ counterpart determined under applied bias of 0 V vs. Ag/AgCl, as presented in Figure 4.6b.

Despite the discernible photocurrent enhancement of BiVO₄ in the presence of RGO, the overall photocurrent of RGO-BiVO₄ is lower than that reported by Ng et al.¹ This could be due to the significantly larger size of the BiVO₄ microcrystals that were employed in this study. Larger particle size deteriorates the charge transport and charge collection

efficiencies of the RGO-BiVO₄ photoanodes used in this study due to poor interparticle contacts between the immobilized BiVO₄ particles and poor BiVO₄/FTO contact, which will be detailed in Chapter 6. Note that the apparent increasing dark current of RGO-BiVO₄ with higher applied bias (i.e., baseline of the LSV curve in Figure 4.6a) is attributed to the specific capacitance of RGO incorporated in the composite. A relatively larger area under the photocurrent-voltage curve has been commonly observed for RGO material, which is associated with the capacitance possessed by RGO.⁴⁰

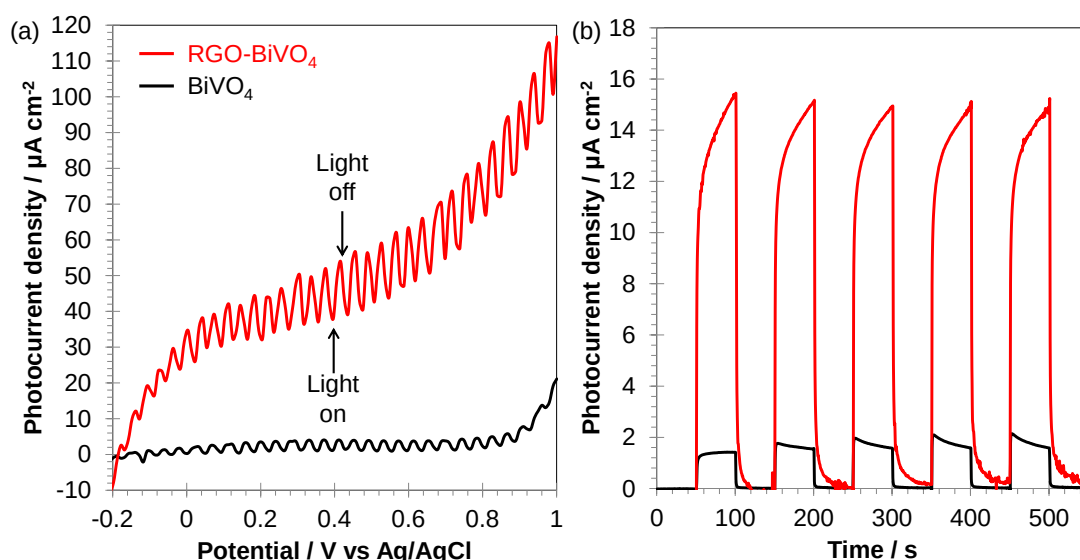


Figure 4.6. (a) Linear sweep voltammetry (LSV) curves under intermittent illumination and (b) chronoamperometry measurements at 0 V vs. Ag/AgCl of a representative BiVO₄ and its corresponding RGO-BiVO₄.

4.3.2.5. Photoluminescence Measurements

The effective improvement in photocurrent generation by RGO-BiVO₄ is ascribed to the ability of RGO to receive and transport electrons away from the excited BiVO₄,¹²⁻¹³ which are otherwise susceptible to recombination with holes. This is corroborated by the perceptible quenching of the band edge emission band of RGO-BiVO₄ at ca. 500 nm

in the steady-state fluorescence spectra (Figure 4.7a) that reflects diminution of electron-hole pair recombination. To delve into the quenching mechanism by RGO, the band edge fluorescence lifetimes for BiVO₄ and RGO-BiVO₄ were determined using time correlated single photon counting (TCSPC) technique. Each time-resolved fluorescence decay curve can be divided into two decay components, in which the fast and the slow components can be related to nonradiative and radiative recombination of electron-hole pairs, respectively.⁴¹ In the absence of RGO, BiVO₄ has a lifetime of 2.93 ns for the fast component (τ_1) and a lifetime of 8.61 ns for the slow component (τ_2), as depicted in Figure 4.7b. Note that these lifetimes decrease in the case of RGO-BiVO₄ (2.02 ns and 6.58 ns for τ_1 and τ_2 , respectively), resulting in the decrease of average lifetime from 8.03 ns for BiVO₄ to 6.05 ns for RGO-BiVO₄. The shorter τ_1 of RGO-BiVO₄ can be ascribed to the efficient transfer of electrons from BiVO₄ to RGO, supporting the beneficial role of RGO in shuttling electrons and suppressing charge recombination in BiVO₄. This electron transfer-mediated lifetime decrease of the fast component in the presence of graphene is consistent with that observed by other research groups.⁴¹⁻⁴²

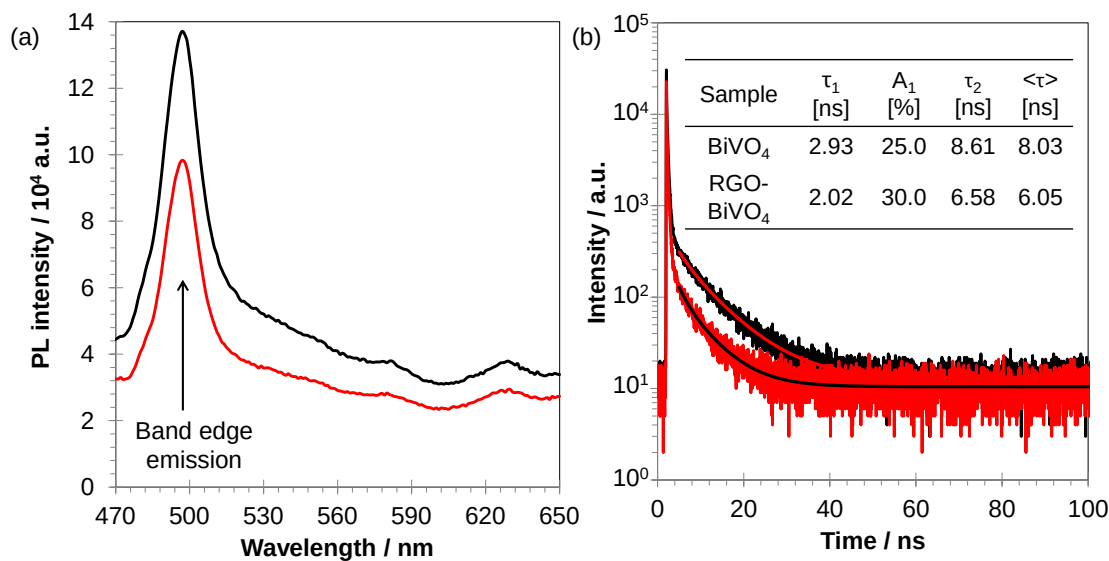


Figure 4.7. (a) Steady-state and (b) time-resolved fluorescence spectra of a representative BiVO₄ and its corresponding RGO-BiVO₄. Inset in panel b shows the parameters of the fitted biexponential functions represented by solid lines.

4.3.3. Effect of BiVO₄ {010}/{110} Relative Exposure Extent on Photoelectrochemical Performance

Comparison of the photoactivity of BiVO₄'s with different growth extents of {010} facets (lower nitric acid concentration produces BiVO₄ particles with higher exposure proportion of {010} facets) and with reference to their corresponding graphene composites, via PEC approach at applied bias of 0 V vs. Ag/AgCl, is plotted in Figure 4.8a. Variation in the relative exposure extent of {010}/{110} facets on BiVO₄ barely affects its photoresponse as demonstrated by the comparable magnitude of photocurrent density amongst all the bare BiVO₄ samples. Conversely, incorporation of RGO into these BiVO₄'s exhibits different degrees of photocurrent enhancement. A correlation between the exposure extent of BiVO₄{010} facets and its photocurrent improvement in the presence of RGO is revealed; the larger the exposed {010} facets on BiVO₄, the greater the extent of photocurrent enhancement after incorporation of RGO. Additionally, a similar correlation also exists in the presence of 0.50 and 0.75 V of

applied biases, as respectively depicted in Figure 4.8b,c. Collation and evaluation of the RGO-induced photocurrent enhancement in the BiVO_4 's (Figure 4.9a) unambiguously show that $\text{BiVO}_4_{0.50\text{M}}$ with the largest exposure extent of {010} facets has the greatest enhancement, followed by $\text{BiVO}_4_{0.75\text{M}}$ and $\text{BiVO}_4_{1.00\text{M}}$, regardless of the magnitude of applied bias.

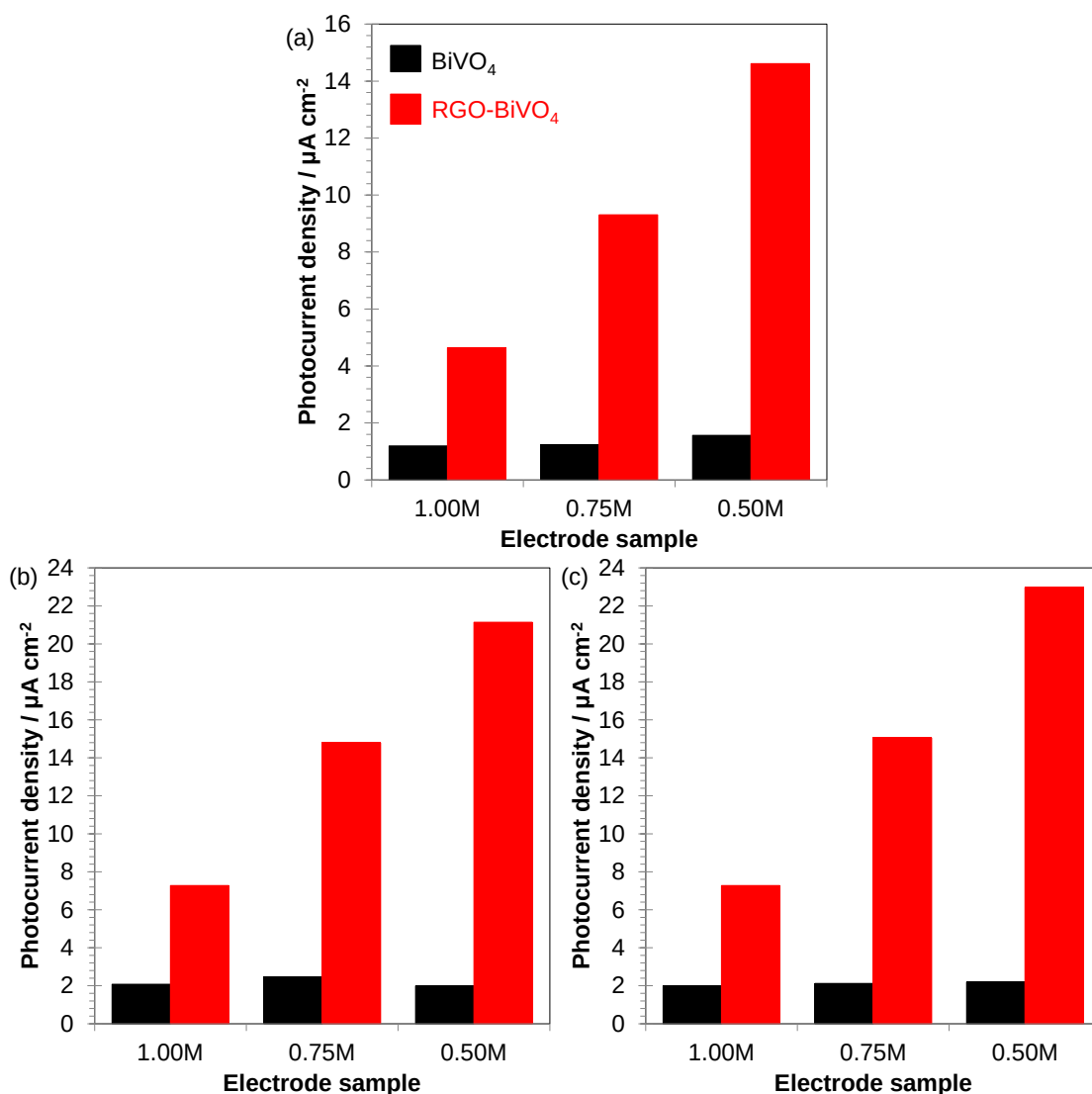


Figure 4.8. Photocurrent generation by the bare BiVO_4 s with different relative exposure extents of {010}/{110} in comparison to their RGO-BiVO_4 composites measured at (a) 0 V, (b) 0.50 V, and (c) 0.75 V vs. Ag/AgCl . Note that the BiVO_4 particle synthesized in lower acid concentration has larger area of {010} facets.

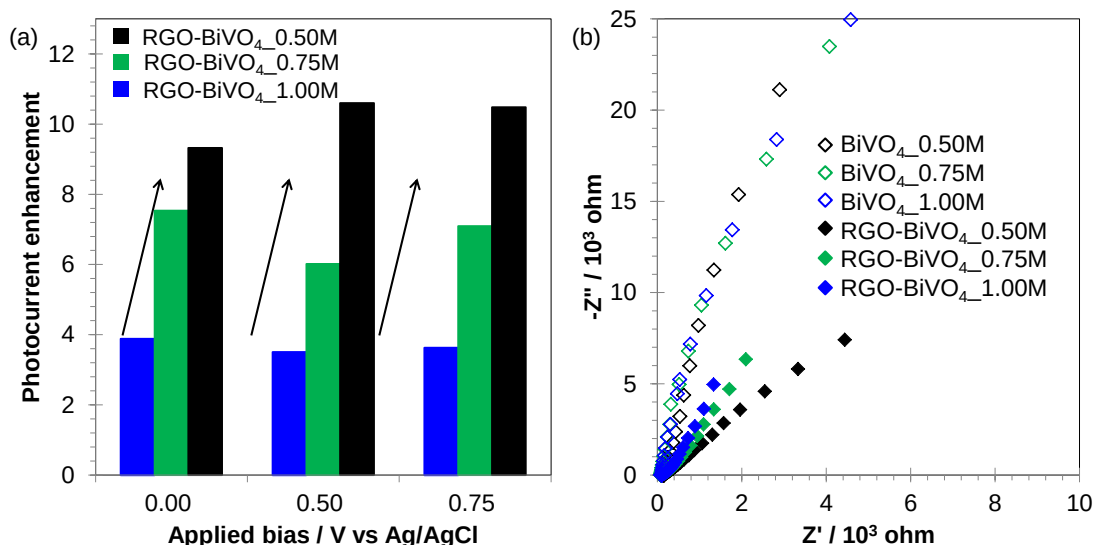


Figure 4.9. (a) Degree of photocurrent enhancement by coupling RGO with the three BiVO_4 samples, determined using three applied biases, namely 0 V, 0.50 V, and 0.75 V vs. Ag/AgCl. (b) Electrochemical impedance spectra of BiVO_4 and RGO- BiVO_4 samples measured at 0 V vs. Ag/AgCl under light condition.

In order to relate PEC performance to charge transfer properties of the photoanodes, electrochemical impedance spectroscopy (EIS) was performed at similar conditions of photocurrent measurement (visible-light-illuminated, 0 V vs. Ag/AgCl) and the results are presented as Nyquist plots in Figure 4.9b. On the one hand, the arcs of the RGO- BiVO_4 composites are markedly smaller than those of bare BiVO_4 's. Given that the arcs in Nyquist plot are associated with charge transfer resistance at the photoelectrode-electrolyte interface,⁴³⁻⁴⁴ the smaller arc radii of the composites suggests that the charge transfer ability of these materials is improved in the presence of RGO, which suppresses charge recombination and renders their enhanced photocurrent densities as opposed to the bare BiVO_4 's. On the other hand, while the arc radii of the bare BiVO_4 's are comparable, the ones exhibited by the RGO- BiVO_4 composites (denoted as RGO-y, where y represents the BiVO_4 sample in which the RGO is incorporated with) follow a decreasing trend of $\text{RGO-BiVO}_4_{1.00\text{M}} > \text{RGO-BiVO}_4_{0.75\text{M}} > \text{RGO-BiVO}_4_{0.50\text{M}}$,

indicating that the charge transfer from RGO-BiVO₄ to FTO substrate becomes easier down the list. This difference in charge transfer ability of the RGO-BiVO₄ composites is in perfect agreement with their activity trend in PEC photocurrent generation, suggesting that different extents of photocurrent enhancement of the composites is originated from their disparity in charge transfer ability. On the basis of intimate interactions between RGO and the {010} and {110} facets of BiVO₄, the well-correlated PEC and EIS results provide a compelling evidence for the constructive effect of having enlarged {010} facets on BiVO₄ to promote charge transfer to the RGO sheets, an electron shuttle.

4.3.4. Density Functional Theory Calculations

Density functional theory was performed to gain insights into the interactions between RGO with the {010} and {110} facets of BiVO₄. For ease of calculation, RGO was assumed as pristine graphene. Figure 4.10a shows the band edges of the BiVO₄{010}, BiVO₄{110} and graphene relative to vacuum before contact. Previous theoretical studies have predicted that it is thermodynamically favorable for an electron to transfer from the {110} facets of BiVO₄ to the {010}.²¹ This is in agreement with our calculations which show that the conduction and valence band edges of the {010} surface are about 0.6 eV lower than that of the {110} surface. The electron effective mass has also been demonstrated to be much lower for the {010} surfaces, implying higher drift velocities of photogenerated electrons on {010} in comparison to on {110}.⁴⁵ In general, the n-type properties of BiVO₄ suggest that its Fermi level (FL) is close to the conduction band edge. The requirement that the FL should be equal across the interface between two materials results in a band bending. From the band edge positions shown in Figure 4.10a, one can estimate the height of the Schottky barrier (ϕ_b)

formed when contact is made, which can be reasonably approximated using equation 4.1:⁴⁶

$$\phi_b = \phi_m - X \quad (4.1)$$

where ϕ_m is the metal (in this case graphene) work function and X is the electron affinity of the semiconductor which is surface dependent. Based on the estimated electron affinity of 4.31 eV for BiVO₄{010} and 3.69 eV for BiVO₄{110}, ϕ_b is 0.09 and 0.71 eV for the graphene/BiVO₄{010} and graphene/BiVO₄{110} interfaces, respectively. The smaller ϕ_b suggests that charge transport from the {010} surface to graphene is easier than from the {110} surface, supporting our experimental observation.

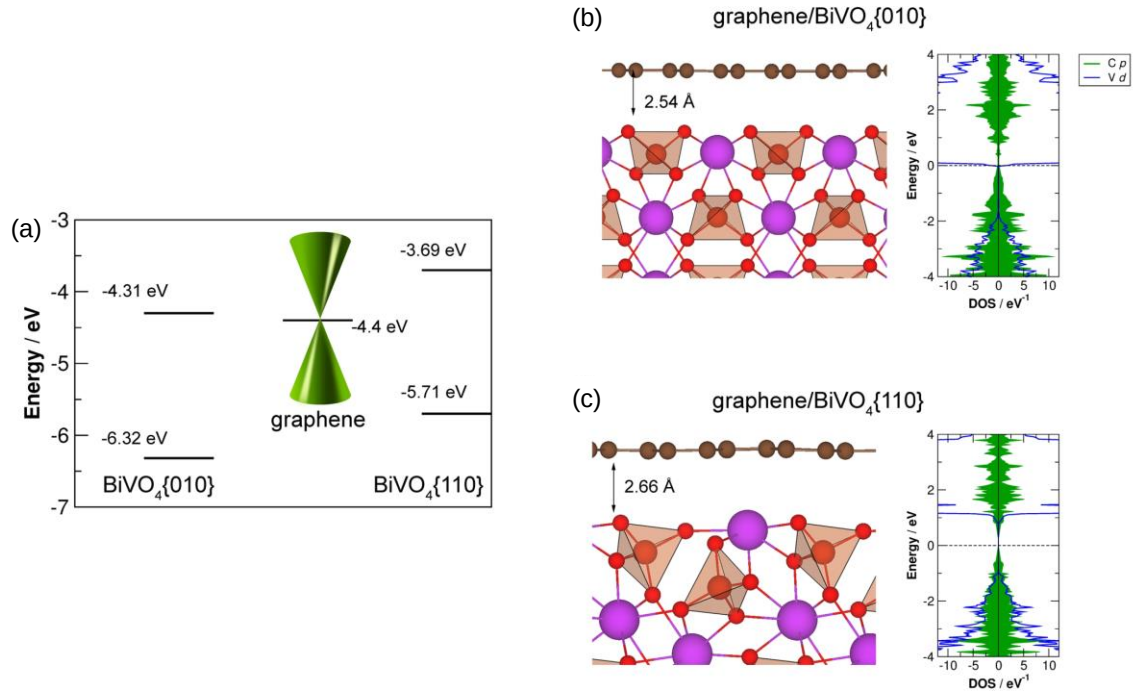


Figure 4.10. (a) The band positions of graphene, {010} and {110} facets of BiVO₄ with respect to vacuum. The small separation in the conduction band minimum (CBM) energies of BiVO₄{010} relative to graphene leads to a small Schottky barrier height. (b) graphene/BiVO₄{010} and (c) graphene/BiVO₄{110} interfaces showing the optimized separations along with the DOS, where the blue lines are the contribution of V d orbitals and the green shaded areas are the contributions of the graphene p orbitals.

The most bound interfaces between graphene/BiVO₄{010} and graphene/BiVO₄{110} are depicted correspondingly in Figure 4.10b,c. Here, the binding energies are calculated as follow

$$E_b = E_{\text{graphene/BiVO}_4} - E_{\text{BiVO}_4} - E_{\text{graphene}} \quad (4.2)$$

Where $E_{\text{graphene/BiVO}_4}$, E_{BiVO_4} , and E_{graphene} are the total energies of the graphene/BiVO₄ composite system, the bare BiVO₄ slab and a graphene sheet, respectively. The binding energies were found to be -2.75 eV for the graphene/BiVO₄{010} interface and -1.96 eV for the graphene/BiVO₄{110} interface. This is also reflected by the shorter surface distance between BiVO₄{010} and graphene as compared to BiVO₄{110} and graphene. Additionally, the density of states (DOS) calculations reveal that the graphene/BiVO₄{010} is metallic. The decomposed DOS (for clarity the Bi and O states as shown in Figure 4.11) shows that states belonging to graphene are responsible for the closure of the gap. On the other hand, the band edge position of {110} facets relative to graphene's FL renders graphene ineffective in completely closing the gap, leading to a gap for the interfacial system of about 0.3 eV.

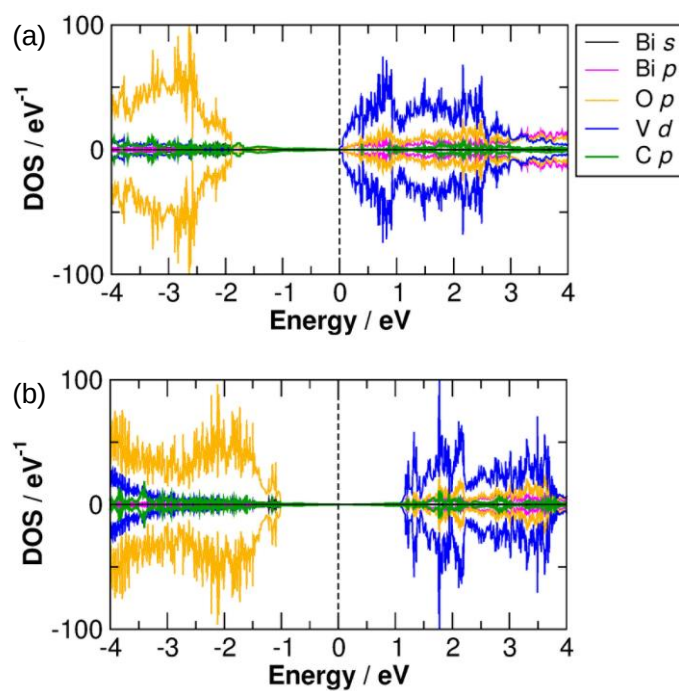


Figure 4.11. Contributions of Bi *s*, Bi *p*, O *p*, V *d*, and C *p* orbitals of the (a) graphene/BiVO₄{010} and (b) graphene/BiVO₄{110} interfaces.

4.4. Summary

Interfacial contact facet of BiVO₄ with RGO was demonstrated to govern the electron transfer ability between the two components. Three dual-faceted BiVO₄ samples with different relative exposure extents of the {010} and {110} facets were separately coupled with RGO via photocatalytic reduction method. The difference in photoactivity of the RGO-BiVO₄ composites was probed using PEC approach. Despite the apparent improvement of photocurrent density magnitude after incorporation of RGO, the enhancement degree was found to correlate with the exposure extent of {010} facets on the dual-faceted BiVO₄. Such a correlation was attributed to the decrease of charge transfer resistance of the RGO-BiVO₄ composite with the presence of larger BiVO₄ {010} surface, as confirmed via EIS measurements. DFT calculations on the electronic properties of the interfaces between graphene and the two facets of BiVO₄ were carried out to support the experimental results. Consistently, the charge transport from BiVO₄ to graphene was calculated to be preferable through the {010} facets than through {110} due to the smaller Schottky barrier, higher binding energy, and metallic characteristic of the graphene/BiVO₄{010} interface.

4.5. References

1. Ng, Y. H.; Iwase, A.; Kudo, A.; Amal, R., Reducing Graphene Oxide on a Visible-Light BiVO₄ Photocatalyst for an Enhanced Photoelectrochemical Water Splitting. *J. Phys. Chem. Lett* **2010**, *1* (17), 2607-2612.
2. Zhang, X.-Y.; Li, H.-P.; Cui, X.-L.; Lin, Y., Graphene/TiO₂ Nanocomposites: Synthesis, Characterization and Application in Hydrogen Evolution from Water Photocatalytic Splitting. *J. Mater. Chem.* **2010**, *20* (14), 2801-2806.
3. Li, N.; Liu, G.; Zhen, C.; Li, F.; Zhang, L.; Cheng, H. M., Battery Performance and Photocatalytic Activity of Mesoporous Anatase TiO₂ Nanospheres/Graphene Composites by Template - Free Self - Assembly. *Adv. Funct. Mater.* **2011**, *21* (9), 1717-1722.
4. Li, Q.; Guo, B.; Yu, J.; Ran, J.; Zhang, B.; Yan, H.; Gong, J. R., Highly Efficient Visible-Light-Driven Photocatalytic Hydrogen Production of CdS-Cluster-Decorated Graphene Nanosheets. *J. Am. Chem. Soc.* **2011**, *133* (28), 10878-10884.
5. Xiang, Q.; Yu, J.; Jaroniec, M., Preparation and Enhanced Visible-Light Photocatalytic H₂-Production Activity of Graphene/C₃N₄ composites. *J. Phys. Chem. C* **2011**, *115* (15), 7355-7363.
6. Zhang, J.; Xiong, Z.; Zhao, X., Graphene–Metal–Oxide Composites for the Degradation of Dyes under Visible Light Irradiation. *J. Mater. Chem.* **2011**, *21* (11), 3634-3640.
7. Zhang, H.; Lv, X.; Li, Y.; Wang, Y.; Li, J., P25-Graphene Composite as a High Performance Photocatalyst. *ACS Nano* **2009**, *4* (1), 380-386.

8. Gao, E.; Wang, W.; Shang, M.; Xu, J., Synthesis and Enhanced Photocatalytic Performance of Graphene-Bi₂WO₆ Composite. *Phys. Chem. Chem. Phys.* **2011**, *13* (7), 2887-2893.
9. Xu, T.; Zhang, L.; Cheng, H.; Zhu, Y., Significantly Enhanced Photocatalytic Performance of ZnO via Graphene Hybridization and the Mechanism Study. *Appl. Catal., B* **2011**, *101* (3), 382-387.
10. Sun, Y.; Wu, Q.; Shi, G., Graphene Based New Energy Materials. *Energy Environ. Sci.* **2011**, *4* (4), 1113-1132.
11. Liu, Q.; Liu, Z.; Zhang, X.; Yang, L.; Zhang, N.; Pan, G.; Yin, S.; Chen, Y.; Wei, J., Polymer Photovoltaic Cells Based on Solution - Processable Graphene and P3HT. *Adv. Funct. Mater.* **2009**, *19* (6), 894-904.
12. Williams, G.; Seger, B.; Kamat, P. V., TiO₂-Graphene Nanocomposites. UV-Assisted Photocatalytic Reduction of Graphene Oxide. *ACS Nano* **2008**, *2* (7), 1487-1491.
13. Lightcap, I. V.; Kosel, T. H.; Kamat, P. V., Anchoring Semiconductor and Metal Nanoparticles on a Two-Dimensional Catalyst Mat. Storing and Shuttling Electrons with Reduced Graphene Oxide. *Nano Lett.* **2010**, *10* (2), 577-583.
14. Bell, N. J.; Ng, Y. H.; Du, A.; Coster, H.; Smith, S. C.; Amal, R., Understanding the Enhancement in Photoelectrochemical Properties of Photocatalytically Prepared TiO₂-Reduced Graphene Oxide Composite. *J. Phys. Chem. C* **2011**, *115* (13), 6004-6009.
15. Xiang, Q.; Yu, J.; Jaroniec, M., Graphene-Based Semiconductor Photocatalysts. *Chem. Soc. Rev.* **2012**, *41* (2), 782-796.

16. Liu, G.; Sun, C.; Yang, H. G.; Smith, S. C.; Wang, L.; Lu, G. Q. M.; Cheng, H.-M., Nanosized Anatase TiO₂ Single Crystals for Enhanced Photocatalytic Activity. *Chem. Commun.* **2010**, 46 (5), 755-757.
17. Iwase, A.; Kudo, A., Photoelectrochemical Water Splitting using Visible-Light-Responsive BiVO₄ Fine Particles Prepared in an Aqueous Acetic Acid Solution. *J. Mater. Chem.* **2010**, 20 (35), 7536-7542.
18. Liu, G.; Jimmy, C. Y.; Lu, G. Q. M.; Cheng, H.-M., Crystal Facet Engineering of Semiconductor Photocatalysts: Motivations, Advances and Unique Properties. *Chem. Commun.* **2011**, 47 (24), 6763-6783.
19. Zhang, L.; Wang, W.; Zhou, L.; Xu, H., Bi₂WO₆ Nano - and Microstructures: Shape Control and Associated Visible - Light - Driven Photocatalytic Activities. *Small* **2007**, 3 (9), 1618-1625.
20. Ohno, T.; Sarukawa, K.; Matsumura, M., Crystal Faces of Rutile and Anatase TiO₂ Particles and Their Roles in Photocatalytic Reactions. *New J. Chem.* **2002**, 26 (9), 1167-1170.
21. Li, R.; Zhang, F.; Wang, D.; Yang, J.; Li, M.; Zhu, J.; Zhou, X.; Han, H.; Li, C., Spatial Separation of Photogenerated Electrons and Holes Among {010} and {110} Crystal Facets of BiVO₄. *Nat. Commun.* **2013**, 4, 1432.
22. Kim, Y.; Shin, D.; Chang, W. J.; Jang, H. L.; Lee, C. W.; Lee, H. E.; Nam, K. T., Hybrid Z - Scheme Using Photosystem I and BiVO₄ for Hydrogen Production. *Adv. Funct. Mater.* **2015**, 25 (16), 2369-2377.
23. Tan, H. L.; Wen, X.; Amal, R.; Ng, Y. H., BiVO₄ {010} and {110} Relative Exposure Extent: Governing Factor of Surface Charge Population and Photocatalytic Activity. *J. Phys. Chem. Lett.* **2016**, 7 (7), 1400-1405.

24. Li, H.; Yu, H.; Quan, X.; Chen, S.; Zhao, H., Improved Photocatalytic Performance of Heterojunction by Controlling the Contact Facet: High Electron Transfer Capacity between TiO₂ and the {110} Facet of BiVO₄ Caused by Suitable Energy Band Alignment. *Adv. Funct. Mater.* **2015**, 25 (20), 3074-3080.
25. Kresse, G.; Furthmüller, J., Efficient Iterative Schemes for Ab Initio Total-Energy Calculations using a Plane-Wave Basis Set. *Phys. Rev. B* **1996**, 54 (16), 11169.
26. Kresse, G.; Joubert, D., From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Phys. Rev. B* **1999**, 59 (3), 1758.
27. Grimme, S., Semiempirical GGA - Type Density Functional Constructed with a Long - Range Dispersion Correction. *J. Comput. Chem.* **2006**, 27 (15), 1787-1799.
28. Mathew, K.; Sundararaman, R.; Letchworth-Weaver, K.; Arias, T.; Hennig, R. G., Implicit Solvation Model for Density-Functional Study of Nanocrystal Surfaces and Reaction Pathways. *J. Chem. Phys.* **2014**, 140 (8), 084106.
29. Crespo-Otero, R.; Walsh, A., Variation in Surface Ionization Potentials of Pristine and Hydrated BiVO₄. *J. Phys. Chem. Lett.* **2015**, 6 (12), 2379-2383.
30. Yu, J.; Kudo, A., Effects of Structural Variation on the Photocatalytic Performance of Hydrothermally Synthesized BiVO₄. *Adv. Funct. Mater.* **2006**, 16 (16), 2163-2169.
31. Kho, Y. K.; Teoh, W. Y.; Iwase, A.; Mädler, L.; Kudo, A.; Amal, R., Flame Preparation of Visible-Light-Responsive BiVO₄ Oxygen Evolution Photocatalysts with Subsequent Activation via Aqueous Route. *ACS Appl. Mater. Interfaces* **2011**, 3 (6), 1997-2004.

32. Meyer, T. J.; Meyer, G. J.; Pfennig, B. W.; Schoonover, J. R.; Timpson, C. J.; Wall, J. F.; Kobusch, C.; Chen, X.; Peek, B. M., Molecular-Level Electron Transfer and Excited State Assemblies on Surfaces of Metal Oxides and Glass. *Inorg. Chem.* **1994**, 33 (18), 3952-3964.
33. Long, M.; Cai, W.; Kisch, H., Visible Light Induced Photoelectrochemical Properties of n-BiVO₄ and n-BiVO₄/p-Co₃O₄. *J. Phys. Chem. C* **2008**, 112 (2), 548-554.
34. Ng, Y. H.; Iwase, A.; Bell, N. J.; Kudo, A.; Amal, R., Semiconductor/Reduced Graphene Oxide Nanocomposites Derived from Photocatalytic Reactions. *Catal. Today* **2011**, 164 (1), 353-357.
35. Moon, I. K.; Lee, J.; Ruoff, R. S.; Lee, H., Reduced Graphene Oxide by Chemical Graphitization. *Nat. Commun.* **2010**, 1, 73.
36. Fan, W.; Lai, Q.; Zhang, Q.; Wang, Y., Nanocomposites of TiO₂ and Reduced Graphene Oxide as Efficient Photocatalysts for Hydrogen Evolution. *J. Phys. Chem. C* **2011**, 115 (21), 10694-10701.
37. Singh, V.; Joung, D.; Zhai, L.; Das, S.; Khondaker, S. I.; Seal, S., Graphene Based Materials: Past, Present and Future. *Prog. Mater Sci.* **2011**, 56 (8), 1178-1271.
38. Tokunaga, S.; Kato, H.; Kudo, A., Selective Preparation of Monoclinic and Tetragonal BiVO₄ with Scheelite Structure and Their Photocatalytic Properties. *Chem. Mater.* **2001**, 13 (12), 4624-4628.
39. Liang, Y.; Tsubota, T.; Mooij, L. P.; van de Krol, R., Highly Improved Quantum Efficiencies for Thin Film BiVO₄ Photoanodes. *J. Phys. Chem. C* **2011**, 115 (35), 17594-17598.

40. Muthoosamy, K.; Bai, R. G.; Abubakar, I. B.; Sudheer, S. M.; Lim, H. N.; Loh, H.-S.; Huang, N. M.; Chia, C. H.; Manickam, S., Exceedingly Biocompatible and Thin-Layered Reduced Graphene Oxide Nanosheets using an Eco-Friendly Mushroom Extract Strategy. *International journal of nanomedicine* **2015**, *10*, 1505.
41. Yu, P.; Wen, X.; Toh, Y.-R.; Lee, Y.-C.; Huang, K.-Y.; Huang, S.; Shrestha, S.; Conibeer, G.; Tang, J., Efficient Electron Transfer in Carbon Nanodot–Graphene Oxide Nanocomposites. *J. Mater. Chem. C* **2014**, *2* (16), 2894-2901.
42. Williams, G.; Kamat, P. V., Graphene–Semiconductor Nanocomposites: Excited-State Interactions between ZnO Nanoparticles and Graphene Oxide. *Langmuir* **2009**, *25* (24), 13869-13873.
43. Jo, W. J.; Jang, J.-W.; Kong, K.-j.; Kang, H. J.; Kim, J. Y.; Jun, H.; Parmar, K. P. S.; Lee, J. S., Phosphate Doping into Monoclinic BiVO₄ for Enhanced Photoelectrochemical Water Oxidation Activity. *Angew. Chem.* **2012**, *124* (13), 3201-3205.
44. Jo, W. J.; Jang, J. W.; Kong, K. j.; Kang, H. J.; Kim, J. Y.; Jun, H.; Parmar, K.; Lee, J. S., Phosphate doping into monoclinic BiVO₄ for enhanced photoelectrochemical water oxidation activity. *Angew. Chem. Int. Ed.* **2012**, *51* (13), 3147-3151.
45. Yang, J.; Wang, D.; Zhou, X.; Li, C., A Theoretical Study on the Mechanism of Photocatalytic Oxygen Evolution on BiVO₄ in Aqueous Solution. *Chem. Eur. J.* **2013**, *19* (4), 1320-1326.
46. Linsebigler, A. L.; Lu, G.; Yates, J. T., Photocatalysis on TiO₂ Surfaces: Principles, Mechanisms, and Selected Results. *Chem. Rev.* **1995**, *95* (3), 735-758.

Chapter 5

Enhancing the Photoactivity of Faceted BiVO₄ via Annealing in Oxygen-Deficient Condition

5.1. Introduction

Earlier studies on thermal annealing have manifested the treatment as a facile route to tailor the grain size, phase composition, and morphology of metal oxide photocatalysts. Provision of thermal energy promotes crystal grain growth for improved crystallinity, thus reducing the number of recombination centers to result in better charge separation.¹⁻³ The temperature dependence of phase transformation processes also allows such heat treatment to facilitate the formation of the more thermodynamically stable photocatalyst.⁴⁻⁶ Furthermore, the lowering of surface free energy in response to heat treatment can also instigate morphological changes in terms of particle size and shape.^{2-3, 7} Alteration of these physicochemical properties affects the charge generation and the kinetic behaviors (including charge separation and transport) of the photoinduced electron-hole pairs, rendering thermal annealing a promising method to improve the activity of various photocatalysts.

In addition to the above-mentioned variation in properties, more recent studies on thermal annealing revealed that the environment in which the treatment occurs has an impact on the defect states of the treated metal oxides.⁸⁻⁹ Generally, annealing atmospheres can be classified into two categories: oxygen-rich and oxygen-deficient.

The typical examples of the former are oxygen (O₂) and air atmospheres, whereas the latter includes nitrogen (N₂), hydrogen (H₂), and argon (Ar) gases. Annealing of metal oxide in oxygen-rich atmosphere was demonstrated to behave differently from that in oxygen-deficient atmosphere: oxygen-rich suppresses oxygen vacancy formation, while oxygen-deficient favors it. Mtangi et al. showed that subjection of ZnO to H₂ and Ar annealing introduced a new defect (possibly oxygen vacancy), which on the other hand was absent after O₂ treatment.⁹ Likewise, Yamada et al. suggested that the oxygen vacancies in nitrogen-doped TiO₂ were increased via N₂ treatment, but decreased after air treatment.¹⁰ While oxygen vacancies are the most prevalent surface structural defects of an oxide material, they are known as the shallow donors in metal oxide photocatalysts.¹¹ Augmentation of oxygen vacancies is therefore beneficial for improving donor densities and facilitating charge transport to enhance the photoactivity of metal oxide materials. Formation of oxygen vacancies has also been claimed to introduce subgap states to extend the light absorption ability of various metal oxides.¹²⁻

14

H₂ annealing or hydrogenation has been utilized as a general strategy to introduce oxygen vacancies in several metal oxides such as ZnO, TiO₂ and WO₃, resulting in significantly enhanced photoelectrochemical (PEC) performance.¹¹ Despite being simple and effective, extra care has to be exercised during its experimental setup as H₂ gas is hazardous. The strong reducing ability of H₂ may also result in undesirable reduction effects. For example, hydrogenation of TiO₂/FTO (fluorine-doped tin oxide) photoelectrode at high temperatures (> 450 °C) was reported to cause damage to the FTO conducting layer due to SnO₂ reduction to Sn metal.¹⁵ This thus restricts the hydrogenation temperature, which then limits the extent of improvement attainable for

the physicochemical properties of a material. Considering these issues, annealing treatment in alternative oxygen-deficient conditions (e.g., N₂ and Ar gases) can be a safer option for controlled generation of oxygen vacancies in metal oxides.

Crystal-facet-engineered BiVO₄ with exposed {010} and {110} facets have been discovered by Li et al. to assist in charge separation of the material.¹⁶ Manipulation of the relative exposure extent of the two facets were found to affect the surface charge population and photoactivity of bare BiVO₄ as well as the interfacial charge interactions between BiVO₄ and graphene, as respectively reported in Chapter 3 and 4. However, such crystal facet engineering approach does not modify the optical and electronic properties of BiVO₄ that can fundamentally enhance its photoactivity. On the contrary, annealing in oxygen-deficient atmospheres such as H₂^{14, 17} and N₂¹³ was shown to be effective in reducing the band gap and increasing the donor density of BiVO₄ via introduction of oxygen vacancies as well as hydrogen impurities in the former and N-doping in the latter. These variations in properties were demonstrated to improve photon absorption and charge transportation for enhanced PEC performance of BiVO₄.

To the best of our knowledge, there is yet any studies investigating the influences of annealing treatment in oxygen-deficient conditions (particularly Ar treatment) on the physicochemical and electronic properties of faceted BiVO₄. Better understanding of the effects can help to further optimize the photoactivity of faceted BiVO₄, which has been demonstrated to possess better charge separation. In this chapter, Ar treatment is elucidated to substantially affect water oxidation activities (both powder suspension (PS) and PEC systems) of dual-faceted BiVO₄, which is highly dependent on the annealing temperature in the range of 300 to 700 °C. This is attributed to the variation in

crystallinity, local structure distortion, optical and electronic properties, and morphology of the BiVO₄ upon heat treatment.

5.2. Experimental

5.2.1. Synthesis of BiVO₄

For this chapter of work, BiVO₄_1.00M as described in Chapter 3 was used. For annealing treatment, the BiVO₄ powder was heated at different temperatures (300, 500, and 700 °C) for 2 h in a tube furnace equipped with continuous flow of Ar gas. Subsequently, the sample was allowed to cool under Ar flow.

5.2.2. Photocatalytic O₂ Evolution

Photocatalytic O₂ evolution was performed in a closed gas circulation system.¹⁸ 300 mg of BiVO₄ powder was dispersed in 150 mL of aqueous 0.05 M AgNO₃ solution (pH 4.5) in a top-irradiation cell with a Pyrex window. Prior to irradiation, the suspension was evacuated to ~ 2 kPa and refilled with Ar. This process was repeated at least five times to remove dissolved gases. For visible light illumination, a 300 W Xe lamp (Oriel) coupled with a 420 nm cutoff filter was used. The light intensity at the flask was 389 mW cm⁻². The oxygen gas evolved during light illumination was analyzed by an online gas chromatograph (Shimadzu GC-8A, TCD, Ar carrier gas).

5.2.3. Photoelectrochemical Measurements

The BiVO₄ powder samples were first made into thin-film electrodes by dropcast method. An electrode was prepared by depositing 6 mL of 1 mg cm⁻³ BiVO₄/ethanol suspension onto 2 cm x 1.5 cm area of FTO conducting substrate. Thereafter, the electrodes were heated in an oven at 150 °C for 2 h. Chronoamperometry measurements

were carried out as described in Chapter 4 with a constant applied potential of 0 V vs. Ag/AgCl.

5.2.4. Facet-Selective Photodepositions of Pt/MnO_x

The facet-selective photodepositions of Pt/MnO_x were done via two approaches: (a) single reduction of PtCl₆²⁻ and (b) simultaneous reduction of PtCl₆²⁻ and oxidation of Mn²⁺. In case (a), 100 mg of BiVO₄ powder was dispersed in 100 mL of aqueous solution containing predetermined amount of chloroplatinic acid (H₂PtCl₆; 2 wt% Pt with respect to BiVO₄). The suspension was irradiated using visible light for 5 h under continuous stirring and deaeration using Ar gas. The product was retrieved by suction filtration, washed with distilled water and dried at 60 °C. Same steps were repeated for case (b) by using an aqueous solution containing both H₂PtCl₆ and manganese (II) nitrate tetrahydrate (Mn(NO₃)₂•4H₂O) with calculated amounts of 2 wt% Pt and 0.5 wt% Mn with respect to BiVO₄. Loadings of Pt and Mn were thereafter determined using inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis, whereby the sample was digested using aqua regia.

5.2.5. Material Characterization

X-ray diffraction (XRD), UV-vis, and Brunauer-Emmett-Teller (BET) surface area analyses were performed as described in Chapter 3, whereas Raman and X-ray photoelectron spectroscopy (XPS) spectra were measured as done in Chapter 4. The crystallite size was estimated from the Scherrer equation using the full width at half-maximum height of the XRD peak at $2\theta = 30.6^\circ$.

Scanning electron microscopy (SEM) images were obtained on a FEI Nova NanoSEM 450 FE-SEM microscope with an operating voltage at 5 kV.

Electron paramagnetic resonance (EPR) measurements were carried out on Bruker EMX-plus operating in the X-band (9.52 GHz) with a microwave power of 2 mW.

5.2.6. Surface Photovoltage Spectroscopy

The BiVO₄ powder samples were first dropcast onto Au substrates to make films. Au substrates were cleaned by sonicating in ethanol, then hydrogen peroxide and potassium hydroxide, and then water for 10 minutes each. BiVO₄ suspensions with concentrations of 5 mg BiVO₄/1 mL water were sonicated for 15 minutes and then 0.05 mL of a suspension was dropcast onto the Au substrate covering a 0.5 cm x 0.5 cm square (the area was controlled with polymer tape). Films were left to dry at room temperature before being heated in an oven at 60 °C for 1 h. Before SPS was performed on the films, each film was treated with a drop of methanol and left to dry at room temperature. All SPS measurements were performed using a gold mesh Kelvin probe (3 mm diameter, Delta PHI Besocke) as the reference mounted inside a home-built vacuum chamber (10⁻⁴ mbar) by a Pfeiffer HiCube 80 Eco turbo pump station. A sample placed in the chamber was illuminated with monochromatic light from a 150 W Xe lamp filtered through an Oriel Cornerstone 130 monochromator (1-10 mW cm⁻²). The measured CPD spectra were corrected for signal drift due to variations in vacuum conditions during the measurements by subtracting a drift background from the raw data. This resulted in the reported CPD values being referenced against the dark CPD voltage. All SPS measurements were taken under vacuum with a scan range of 1 eV to 5 eV. The SPS measurements were performed by Ms. Alexandra T. De Denko and Prof. Frank E. Osterloh from the Department of Chemistry at University of California, United States.

5.3. Results and Discussion

5.3.1. Photocatalytic O₂ Evolution and Photoelectrochemical Photocurrent

Dual-faceted BiVO₄ with dominating oxidation functional {110} facets was synthesized using solid-liquid state reaction described in Chapter 3 with 1.00M of HNO₃ solution and annealed under Ar atmosphere at different temperatures, namely, 300, 500, and 700 °C. Herein, the treated BiVO₄ samples are denoted as ArT, where T represents the annealing temperature. The effect of Ar treatment on the photoactivity of BiVO₄ was determined using the water oxidation reaction via two approaches: PS and PEC method. In the PS system, BiVO₄ powder was suspended in an aqueous silver nitrate (AgNO₃) solution in which the O₂ gas evolved during visible light ($\lambda > 420$ nm) illumination was monitored. Evidently, Ar treatment affects the photocatalytic water oxidation activity of BiVO₄, as depicted in Figure 5.1a. While annealing at a moderately low temperature of 300 °C barely altered the water oxidation photoactivity of BiVO₄ as compared to the as-synthesized (untreated) BiVO₄, the water oxidation rate was greatly improved for the BiVO₄ annealed at 500 °C, but considerably impaired when the annealing temperature was further increased to 700 °C. In contrast to other samples that showed ongoing O₂ gas evolution throughout 4 h illumination, the amount of O₂ gas generated by Ar700 sample plateaued after 1 h of illumination.

For the PEC system, the BiVO₄ powder samples were made into electrodes via dropcast method using FTO as the substrates. Upon light irradiation on the BiVO₄ photoanode, concurrent with hole-mediated water oxidation reaction on the surface of the photoanode, electrons are drawn off as current through the external circuit to the counter electrode. Comparison of the photocurrent magnitude is thus another technique to evaluate the BiVO₄'s photoactivity in response to the annealing treatment under Ar

environment at different temperatures. Figure 5.1b compares the anodic photocurrent densities of the untreated BiVO₄ with the Ar-treated samples, measured at an applied potential of 0 V vs. Ag/AgCl at pH 6 under visible light ($\lambda > 420$ nm) irradiation from the backside. Interestingly, the BiVO₄ samples exhibit similar behavior in PEC photocurrent generation with that of PS water oxidation activity trend, that is Ar700 < untreated $\approx$ Ar300 < Ar500.

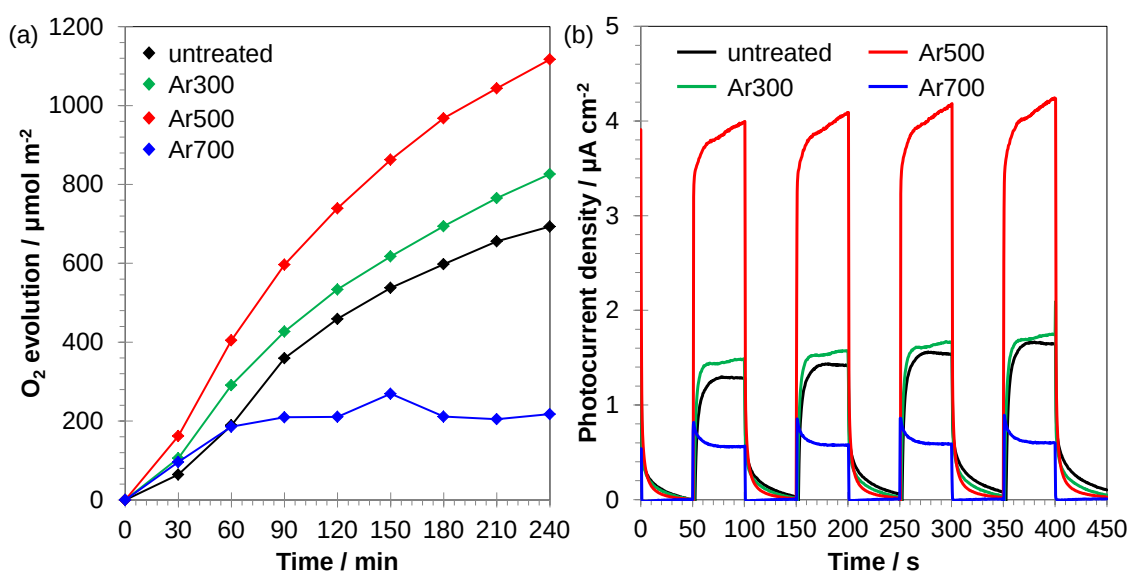


Figure 5.1. (a) Photocatalytic O₂ evolution normalized with respect to BiVO₄ surface area and (b) PEC photocurrent generation from BiVO₄ samples annealed at 300, 500, and 700 °C under Ar atmosphere in comparison to the as-synthesized (untreated) sample.

5.3.2. Structural, Physical, and Optical Properties at Different Annealing Temperatures

To understand the interplay between Ar annealing treatment and the structural, physical, and optical properties of BiVO₄, X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) surface area, Raman, and UV-vis diffuse reflectance measurements were carried out for each BiVO₄ sample, as delineated below. XRD patterns in Figure 5.2a show that the single-phase scheelite-monoclinic structure of the as-synthesized BiVO₄ was

preserved after Ar annealing treatment at different temperatures in the range of 300 – 700 °C. Crystallite size (Table 5.1) estimation using the Scherrer equation indicates the BiVO₄ crystals enlarge with the increase of annealing temperature, particularly for those with relatively higher temperatures of 500 and 700 °C. Consistently, BET measurements also show a gradual decrease of the specific surface area of the treated BiVO₄ samples with increasing annealing temperature, suggesting an increase of particle size upon heating. In particular, the specific surface area is halved from 2.3 m² g⁻¹ for the untreated BiVO₄ to 1.1 m² g⁻¹ for Ar700 (Table 5.1). The increase of crystallite size that is indicative of improved crystallinity has been commonly reported for thermal treatment of oxide semiconductors, be it in air or oxygen-deficient ambient.^{1, 19-21} Such enhanced crystallinity ensuing from Ar treatment is supported by the substantially narrower Raman peaks of the Ar-treated BiVO₄ samples compared to the untreated BiVO₄,^{17, 22} as displayed in Figure 5.2b. In fact, the peak width gradually decreases as the annealing temperature increases.

The Raman spectra of all samples exhibit the characteristic vibrational bands of BiVO₄.²³ Specifically, the 324 and 366 cm⁻¹ bands are related to the deformation modes of VO₄³⁻ tetrahedron, whereas the bands at 710 and 818 cm⁻¹ correspond to the respective asymmetric and symmetric stretching modes of V-O bond.^{22, 24} Raman spectroscopy has been demonstrated as a useful technique that is sensitive to the variation in the local structure of BiVO₄.^{18, 25} For this, Raman analysis was performed and confirmed using more than one arbitrarily chosen location on each of the BiVO₄ powder samples. Enlarged view of the dominant 818 cm⁻¹ band (inset in Figure 5.2b) shows that it is shifted to higher frequencies with greater annealing temperatures, suggesting the decrease of V-O bond length according to the empirical correlation

between Raman stretching frequencies and V-O bond lengths.²⁶⁻²⁷ The position of the dominant Raman band and the corresponding V-O bond length for each sample are listed in Table 5.1. Owing to the Bi³⁺ electron lone-pair-induced distortion of the VO₄³⁻ tetrahedron in monoclinic BiVO₄, shorter V-O bond length infers greater lone-pair distortion around the Bi³⁺ cation, thus leading to greater overlap between the Bi 6s and O 2p orbitals at the valence band. Such greater orbital overlap has been reported to prompt enhanced photogenerated hole migration to the surface of BiVO₄ to conduct water oxidation reaction.²⁵

The variation in BiVO₄'s local structure distortion (i.e., degree of orbital overlap) by Ar annealing treatment is reinforced by the change in its optical properties as reflected in the UV-vis diffuse reflectance spectra (Figure 5.2c). Although all samples display optical absorption in the visible light region, the absorption edges of the Ar-treated samples are red-shifted with respect to that of the untreated BiVO₄, as most significantly evinced by Ar700. Band gap energy estimation from the absorption edges indicates the band gap of BiVO₄ decreases as the annealing temperature increases (Table 5.1).

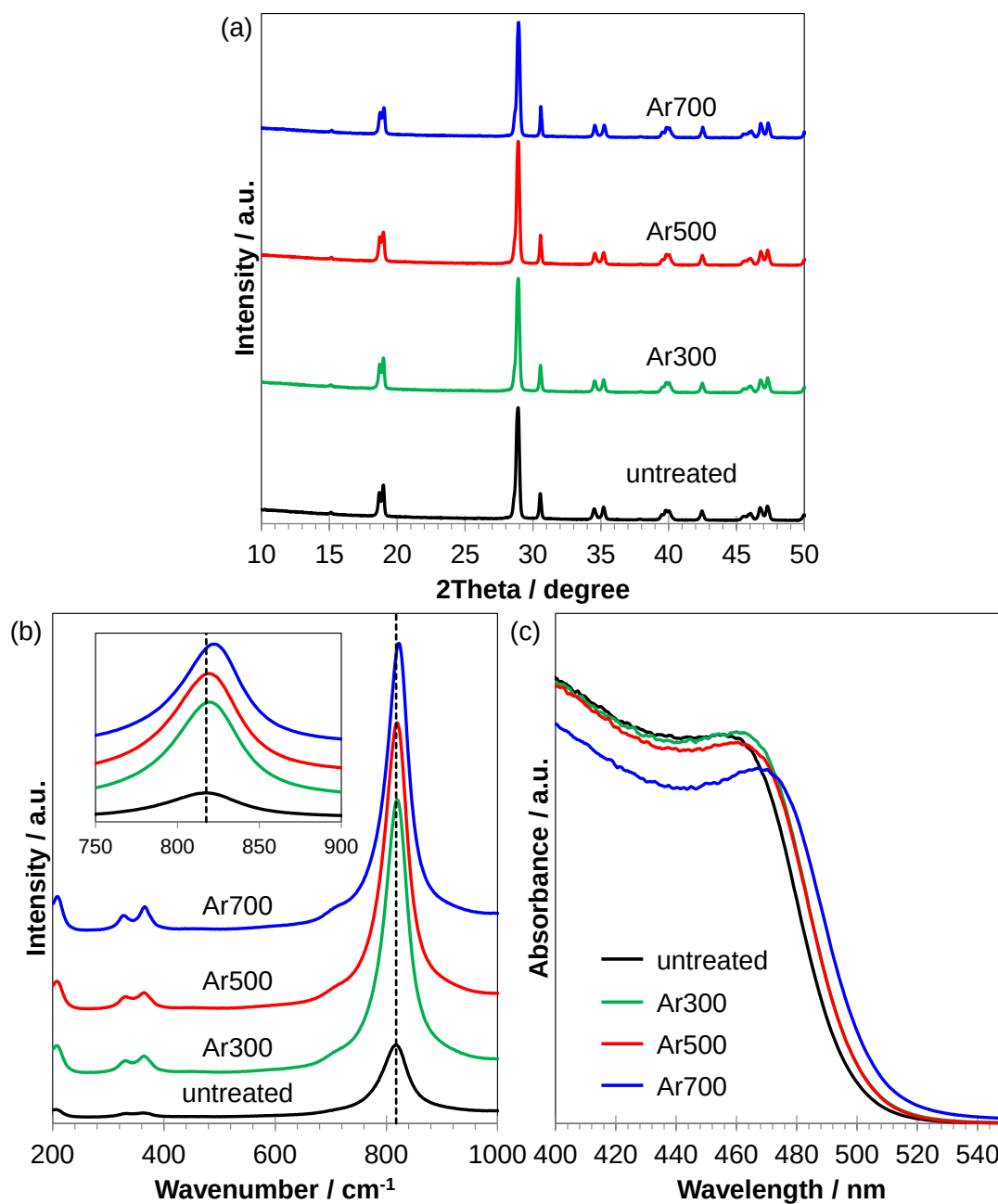


Figure 5.2. (a) XRD diffraction peaks, (b) Raman, and (c) UV-vis spectra of BiVO_4 before and after Ar annealing treatment at 300, 500, and 700 °C.

Table 5.1. Effects of Ar annealing treatment on the crystallite size, specific surface area, local structure, and band gap energy of BiVO₄.

Sample	Crystallite size [nm]	Specific surface area [m ² g ⁻¹]	Raman band [cm ⁻¹]	V-O bond length ^a [Å]	Band gap [eV]
untreated	81	2.3	818	1.701	2.49
Ar300	85	2.1	819	1.700	2.47
Ar500	112	1.9	819	1.700	2.47
Ar700	272	1.1	823	1.698	2.44

$$^a)v[\text{cm}^{-1}] = 21349 \exp(-1.9176R[\text{Å}]).^{26-27}$$

5.3.3. Surface Photovoltage Spectroscopy

In order to probe the photochemical charge separation in as-synthesized and Ar-annealed BiVO₄ samples, surface photovoltage spectroscopy (SPS) measurements were conducted on thin films of the particles on a gold substrate. SPS sensitively measures photochemical charge transport and detects interfacial trap sites²⁸⁻²⁹ and defect states.³⁰⁻³¹ This is achieved by following the light-induced change in the contact potential difference (ΔCPD vs. gold (Au) reference) of the BiVO₄ films as a function of the illumination energy, using a Kelvin probe. Measurements were conducted in vacuum after wetting the films with a drop of methanol. Methanol acts as a sacrificial electron donor and improves the photovoltage signal from BiVO₄ by reacting with the photoholes.³²

The SPS spectrum of the untreated BiVO₄ is shown in Figure 5.3a. A negative ΔCPD signal develops at photon energies near the optical band gap of the material and reaches a local maximum of -0.12 V at 3.0 eV. The spectrum resembles those previously measured for BiVO₄ nanoparticles.³³ Similarly, the photovoltage signal in Figure 5.3a can be attributed to the injection of photoelectrons from BiVO₄ into the Au substrate as shown in the energy diagram in Figure 5.3c. Based on the difference between the work

function of the Au substrate (5.3 eV) and the conduction band edge of BiVO₄ (4.76 eV), electrons injecting into the Au can produce a maximum photovoltage of $[-5.3 \text{ eV} - (-4.76 \text{ eV})]/e = -0.54 \text{ V}$. The lower experimental value of -0.12 V is ascribed to low electron mobility in the BiVO₄ particulate film, which restricts charge separation in BiVO₄ particles in direct contact with the Au substrate. This is confirmed by the absence of stronger photovoltage signals in thicker films (data not shown). The SPS spectrum in Figure 5.3a further shows that the photovoltage does not revert to zero at the end of the scan. This means that the charge separation is irreversible, likely to trapping of photogenerated holes near the particle surface or reaction with surface adsorbed methanol molecules.

Figure 5.3b shows the surface photovoltage spectra for the Ar-annealed samples (data in Table 5.2). The spectra for the Ar300 and Ar500 samples are similar to the untreated BiVO₄. However, for Ar700, the photovoltage spectrum is inverted. Furthermore, changes are observed in the photoonset across the sample series, as shown in Figure 5.3d. These variations indicate changes in the defect state concentration in the BiVO₄ particles. For example, the Ar500 and Ar700 samples have photoonsets at 2.08 and 2.10 eV, approximately 0.3 eV below their optical band gaps (Table 5.2), whereas the photoonsets for the untreated BiVO₄ and Ar300 are at 2.25 eV and at 2.43 eV. This shows that thermal annealing modifies the electronic structure of the BiVO₄ particles. Annealing at 300 °C removes defects in Ar300, as supported by the slight increase of its crystallinity based on the XRD results, and pushes the photoonset closer to the optical band gap of the material. Annealing at 500 °C or higher produces new subgap states near the conduction or valence band edge, which are responsible for the earlier onset in Ar500 and Ar700. In Ar500, these subgap states also improve charge transport through

the BiVO_4 film, allowing for a photovoltage of -0.181 V (the largest in the sample series). However, in Ar700, the subgap states cause trapping of electrons and reversal of the charge transfer direction. Overall, the SPS results show that argon annealing induces changes in charge transport and trapping across the BiVO_4 series, depending on the temperature.

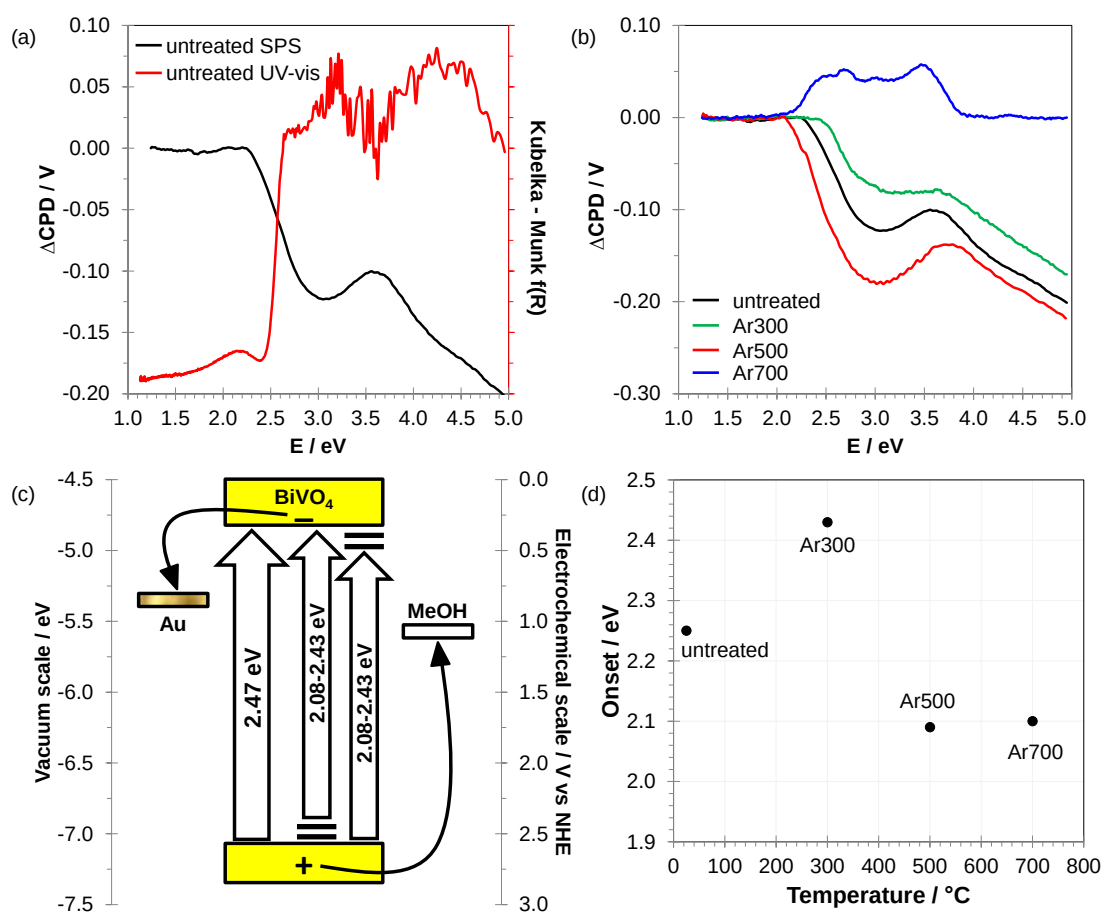


Figure 5.3. (a) SPS spectrum for the untreated BiVO_4 overlaid with its UV-vis absorption spectrum. (b) SPS spectra for all the samples. (c) Energy diagram showing charge separation in the BiVO_4 /Au system. The position of the subgap states is tentative. (d) A graph showing variation of the SPS onsets with annealing temperature.

Table 5.2. The Δ CPD value at the local maximum and SPS photoonset for each film.

Sample	Δ CPD [V]	Photoonset [eV]
untreated	-0.123	2.25
Ar300	-0.081	2.43
Ar500	-0.181	2.08
Ar700	+0.057	2.10

5.3.4. X-ray Photoelectron and Electron Paramagnetic Resonance Spectroscopies

X-ray photoelectron spectroscopy (XPS) analysis was utilized to determine the change in surface chemical states of the Ar-treated BiVO₄ samples. Figure 5.4a-c show the core levels of V 2p, O 1s, and Bi 4f XPS spectra of the samples. The V 2p XPS spectra (Figure 5.4a) of all samples exhibit V 2p_{3/2} and V 2p_{1/2} peaks at 516.9 and 524.6 eV, respectively, that are consistent with the values reported for BiVO₄.¹⁴ Each of the V 2p_{3/2} peak can be deconvoluted into two components V⁵⁺ and V⁴⁺ with the latter appearing at lower binding energy. The asymmetric nature of O 1s signal (Figure 5.4b) indicates the presence of two oxygen species, namely, surface lattice oxygen (O_{latt}) and adsorbed oxygen (O_{ads}) with respective binding energies of 530.0 and 531.7 eV. Since both V⁴⁺ and O_{ads} are associated with oxygen vacancies,³⁴⁻³⁵ the presence of these two species confirms that oxygen vacancies exist on the surface of all samples. Despite SPS photoonset observations suggesting that new subgap states (likely to be oxygen vacancies) are present on Ar500 and Ar700, a corresponding increase of both the V⁴⁺ and O_{ads} species was not observed in the V 2p and O 1s XPS spectra of the two samples. This may be attributed to the minute variation of the oxygen vacancy density between the samples, which is beyond the sensitivity of XPS. As for the Bi 4f XPS spectra (Figure 5.4c), all samples display two distinct peaks located at around 159.3 and 164.6 eV which can be assigned to Bi 4f_{7/2} and Bi 4f_{5/2}, respectively, corresponding to Bi³⁺

typically reported for BiVO₄.³⁶⁻³⁷ Notably, an apparent broadening of these peaks with discernible shoulders at a higher binding energy is observed solely for Ar700. Deconvolution suggests that there are additional peaks at 160.4 and 165.6 eV, which are indicative of Bi centers with a higher oxidation state and can be attributed to surface bismuth vacancies.³⁸ The result substantiates the presence of bismuth vacancies on the surface of Ar700.

It is known that the oxygen vacancy-related V⁴⁺ is paramagnetic. The relative density of oxygen vacancies of the BiVO₄ samples could be quantified by comparing their relative amount of V⁴⁺ using electron paramagnetic resonance (EPR) spectroscopy, which is highly sensitive for paramagnetic states even at extremely low concentrations.³⁹ Figure 5.4d compares the room temperature EPR spectra of all samples, whereby a signal centered at $g = 1.977$ (corresponds to the g value reported for paramagnetic V⁴⁺)⁴⁰ is observed for each sample. Importantly, while the EPR signal of Ar300 is comparable to that of the untreated BiVO₄, the signal for Ar500 is markedly increased. These EPR results are in accordance with the SPS photoonset, inferring that the new subgap states for Ar500 arises from the formation of more oxygen vacancies. However, further increase of the annealing temperature to 700 °C diminishes the oxygen vacancy density, as indicated by the weaker EPR signal of Ar700 relative to that of Ar500. On the basis of the lower V⁴⁺ concentration but comparable SPS photoonset of Ar700 in comparison to Ar500, the subgap states of Ar700 are thus concluded to comprise both oxygen and bismuth vacancies, whereby the latter was validated by the Bi 4f XPS results discussed earlier.

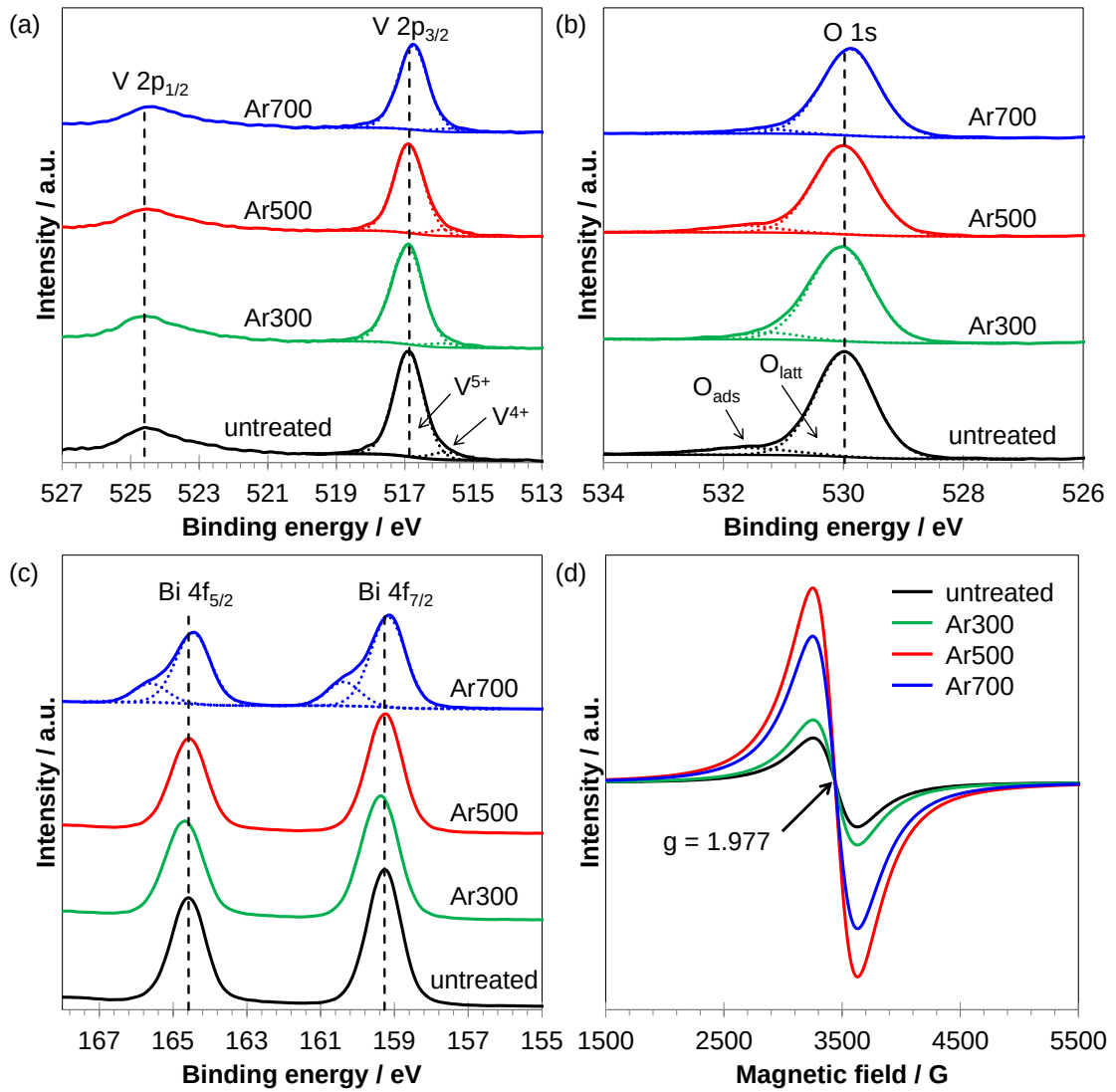


Figure 5.4. High-resolution XPS spectra of the (a) V 2p, (b) O 1s, and (c) Bi 4f core levels of the BiVO_4 samples before and after Ar annealing treatment at different temperatures. (d) The corresponding room temperature EPR spectra of all samples.

5.3.5. Effects of Ar Treatment on the Structural, Electronic, and Morphological Properties of Dual-Faceted BiVO_4

The results of the above-mentioned spectroscopic characterization techniques verify that Ar annealing treatment improves the crystallinity and affects the local structure distortion of BiVO_4 , which play a role in governing the photoactivity of BiVO_4 . Higher crystallinity signifies presence of less number of recombination sites to abate charge

recombination, whereas greater orbital overlap allows better delocalization of photogenerated electrons and holes. These changes lead to more efficient charge separation which then explains the best activity exhibited by Ar500, in both the PS water oxidation reaction and the PEC photocurrent generation. The EPR results also revealed and confirmed that annealing treatment in the oxygen-deficient Ar atmosphere boosts oxygen vacancy formation in BiVO₄, particularly at a temperature of 500 °C or higher. The considerable augmentation of oxygen vacancies in Ar500 is another factor contributing to its superior photoactivity. Oxygen vacancies have been predicted by the density functional theory (DFT) calculations as shallow donors in monoclinic BiVO₄ with low formation energies,^{17, 41} which can increase the donor densities of the material for enhanced charge transport. These advantages of oxygen vacancies in BiVO₄ were demonstrated in numerous studies related to hydrogenation treatment,^{14, 17, 42-43} whereby the H₂-treated BiVO₄ showed better PEC water oxidation performance than that of the air-annealed sample.

Likewise, given that the crystallinity of Ar300 is only slightly improved compared to the untreated BiVO₄ and they both have comparable density of oxygen vacancies, it is reasonable to conclude that their photoactivities are comparable. Based on the most profound changes of structural, optical, and electronic properties exhibited by Ar700, a corresponding improvement in its photoactivity may be initially envisaged. However, the performance of Ar700 in the two activity tests executed was considerably poorer than that of the untreated BiVO₄. Normalization of the photocatalytic O₂ evolution activity of BiVO₄ samples with respect to surface area (Figure 5.1a) indicates that the poor performance of Ar700 was not due to the lost its surface area. Instead, it can be due to the creation of surface bismuth vacancies as corroborated by XPS analysis.

Surface bismuth vacancy formation is possibly due to bismuth volatilization at high-temperature annealing, a phenomenon which has commonly been observed in the sintering process of bismuth-containing ceramic materials, contributing to the loss of bismuth element.⁴⁴ This is especially significant at elevated temperatures. DFT calculations by Yin et al.⁴¹ and Wang et al.¹⁷ collectively suggest that bismuth vacancies are shallow acceptors in monoclinic BiVO₄. The creation of surface bismuth vacancies thus encourages undesirable electron trapping on Ar700 (as supported by the positive SPS Δ CPD signal), confining the photogenerated electrons and impeding their reaction with Ag⁺ ions, leading to poor O₂ generation. Similarly, the trapping phenomenon hampers electron transfer efficiencies of the Ar700 photoanode to result in low photocurrent generation by this sample.

Aside from the induced surface bismuth vacancies, the exceptionally poor photoactivity of Ar700 can also be ascribed to the well-defined crystal facets of the BiVO₄ diminishing under annealing treatment at high temperature. Figure 5.5 presents the scanning electron microscopy (SEM) images of the Ar-treated samples along with the untreated BiVO₄. The morphology of the Ar700 particles has evidently changed with regards to that of the other samples. As illustrated in Figure 5.5a, the untreated BiVO₄ particles are dual-faceted with exposed {010} and {110} facets, where the facet assignments are schematically depicted in the inset based on Chapter 3. While the well-developed {010} and {110} facets are conserved in Ar300 and Ar500 (Figure 5.5b, c, respectively), they diminished in Ar700 (Figure 5.5d) whereby the particles become rounded with ridged surface.

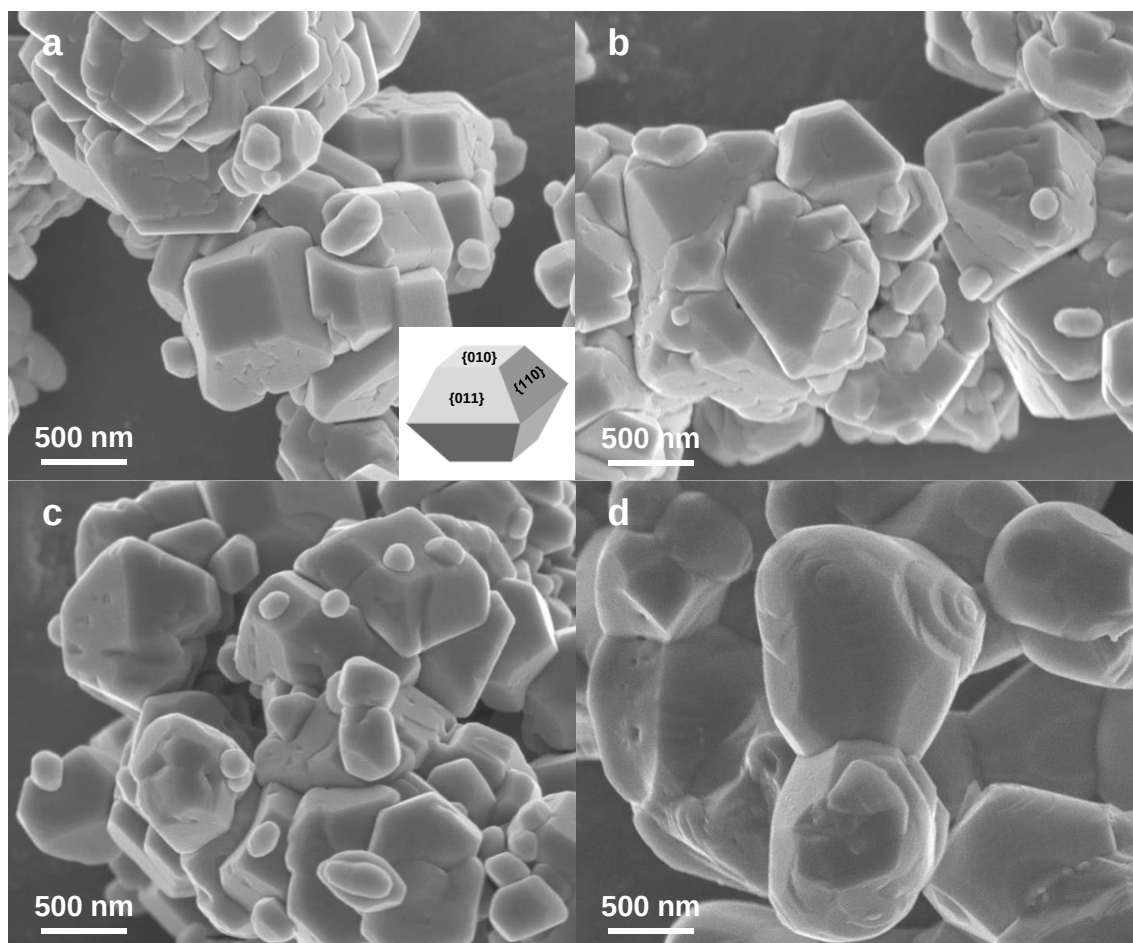


Figure 5.5. SEM images of the (a) untreated BiVO_4 and Ar-treated BiVO_4 samples prepared at (b) 300, (c) 500, and (d) 700 °C.

{010} and {110} have been revealed as the redox functional facets of monoclinic BiVO_4 , in which photogenerated electrons and holes are spatially separated on the two surfaces.¹⁶ Therefore, the presence of well-developed {010} and {110} facets is essential for efficient charge separation. In order to validate the crystal-facet-mediated charge separation, the BiVO_4 samples with and without the well-defined facets (represented by the untreated BiVO_4 and Ar700, respectively) were separately suspended in an aqueous solution containing platinum (Pt) salt and irradiated with visible light ($\lambda > 420$ nm). Reduction of the Pt salt by receiving photogenerated electrons from BiVO_4 forms metal Pt on the surface of the photocatalyst. This is

generally known as the photoreduction process. After a 5 h illumination, the powder samples were collected and observed using a SEM microscope. The deposition of Pt metal is verified with the presence of small particles on the surface of the untreated BiVO₄ (Figure 5.6c) and Ar700 (Figure 5.6d), which surfaces are otherwise particle-free (Figure 5.6a, b, respectively) prior to their exposure to Pt salt under illumination. Note that the Pt particles are solely deposited on the {010} surface of the untreated BiVO₄, suggesting that the photogenerated electrons are mainly available on the {010}, which is in perfect agreement with that observed by Li et al.¹⁶ Such discernible selectivity of Pt deposition on the {010} facet is clearly undermined in Ar700, where the Pt particles are randomly deposited on the surfaces with diminished {010} and {110} facets. The better selectivity of Pt deposition on the untreated BiVO₄ as opposed to Ar700 thus manifests better charge separation in BiVO₄ with well-developed {010} and {110} facets.

Apart from the single photodeposition of Pt metal, the role of {010} and {110} facets in facilitating charge separation was further substantiated by simultaneous photodeposition of Pt and manganese oxide (MnO_x). In the presence of both Pt and manganese (Mn) salts, Li et al. have demonstrated that the latter can be oxidized to produce insoluble sponge-like MnO_x by accepting holes from the light-activated BiVO₄ when the electrons are involved in the reduction of the former to form Pt particles.¹⁶ Figure 5.6e,f displays the SEM images of Pt and MnO_x deposited on the untreated BiVO₄ and Ar700, respectively. The successful depositions of Pt and MnO_x on the untreated BiVO₄ (1.33 wt% Pt and 0.53 wt% Mn) and Ar700 (1.51 wt% Pt and 0.58 wt% Mn) were confirmed using inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis, whereby loadings of Pt and Mn were found to be comparable between both samples. In the case of the untreated, well-faceted BiVO₄, sponge-like MnO_x deposits

are primarily formed on the {110} facets, whereas the Pt particles are selectively deposited on the {010} surfaces. The SEM image clearly shows that other than the deposition of Pt particles, the {010} surface is completely free of the MnO_x deposits. This highly selective deposition of Pt on the {010} facets and MnO_x on the {110} facets marks good charge separation in BiVO₄ with well-developed facets, whereby photogenerated electrons and holes are preferentially driven to the {010} and {110} surfaces, respectively. On the other hand, the surfaces of Ar700 particles with diminished {010} and {110} facets are fully covered by sponge-like MnO_x with patches of Pt agglomerates noticeable, indicating the lack of charge separation in this sample.

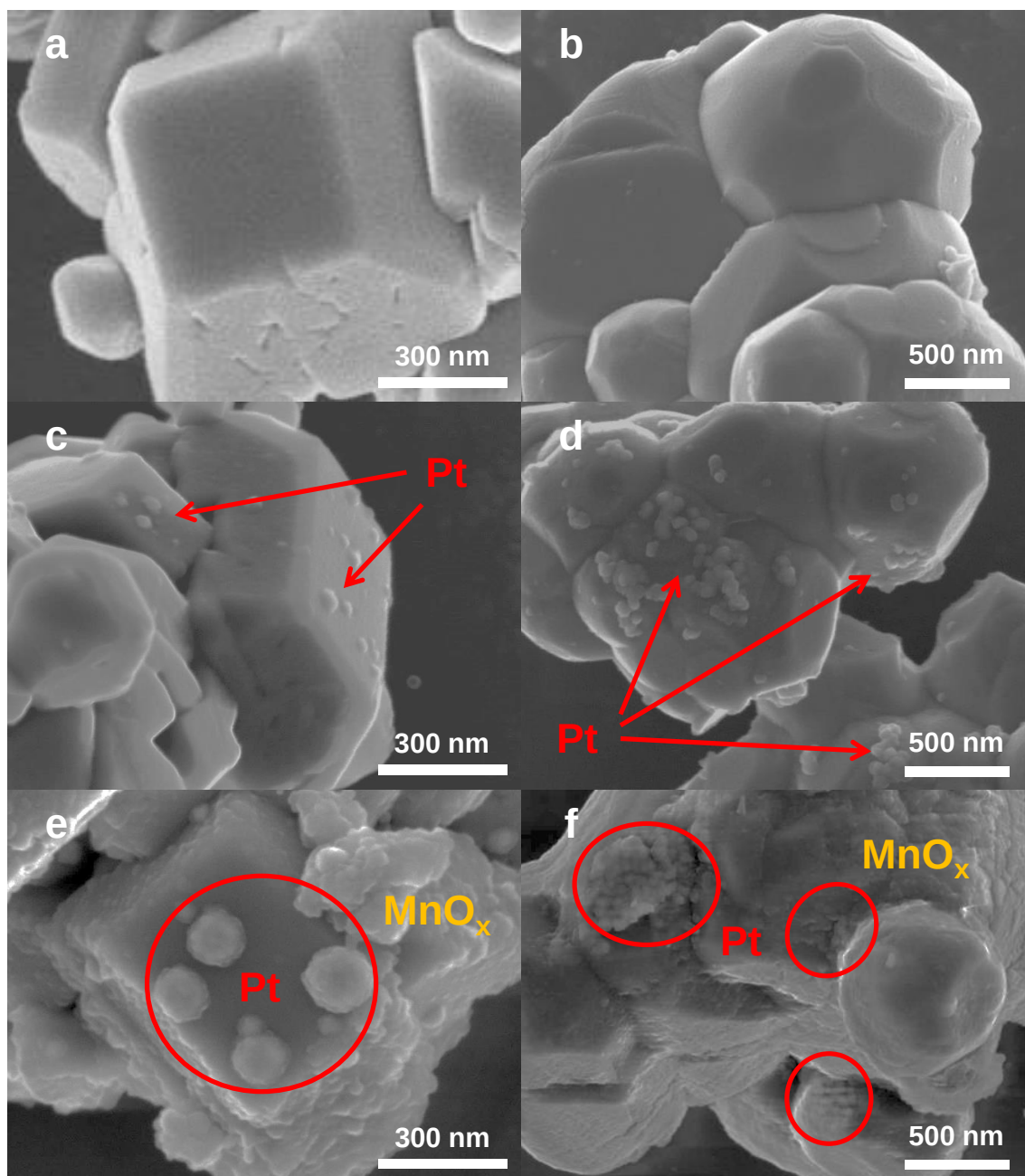


Figure 5.6. SEM images of the (a) untreated BiVO_4 , (b) Ar700, (c) Pt-loaded untreated BiVO_4 , (d) Pt-loaded Ar700, (e) Pt/ MnO_x -loaded untreated BiVO_4 , and (f) Pt/ MnO_x -loaded Ar700. (e) highlights facet-selective depositions of Pt and MnO_x on the untreated BiVO_4 with well-developed $\{010\}$ and $\{110\}$ facets.

5.4. Summary

Ar annealing was demonstrated to affect the activity of dual-faceted BiVO₄ for photocatalytic O₂ generation and PEC photocurrent generation, attributing to the variation in physicochemical and electronic properties of the material. XRD, Raman, UV-vis, SPS, and EPR spectroscopic characterizations revealed that not only did Ar annealing enhance the crystallinity, local structure distortion, and optical properties of BiVO₄, but also introduces new subgap states attributed to oxygen vacancies. Higher annealing temperature induces better crystallinity, greater orbital overlap, and smaller band gap as well as favors oxygen vacancy formation, while improving charge separation, transport, and photoactivity of BiVO₄. Despite Ar700 having the most significant changes on the aforesaid properties, Ar500 displayed the best activity in both the PS and PEC systems. This is due to the introduction of additional surface bismuth vacancies and diminution of well-developed facets upon annealing at a high temperature of 700 °C, subsequently resulting in the deterioration of photochemical charge separation and photoactivity of the BiVO₄.

5.5. References

1. Reddy, B. M.; Khan, A.; Yamada, Y.; Kobayashi, T.; Lorient, S.; Volta, J.-C., Structural Characterization of CeO₂-MO₂ (M=Si⁴⁺, Ti⁴⁺, and Zr⁴⁺) Mixed Oxides by Raman Spectroscopy, X-Ray Photoelectron Spectroscopy, and Other Techniques. *J. Phys. Chem. B* **2003**, *107* (41), 11475-11484.
2. Kang, H. S.; Kang, J. S.; Kim, J. W.; Lee, S. Y., Annealing Effect on the Property of Ultraviolet and Green Emissions of ZnO Thin Films. *J. Appl. Phys.* **2004**, *95* (3), 1246-1250.
3. Yu, J.; Wang, B., Effect of Calcination Temperature on Morphology and Photoelectrochemical Properties of Anodized Titanium Dioxide Nanotube Arrays. *Appl. Catal., B* **2010**, *94* (3), 295-302.
4. Bhattacharya, A. K.; Mallick, K. K.; Hartridge, A., Phase Transition in BiVO₄. *Mater. Lett.* **1997**, *30* (1), 7-13.
5. Hanaor, D.; Sorrell, C., Review of the Anatase to Rutile Phase Transformation. *J. Mater. Sci.* **2011**, *46* (4), 855-874.
6. Yu, J.-G.; Yu, H.-G.; Cheng, B.; Zhao, X.-J.; Yu, J. C.; Ho, W.-K., The Effect of Calcination Temperature on the Surface Microstructure and Photocatalytic Activity of TiO₂ Thin Films Prepared by Liquid Phase Deposition. *J. Phys. Chem. B* **2003**, *107* (50), 13871-13879.
7. Ng, C.; Ng, Y. H.; Iwase, A.; Amal, R., Influence of Annealing Temperature of WO₃ in Photoelectrochemical Conversion and Energy Storage for Water Splitting. *ACS Appl. Mater. Interfaces* **2013**, *5* (11), 5269-5275.
8. Hyam, R. S.; Lee, J.; Cho, E.; Khim, J.; Lee, H., Effect of Annealing Environments on Self-Organized TiO₂ Nanotubes for Efficient Photocatalytic Applications. *J. Nanosci. Nanotechnol.* **2012**, *12* (12), 8908-8912.

9. Mtangi, W.; Auret, F. D.; Meyer, W.; Legodi, M.; van Rensburg, P. J.; Coelho, S.; Diale, M.; Nel, J., Effects of Hydrogen, Oxygen, and Argon Annealing on the Electrical Properties of ZnO and ZnO Devices Studied by Current-Voltage, Deep Level Transient Spectroscopy, and Laplace DLTS. *J. Appl. Phys.* **2012**, *111* (9), 094504.
10. Yamada, K.; Yamane, H.; Matsushima, S.; Nakamura, H.; Ohira, K.; Kouya, M.; Kumada, K., Effect of Thermal Treatment on Photocatalytic Activity of N-Doped TiO₂ Particles under Visible Light. *Thin Solid Films* **2008**, *516* (21), 7482-7487.
11. Wang, G.; Ling, Y.; Li, Y., Oxygen-Deficient Metal Oxide Nanostructures for Photoelectrochemical Water Oxidation and Other Applications. *Nanoscale* **2012**, *4* (21), 6682-6691.
12. Chae, Y.; Mori, S.; Suzuki, M., Visible-Light Photocatalytic Activity of Anatase TiO₂ Treated with Argon Plasma. *Thin Solid Films* **2009**, *517* (14), 4260-4263.
13. Kim, T. W.; Ping, Y.; Galli, G. A.; Choi, K.-S., Simultaneous Enhancements in Photon Absorption and Charge Transport of Bismuth Vanadate Photoanodes for Solar Water Splitting. *Nat. Commun.* **2015**, *6*, 8769.
14. Singh, A. P.; Kodan, N.; Dey, A.; Krishnamurthy, S.; Mehta, B. R., Improvement in the Structural, Optical, Electronic and Photoelectrochemical Properties of Hydrogen Treated Bismuth Vanadate Thin Films. *Int. J. Hydrogen Energy* **2015**, *40* (12), 4311-4319.
15. Wang, G.; Wang, H.; Ling, Y.; Tang, Y.; Yang, X.; Fitzmorris, R. C.; Wang, C.; Zhang, J. Z.; Li, Y., Hydrogen-Treated TiO₂ Nanowire Arrays for Photoelectrochemical Water Splitting. *Nano Lett.* **2011**, *11* (7), 3026-3033.

16. Li, R.; Zhang, F.; Wang, D.; Yang, J.; Li, M.; Zhu, J.; Zhou, X.; Han, H.; Li, C., Spatial Separation of Photogenerated Electrons and Holes Among {010} and {110} Crystal Facets of BiVO₄. *Nat. Commun.* **2013**, *4*, 1432.
17. Wang, G.; Ling, Y.; Lu, X.; Qian, F.; Tong, Y.; Zhang, J. Z.; Lordi, V.; Rocha Leao, C.; Li, Y., Computational and Photoelectrochemical Study of Hydrogenated Bismuth Vanadate. *J. Phys. Chem. C* **2013**, *117* (21), 10957-10964.
18. Kho, Y. K.; Teoh, W. Y.; Iwase, A.; Mädler, L.; Kudo, A.; Amal, R., Flame Preparation of Visible-Light-Responsive BiVO₄ Oxygen Evolution Photocatalysts with Subsequent Activation via Aqueous Route. *ACS Appl. Mater. Interfaces* **2011**, *3* (6), 1997-2004.
19. Maeda, K., Effects of the Physicochemical Properties of Rutile Titania Powder on Photocatalytic Water Oxidation. *ACS Catal.* **2014**, *4* (6), 1632-1636.
20. Chang, J.; Lin, W.; Hon, M.-H., Effects of Post-Annealing on the Structure and Properties of Al-Doped Zinc Oxide Films. *Appl. Surf. Sci.* **2001**, *183* (1), 18-25.
21. Nunes, P.; Fernandes, B.; Fortunato, E.; Vilarinho, P.; Martins, R., Performances Presented by Zinc Oxide Thin Films Deposited by Spray Pyrolysis. *Thin Solid Films* **1999**, *337* (1), 176-179.
22. Gotić, M.; Musić, S.; Ivanda, M.; Šoufek, M.; Popović, S., Synthesis and Characterisation of Bismuth(III) Vanadate. *J. Mol. Struct.* **2005**, *744–747* (0), 535-540.
23. Tan, H. L.; Tahini, H. A.; Wen, X.; Wong, R. J.; Tan, X.; Iwase, A.; Kudo, A.; Amal, R.; Smith, S. C.; Ng, Y. H., Interfacing BiVO₄ with Reduced Graphene Oxide for Enhanced Photoactivity: A Tale of Facet Dependence of Electron Shuttling. *Small* **2016**, *12* (38), 5295-5302.

24. Liu, J.; Wang, H.; Wang, S.; Yan, H., Hydrothermal Preparation of BiVO₄ Powders. *Mater. Sci. Eng., B* **2003**, *104* (1), 36-39.
25. Yu, J.; Kudo, A., Effects of Structural Variation on the Photocatalytic Performance of Hydrothermally Synthesized BiVO₄. *Adv. Funct. Mater.* **2006**, *16* (16), 2163-2169.
26. Brown, I. t.; Wu, K. K., Empirical Parameters for Calculating Cation–Oxygen Bond Valences. *Acta Crystallogr., Sect. B* **1976**, *32* (7), 1957-1959.
27. Hardcastle, F. D.; Wachs, I. E., Determination of Vanadium-Oxygen Bond Distances and Bond Orders by Raman Spectroscopy. *J. Phys. Chem.* **1991**, *95* (13), 5031-5041.
28. Waller, M. R.; Townsend, T. K.; Zhao, J.; Sabio, E. M.; Chamousis, R. L.; Browning, N. D.; Osterloh, F. E., Single-Crystal Tungsten Oxide Nanosheets: Photochemical Water Oxidation in the Quantum Confinement Regime. *Chem. Mater.* **2012**, *24* (4), 698-704.
29. Osterloh, F. E.; Holmes, M. A.; Chang, L.; Moulé, A. J.; Zhao, J., Photochemical Charge Separation in Poly (3-Hexylthiophene)(P3HT) Films Observed with Surface Photovoltage Spectroscopy. *J. Phys. Chem. C* **2013**, *117* (51), 26905-26913.
30. Beranek, R.; Neumann, B.; Sakthivel, S.; Janczarek, M.; Dittrich, T.; Tributsch, H.; Kisch, H., Exploring the Electronic Structure of Nitrogen-Modified TiO₂ Photocatalysts through Photocurrent and Surface Photovoltage Studies. *Chem. Phys.* **2007**, *339* (1), 11-19.
31. Zhao, J.; Osterloh, F. E., Photochemical Charge Separation in Nanocrystal Photocatalyst Films: Insights from Surface Photovoltage Spectroscopy. *J. Phys. Chem. Lett.* **2014**, *5* (5), 782-786.

32. Yang, Y.; Wang, J.; Zhao, J.; Nail, B. A.; Yuan, X.; Guo, Y.; Osterloh, F. E., Photochemical Charge Separation at Particle Interfaces: The n-BiVO₄-p-Silicon System. *ACS Appl. Mater. Interfaces* **2015**, 7 (10), 5959-5964.
33. Wang, J.; Osterloh, F. E., Limiting Factors for Photochemical Charge Separation in BiVO₄/Co₃O₄, A Highly Active Photocatalyst for Water Oxidation in Sunlight. *J. Mater. Chem. A* **2014**, 2 (24), 9405-9411.
34. Jiang, H.; Dai, H.; Meng, X.; Ji, K.; Zhang, L.; Deng, J., Porous Olive-Like BiVO₄: Alchoho-Hydrothermal Preparation and Excellent Visible-Light-Driven Photocatalytic Performance for the Degradation of Phenol. *Appl. Catal., B* **2011**, 105 (3), 326-334.
35. Liu, Y.; Dai, H.; Deng, J.; Zhang, L.; Au, C. T., Three-Dimensional Ordered Macroporous Bismuth Vanadates: PMMA-Templating Fabrication and Excellent Visible Light-Driven Photocatalytic Performance for Phenol Degradation. *Nanoscale* **2012**, 4 (7), 2317-2325.
36. Zhang, Y.; Guo, Y.; Duan, H.; Li, H.; Sun, C.; Liu, H., Facile Synthesis of V⁴⁺ Self-Doped,[010] Oriented BiVO₄ Nanorods with Highly Efficient Visible Light-Induced Photocatalytic Activity. *Phys. Chem. Chem. Phys.* **2014**, 16 (44), 24519-24526.
37. Su, J.; Zou, X.-X.; Li, G.-D.; Wei, X.; Yan, C.; Wang, Y.-N.; Zhao, J.; Zhou, L.-J.; Chen, J.-S., Macroporous V₂O₅-BiVO₄ Composites: Effect of Heterojunction on the Behavior of Photogenerated Charges. *J. Phys. Chem. C* **2011**, 115 (16), 8064-8071.
38. Zhang, L.; Wang, W.; Jiang, D.; Gao, E.; Sun, S., Photoreduction of CO₂ on BiOCl Nanoplates with the Assistance of Photoinduced Oxygen Vacancies. *Nano Res.* **2015**, 8 (3), 821-831.

39. Che, M.; Védrine, J. C., *Characterization of Solid Materials and Heterogeneous Catalysts: From Structure to Surface Reactivity*. John Wiley & Sons: Weinheim, Germany, **2012**.
40. Gupta, S.; Khanijo, N.; Mansingh, A., The Influence of V⁴⁺ Ion Concentration on the EPR Spectra of Vanadate Glasses. *J. Non-Cryst. Solids* **1995**, *181* (1), 58-63.
41. Yin, W.-J.; Wei, S.-H.; Al-Jassim, M. M.; Turner, J.; Yan, Y., Doping Properties of Monoclinic BiVO₄ Studied by First-Principles Density-Functional Theory. *Phys. Rev. B* **2011**, *83* (15), 155102.
42. Gan, J.; Lu, X.; Rajeeva, B. B.; Menz, R.; Tong, Y.; Zheng, Y., Efficient Photoelectrochemical Water Oxidation over Hydrogen - Reduced Nanoporous BiVO₄ with Ni–Bi Electrocatalyst. *ChemElectroChem* **2015**, *2* (9), 1385-1395.
43. Zhang, Y.; Wang, D.; Zhang, X.; Chen, Y.; Kong, L.; Chen, P.; Wang, Y.; Wang, C.; Wang, L.; Liu, Y., Enhanced Photoelectrochemical Performance of Nanoporous BiVO₄ Photoanode by Combining Surface Deposited Cobalt-Phosphate with Hydrogenation Treatment. *Electrochim. Acta* **2016**, *195*, 51-58.
44. König, J.; Spreitzer, M.; Jančar, B.; Suvorov, D.; Samardžija, Z.; Popovič, A., The Thermal Decomposition of K_{0.5}Bi_{0.5}TiO₃ Ceramics. *J. Eur. Ceram. Soc.* **2009**, *29* (9), 1695-1701.

Chapter 6

Exploring Different Roles of Particle Size in Photoelectrochemical and Photocatalytic Water Oxidation on BiVO_4

6.1. Introduction

An ongoing effort in the research community has been devoted into the development of photocatalysts for solar water splitting to produce H_2 as a clean and renewable energy carrier. Because of the limited availability of photocatalyst materials capable of visible-light-driven water splitting into H_2 and O_2 , great attention has thus been directed into developing visible-light-responsive photocatalysts active for evolution of either H_2 or O_2 from water in the presence of sacrificial reagents to realize the overall water splitting via a Z-scheme photocatalysis system. The said system involves a two-step photoexcitation of the H_2 - and O_2 -evolving photocatalysts present in a single medium containing a suitable electron mediator.¹⁻⁴ Although H_2 is the primarily sought after reaction product, an efficient O_2 -evolving photocatalyst is equally important to attain effective overall water splitting.

Monoclinic BiVO₄, with its valence band composed of hybridized Bi 6s and O 2p orbitals,⁵⁻⁶ has a relatively narrower bandgap (2.4 - 2.5 eV) compared to other metal oxide semiconductor photocatalysts and it is highly active for water oxidation. While early work on BiVO₄ mainly concentrated on the powder suspension (PS) system for photocatalytic O₂ evolution,^{5, 7-8} more recent studies have also shown its feasibility for water oxidation via the photoelectrochemical (PEC) system, in which the n-type BiVO₄ is employed as the particulate photoanode.^{6, 9-15} The performance of BiVO₄ is generally limited by its slow water oxidation kinetics¹⁶ and poor electron transport properties.¹⁰ Despite successful demonstration of the introduction of various water oxidation catalysts (e.g. Co-Pi,¹⁶⁻¹⁹ NiOOH¹² and FeOOH^{12, 14, 20}) and donor-type dopants (Mo²¹⁻²² and W^{11, 18, 23}) in circumventing the respective limitations, the efficiency of BiVO₄ is still greatly impaired by its intrinsically low carrier mobility.²⁴

In this regard, nanoscaling has been widely employed to reduce the photocatalyst size to shorten the charge transport pathways as well as to provide larger surface active sites, subsequently promoting minority carrier extraction and charge transfer kinetics.^{12, 25-27} However, reduction of particle size is generally achieved at the expense of crystallinity, at which the density of surface defects is increased and results in augmented surface recombination. Such conflicting transformation of properties ensuing from nanoscaling thus renders particle size an intricate issue in governing the photoactivities in particulate PEC and PS systems.

The charge separation mechanisms in the two systems are essentially different. In PS system containing n-type semiconductor, charge separation relies on the thickness of space charge layer (SCL) formed at the photocatalyst/electrolyte interface to drive photogenerated holes to the electrolyte and electrons to the bulk.^{26, 28} On the contrary,

charge separation is facilitated by an externally applied potential in the particulate PEC system to draw electrons out from the illuminated photoanode to the counter electrode.²⁸ The difference in charge separation mechanisms of the two systems suggests that different particle qualities (e.g., size and crystallinity) are required to improve their performance in the respective system. With these, Hong et al. reported that particle size has an opposite effect on the water oxidation performance of WO₃ in the PS (proportional to the particle size) and particulate PEC (inversely proportional) systems.²⁸

To date, the beneficial effects of nanostructured BiVO₄ have been extensively shown in the particulate PEC system for water oxidation,^{9, 12-15} whereas studies on the influence of particle size on photocatalytic O₂ generation performance of suspended BiVO₄ is relatively scarce. For example, nanosized BiVO₄ particles (< 100 nm) prepared by Kho et al.²⁹ via flame spray pyrolysis showed poor photocatalytic O₂ evolution activity despite their high specific surface area. Similarly, Iwase and Kudo³⁰ observed poor photocatalytic performance of small and spherical BiVO₄ particles in comparison to the significantly larger and well-crystalline BiVO₄ particles.

The dual-faceted BiVO₄ samples being investigated in Chapters 3-5 are microcrystals. Despite the crystal-facet-engineered BiVO₄ was demonstrated to facilitate spatial separation of the photogenerated charges,³¹ the water oxidation photoactivity of the faceted BiVO₄ microcrystal in comparison to smaller or nanosized BiVO₄ remains unclear. In this chapter, we provide an explicit study comparing the nanoscaling effect on photoactivity of BiVO₄ in the particulate PEC and PS systems, which are seemingly similar for water oxidation yet different in the working principle and the charge separation mechanisms present within the photocatalyst. For this purpose,

BiVO₄_0.50M as described in Chapter 3 was employed in this work in addition to two other BiVO₄ samples of smaller particle size. Contrary behavior of BiVO₄'s photoactivity dependence on the particle size was exhibited in the two systems (inversely and directly dependent on particle size in the PEC and PS systems, respectively). Detailed investigation on the interplay between the physical properties (size, crystallinity, interparticle and BiVO₄/FTO substrate contacts) and the photoactivities of BiVO₄ in PEC and PS systems indicate different features govern the activity of BiVO₄ photocatalyst in the two systems, namely, charge transport in the former and charge separation in the latter.

6.2. Experimental

6.2.1. Synthesis of BiVO₄

All BiVO₄ samples were synthesized using solid-liquid state reaction in which the bismuth- and vanadium-containing precursors were mixed in an acidic aqueous solution (50 mL) at room temperature. For Sample A, BiVO₄_0.50M as described in Chapter 3 was used. To synthesis sample B, 10 mmol of bismuth (III) nitrate pentahydrate (Bi(NO₃)₃·5H₂O) and 5 mmol of V₂O₅ were stirred in 0.75 M of nitric acid for 2 days. On the other hand, sample C was obtained by stirring equimolar amounts (5 mmol) of Bi₂O₃ and V₂O₅ in 1 M of acetic acid for 16 days. The resulting vivid yellow suspension from each of the preparation methods was collected by suction filtration, followed by washing with distilled water and dried at 110 °C. Additionally, sample C was treated by air calcination at 400 °C for 1 h.

6.2.2. Material Characterization

The morphology of the BiVO₄ samples was examined using a Hitachi S900 scanning electron microscope (SEM) operated at 4 kV. The resulting SEM images were then used for particle size measurements using Image-J software.

Brunauer-Emmett-Teller (BET) surface area, X-ray diffraction, and UV-vis diffuse reflectance spectra measurements were carried out as described in Chapter 3. The crystallite size was estimated by Scherrer equation using the full width at half-maximum height of the XRD peak at $2\theta = 30.6^\circ$. X-ray photoelectron spectroscopy (XPS) was performed as described in Chapter 4.

Cross sections of the BiVO₄/FTO with different particle sizes of BiVO₄ were observed on a FEI Nova NanoSEM 450 field-emission SEM, in which the electrode sample was tilted by 10° .

6.2.3. Preparation of Electrodes

The particulate electrodes used for PEC measurements, electrochemical impedance spectroscopy (EIS) and SEM imaging of the BiVO₄/FTO cross sections were prepared by dropcasting the BiVO₄ powder samples on conductive fluorine-doped tin oxide (FTO) substrates as described in Chapter 5. For improving the adhesion of BiVO₄ particles onto the glass substrate, the obtained electrodes were heated at 300°C in air for 2 h. The morphology and size of the BiVO₄ particles were preserved after heat treatment.

6.2.4. Photoelectrochemical Measurements (PEC System)

PEC measurements were performed in a three-electrode cell setup as described in Chapter 4. N₂-saturated 0.1 M sodium sulfate (Na₂SO₄) with or without methanol (10

vol %) was used as the electrolyte for all the electrochemical measurements. The current-potential (I-V) curves were recorded using an Autolab potentiostat (Model PGSTAT302N) at a potential scan rate of 0.02 V s⁻¹. Electrochemical impedance spectroscopy (EIS) measurements were also conducted in the same setup with 0.1 M Na₂SO₄ as the electrolyte. The Nyquist plots were attained with an AC potential of 5 mV amplitude at 0 V vs. Ag/AgCl in the frequency range of 100 kHz to 0.01 Hz.

6.2.5. Photocatalytic Reaction (PS System)

Photocatalytic O₂ evolution was carried out in an enclosed top-irradiation cell with a Pyrex window, as described in Chapter 3.

6.3. Results and Discussion

6.3.1. Morphological, Structural and Optical Properties

BiVO₄ samples with different particle sizes were prepared via a similar solid-liquid state reaction at room temperature, at which bismuth- and vanadium-containing precursors were dissolved and precipitated in acidic aqueous solution to form BiVO₄. Stirring of bismuth (III) oxide (Bi₂O₃) and vanadium (V) oxide (V₂O₅) in nitric acid (HNO₃) resulted in large and square platelike BiVO₄ particles with smooth and clear faces,³² denoted as sample A shown in Figure 6.1a. Although replacement of Bi₂O₃ with bismuth (III) nitrate pentahydrate (Bi(NO₃)₃·5H₂O) as the Bi precursor led to the formation of smaller BiVO₄ particles with irregular shape (sample B; Figure 6.1b),³³ substitution of HNO₃ with acetic acid (CH₃COOH) as the reaction medium produced the smallest spherical BiVO₄ particles (sample C; Figure 6.1c).³⁰ To achieve the same crystal phase as that of sample A and B, we treated sample C was treated with post-calcination at an elevated temperature of 400 °C for its phase transition from scheelite-

tetragonal to scheelite-monoclinic. Size measurement of 200 particles randomly selected from the scanning electron microscopy (SEM) images indicate that sample A, B and C have an average size of 833 ± 249 nm (determined by the width of the square particles), 374 ± 171 nm and 123 ± 24 nm, respectively. The histograms corresponding to the particle size distribution of each sample are displayed in Figure 6.1d-f. BET surface area analysis shows an increasing trend from $2.1 \text{ m}^2 \text{ g}^{-1}$ for sample A, to $2.9 \text{ m}^2 \text{ g}^{-1}$ for sample B and $5.4 \text{ m}^2 \text{ g}^{-1}$ for sample C. The average particle sizes of all samples were also estimated from their BET surface areas by the equation $d = 6000/(SSA\rho)$, where SSA = BET surface area and ρ = specific density of BiVO₄ (6.1 g cm^{-3}), as listed in Table 6.1. Although discrepancies exist between the values estimated from the SEM images and BET areas, they are in agreement showing the decrease of particle size from sample A to sample C.

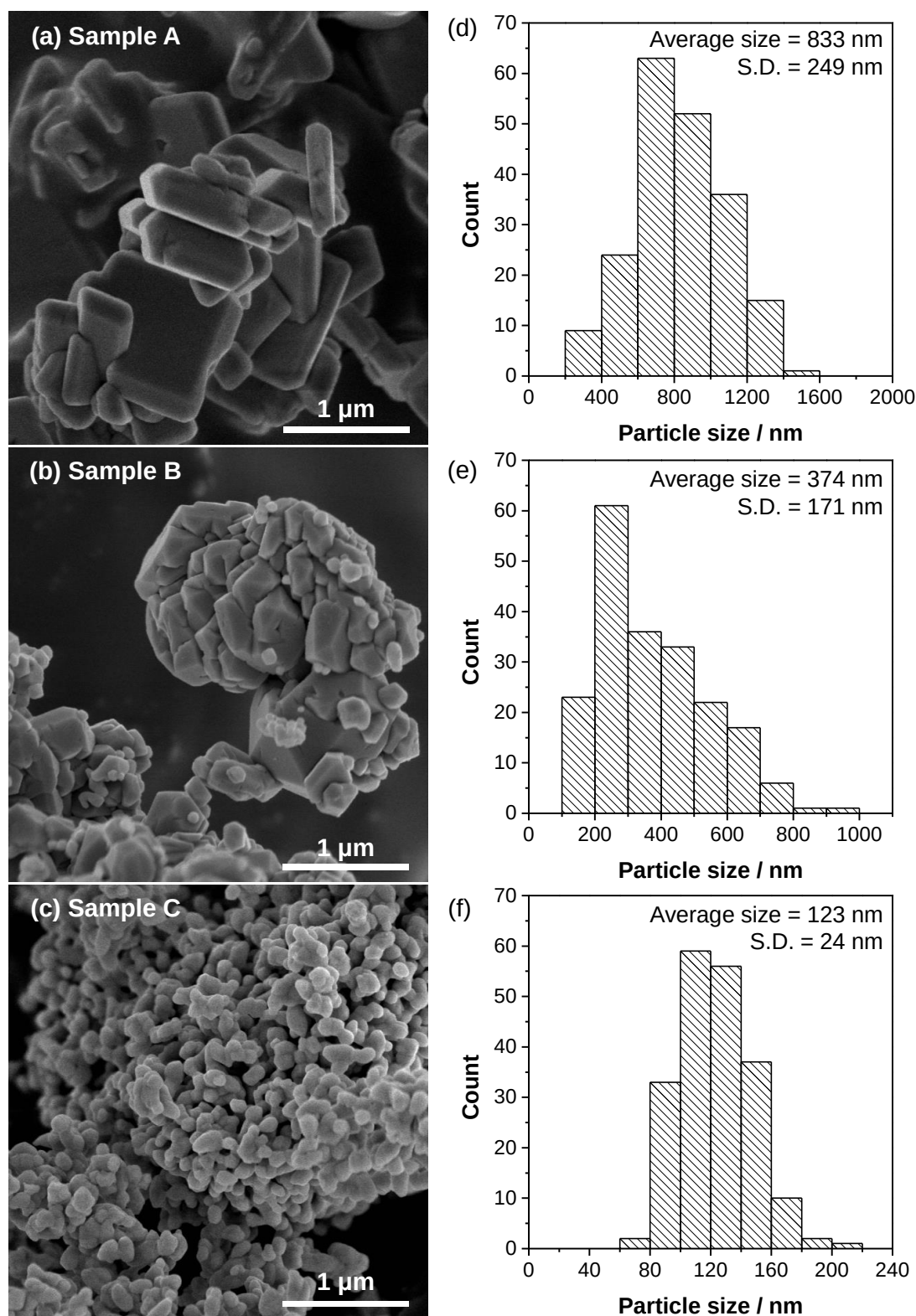


Figure 6.1. SEM images of (a) sample A, (b) sample B, and (c) sample C. (d-f) Particle size distribution histograms of sample A, B, and C, respectively. Each histogram was constructed by the measurements of 200 particles.

Table 6.1. Physical and optical properties of the as-prepared BiVO₄ samples.

	Bi precursor	Acid aqueous solution, concentration [M]	Particle size [nm]		BET surface area [m ² g ⁻¹]	Crystallite size [nm]	Band gap [eV]
			SEM	BET			
A	Bi ₂ O ₃	HNO ₃ , 0.5	833 ± 249	468	2.1	91	2.49
B	Bi(NO ₃) ₃ ·5H ₂ O	HNO ₃ , 0.75	374 ± 171	339	2.9	89	2.48
C	Bi ₂ O ₃	CH ₃ COOH, 1.0	123 ± 24	182	5.4	72	2.57

Figure 6.2a displays the XRD patterns of the BiVO₄ samples. The discernible peak splitting at 18.5, 35 and 46 ° of 2θ signifies that all samples have a single scheelite-monoclinic phase.⁸ Despite the supposedly split peak at 18.5 ° as a characteristic diffraction fingerprint of scheelite-monoclinic BiVO₄, the seemingly singlet for sample C can be attributed to the low crystallinity of the BiVO₄ particles obtained using aqueous CH₃COOH solution.³⁰ Note that the peak resolution worsens from sample A to sample C, which is readily demonstrated by the split peaks at 18.5 ° and 35 ° (illustrated in the insets), indicating that the crystallinity deteriorates as the particle size decreases. This observed particle size dependent crystallinity is supported by the gradual decrease of crystallite size from sample A to sample C (Table 6.1), as estimated using the Scherrer equation. The considerably larger particle size of each sample in comparison to the crystallite size suggests that the BiVO₄ samples used in this study are composed of multidomain crystals (i.e., non-single crystal). Although all BiVO₄ samples exhibit the typical optical absorption in the visible-light region, the absorption edge of sample C is slightly blue-shifted compared to that of sample A and B (Figure 6.2b). Such blue shift in absorption edge of sample C is in agreement with that reported by Iwase and Kudo.³⁰ The band gap energies were estimated as 2.49 eV, 2.48 eV and 2.57 eV for samples A, B and C, respectively. Table 6.1 summarizes the physical and optical properties of the as-prepared BiVO₄ for ease of comparison.

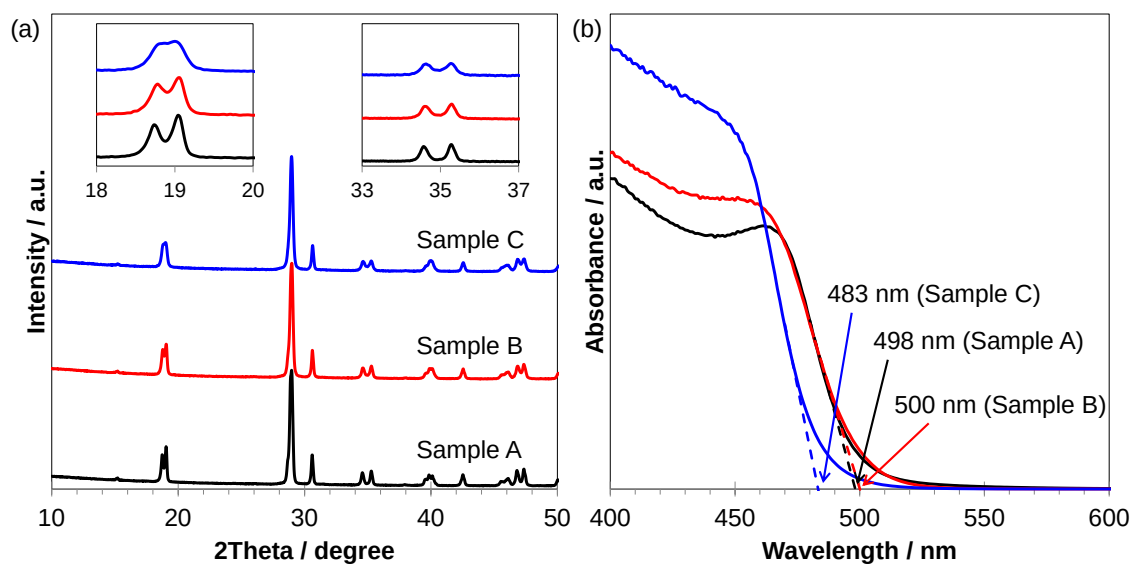


Figure 6.2. (a) XRD diffraction patterns and (b) UV-vis diffuse reflectance spectra of sample A (black line), B (red line), and C (blue line). Insets in panel a illustrate the enlarged XRD diffraction patterns showing the peak splitting at around 18.5 ° (left) and 35 ° (right).

6.3.2. Surface Chemical States

X-ray photoelectron spectroscopy (XPS) measurements were carried out to compare the surface qualities of the BiVO₄ samples with different particle sizes. Figure 6.3 shows the core levels Bi 4f, V 2p and O 1s XPS spectra of all samples. The Bi 4f_{7/2}, Bi 4f_{5/2}, V 2p_{3/2}, V 2p_{1/2}, and O 1s peaks for both sample A and B are found at 159.4, 164.7, 517.1, 524.9, and 530.2 eV, respectively, which correspond to the Bi³⁺, V⁵⁺, and O²⁻ in BiVO₄.³⁴⁻³⁵ In comparison to sample A and B, these peaks of sample C are consistently shifted by -0.4 eV. This can be ascribed to the surface effect of nanosized materials, whereby an increase in the ratio of surface to bulk atoms has been found to result in negative binding energy shift.³⁶ Deconvolution of the V 2p_{3/2} peak (Figure 6.3b) suggests that there is an additional peak for both sample B and C at higher binding energies located at 518.3 eV for sample B and 518.0 eV for sample C. These peaks are attributable to the presence of V⁵⁺ in V₂O₅ originated from the V precursor.³⁴ Likewise, deconvolution of the asymmetric O 1s peaks of both samples B and C (Figure 6.3c) reveals the presence of an additional peak located at the binding energies 1.2 and 1.5 eV higher than the O 1s peaks of the respective samples. The chemical shift within the range of 1.2–1.5 eV agrees well with that between hydroxyl oxygen (OH) and lattice oxygen (O²⁻) of metal oxide,³⁷ suggesting that the additional peak for both samples B and C corresponds to the OH groups present at the defect sites.³⁸ Dissociation of water molecules preferably occurs at the surface defects of photocatalyst, resulting in the hydroxylation of the surface where OH groups are bind to the defect sites.³⁹ It is noteworthy that sample C shows a relatively higher OH/O²⁻ ratio compared to sample B (0.23 and 0.18, respectively), indicating that the former has a higher density of surface defects ensuing from particle size reduction. These XPS results thus suggest the

increase of surface defect density from sample A to C, which explains their decreasing crystallinity as observed from the XRD analysis (Figure 6.2a).

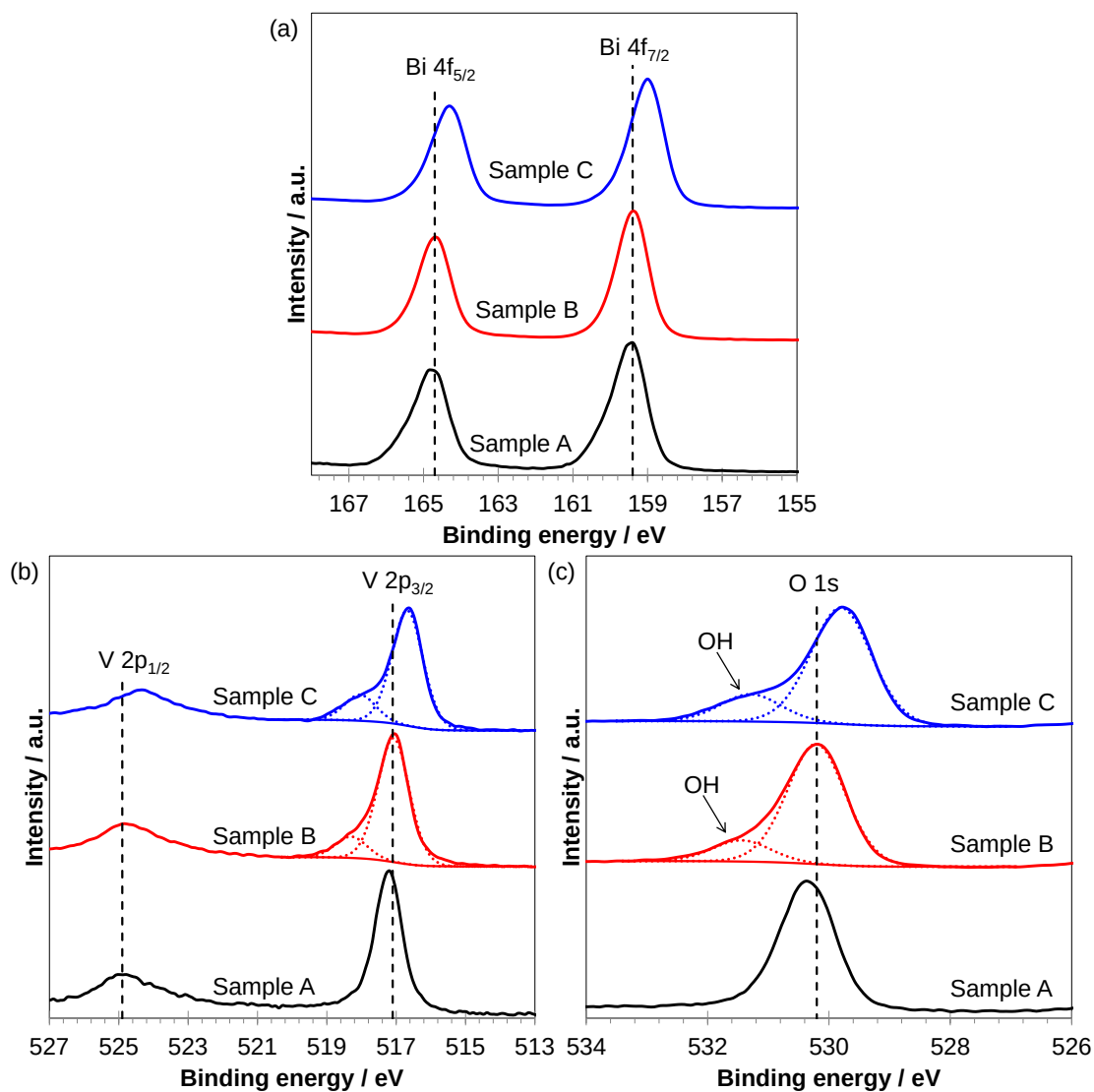


Figure 6.3. XPS spectra of the (a) Bi 4f, (b) V 2p and (c) O 1s core levels of sample A, B, and C.

6.3.3. Photoelectrochemical Measurements

To evaluate the particle size effect on the PEC water oxidation performance of BiVO₄ under visible-light illumination (of wavelength, $\lambda > 420$ nm), the powder samples were each made into an electrode via a dropcast method using conductive fluorine-doped tin oxide (FTO) glass as the substrate. Figure 6.4a depicts the current-potential (I-V) curves of the BiVO₄ particulate photoanodes under dark and light conditions. Upon light illumination, all samples exhibit anodic photocurrent which is a typical photoresponse of the n-type BiVO₄. Improved magnitude of photocurrent density was observed as the BiVO₄ particle size decreased over the range of potentials studied. As opposed to sample A that portrays steady growth of photocurrent with the applied potential, sample B and C reach a saturated photocurrent at a low potential of -0.30 V vs. Ag/AgCl, suggesting a more efficient charge separation and transportation in the photoanodes made with smaller BiVO₄ particles.⁴⁰ Additionally, the onset potential (estimated by the interception between dark and light curves⁴¹) was found to be progressively shifted to a more negative potential with the decrease of BiVO₄ particle size, as evidenced by the magnified view of I-V curves in the range of -0.65 to -0.35 V vs. Ag/AgCl (inset in Figure 6.4a). A low onset potential is favorable for efficient PEC water splitting reactions in view of the requirement of low energy input (i.e., the applied potential).⁴⁰⁻⁴¹ The negative shift of both the saturation and onset potentials for the photoanodes with smaller BiVO₄ particles thus infers enhanced PEC performance through decreasing BiVO₄ particle size. In order to understand the origin of the improved PEC performance for BiVO₄ with smaller particle size, the electrochemical properties of each BiVO₄ photoanode was determined using electrochemical impedance spectroscopy (EIS). Figure 6.4b presents the Nyquist plots of all samples measured at 0 V vs. Ag/AgCl under dark condition. The arc radius decreases from sample A to sample C, suggesting

an improving charge transfer ability of the photoanode accompanying the BiVO_4 particle size decrease, which correlates well with the activity trend in the PEC photocurrent generation.

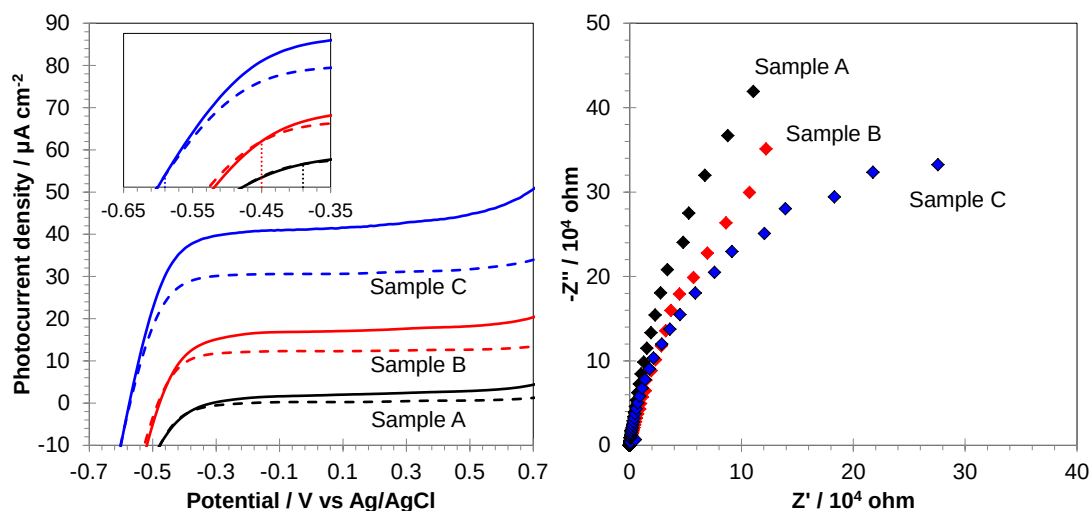


Figure 6.4. (a) I-V curves under dark (dashed line) and light (full line) conditions with a scan rate of 0.02 Vs^{-1} and (b) Nyquist plots of samples A, B, and C obtained in $0.1 \text{ M Na}_2\text{SO}_4$ solution. The inset in panel a illustrates the magnified view of the I-V curves showing the onset potential of each sample.

The charge transfer efficiency of the photoanode is determined by both the electrons and holes, whereby the former migrate to the BiVO₄/FTO interface to be drawn off as current and the latter to the BiVO₄/electrolyte interface to conduct water oxidation reaction. The possibility of hole transfer as the limiting factor of the charge transfer efficiency of a photoanode can be eradicated by the addition of a hole scavenger. Figure 6.5 compares the I-V curves of all BiVO₄ photoanodes obtained with and without methanol (hole scavenger) addition. Consistent with that reported in the literature,^{6, 42} significant improvement of photocurrent and negative shift of onset potential were observed for each sample in the presence of the hole-scavenging methanol as compared to that measured in the absence of methanol. Importantly, in the presence of methanol, BiVO₄ with smaller particle size also exhibits higher photocurrent density as well as lower saturation and onset potentials, similar to that observed in the absence of methanol. The results thus infer electron transfer as the governing factor of the improved charge transfer ability of BiVO₄ photoanode with smaller particle size.

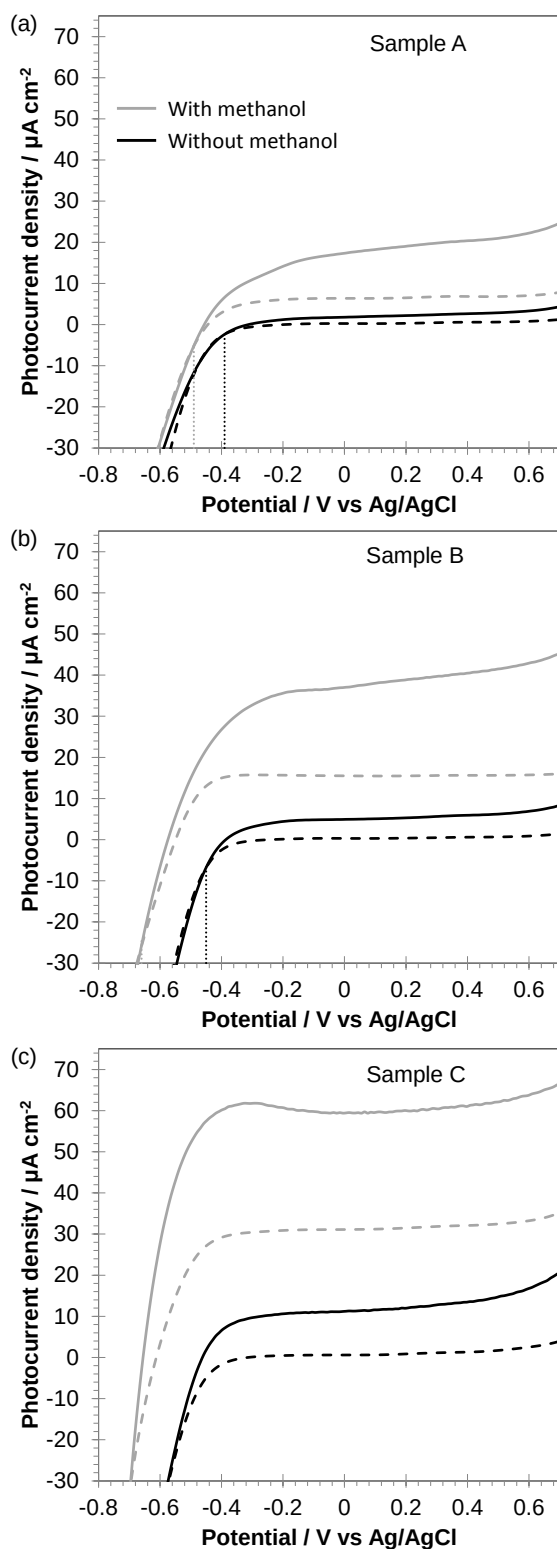


Figure 6.5. Comparison of the I-V curves of (a) sample A, (b) sample B, and (c) sample C under dark (dashed line) and light (full line) conditions with a scan rate of 0.02 Vs^{-1} in $0.1 \text{ M Na}_2\text{SO}_4$ without additives (black lines) and after addition of 10 vol % methanol (gray lines).

6.3.4. Effect of Particle Size on Interparticle and Particle/FTO Contacts in BiVO₄ Particulate Electrode

Given that the photogenerated electrons have to be transported to the back conducting substrate at the photoanode to be drawn off as current, the nature of the interparticle contacts as well as the contact between the particles and the substrate are the key features controlling the electron transport properties of the photoanode and thus the electron transfer efficiency at the particle/substrate interface.³⁰ With respect to these aspects, the cross sections of sample A, B, and C on FTO substrates were observed under SEM and the corresponding images are displayed in Figure 6.6. At a lower magnification, void spaces can be observed within the network of sample A particles (Figure 6.6a). The size of these void spaces shrinks as the BiVO₄ particle size decreases, as depicted by the sample B electrode in Figure 6.6b and sample C electrode in Figure 6.6c, suggesting a more compact particle network and better interparticle contacts with the presence of smaller particles. At a higher magnification focusing on the BiVO₄/FTO interface, the contact of sample A particles and the FTO substrate (Figure 6.6d) is evidently poor due to stacking up of the large particles. Such BiVO₄/FTO contact is improved in sample B and C electrodes (Figure 6.6e,f, respectively). Because of the comparable size of sample C particles with the rough surface of the FTO substrate, elemental energy-dispersive X-ray spectroscopy (EDS) mapping (Figure 6.7) was carried out to aid in identifying the interface between sample C particles with the FTO substrate, as outlined in Figure 6.6f. Clearly, sample C particles with the smallest size are uniformly distributed on the FTO substrate, establishing the most intimate contact with the substrate compared to the other two samples. The SEM images of the BiVO₄/FTO interfaces provide compelling evidence that the superior PEC performance of BiVO₄ with smaller particle sizes arises from the improved BiVO₄ particles contact

with the electron collecting FTO substrate on top of the enriched interparticle contacts. These contacts ensure effective interparticle charge transport and thus efficient collection of photogenerated electrons at the FTO back substrate to render higher photocurrent generation.

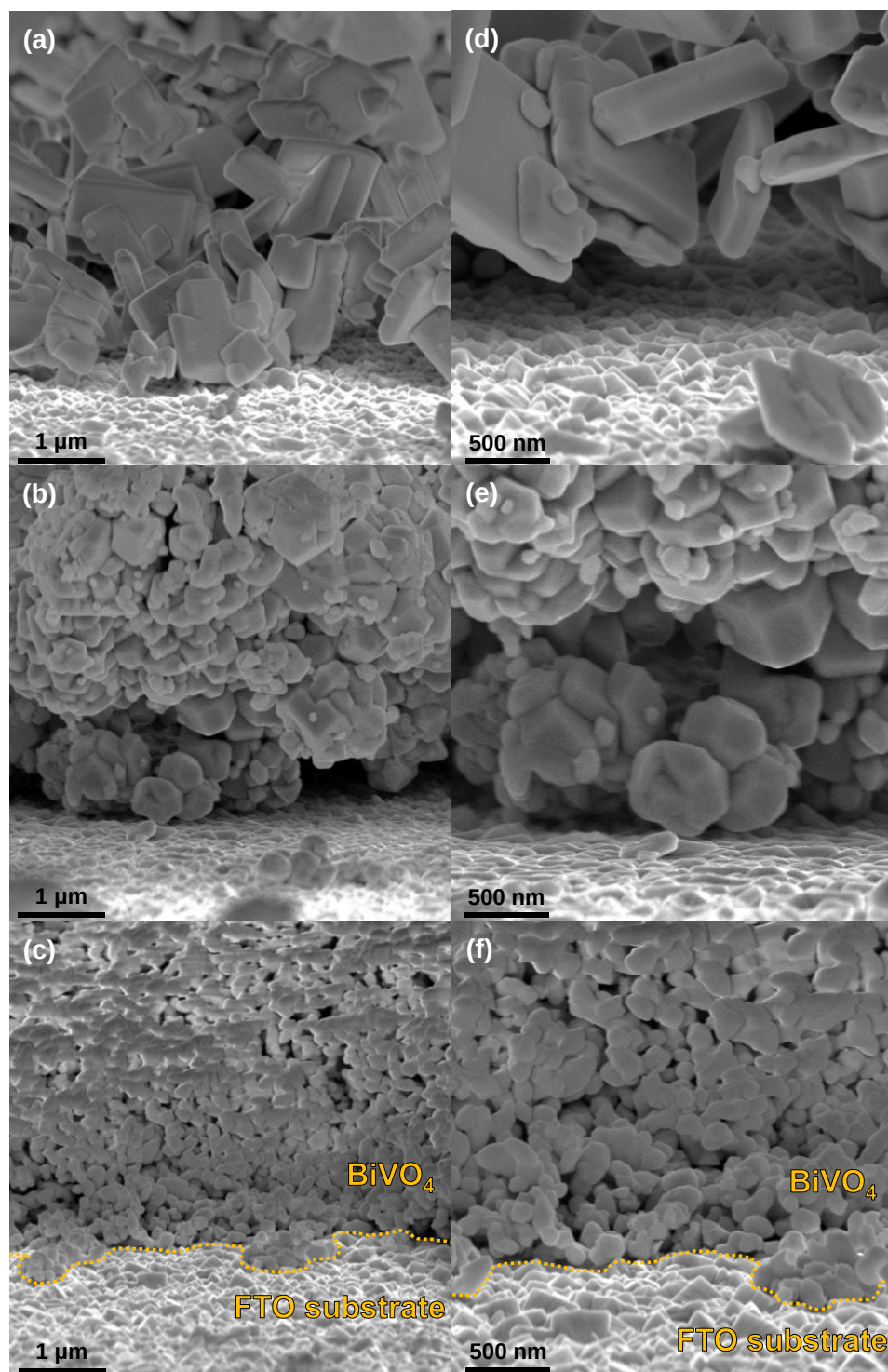


Figure 6.6. SEM images of the cross sections of (a) sample A, (b) sample B, and (c) sample C BiVO_4 particles on FTO conducting glass. (d-f) Higher magnification of the SEM images of sample A, B, and C interfaces with FTO, respectively.

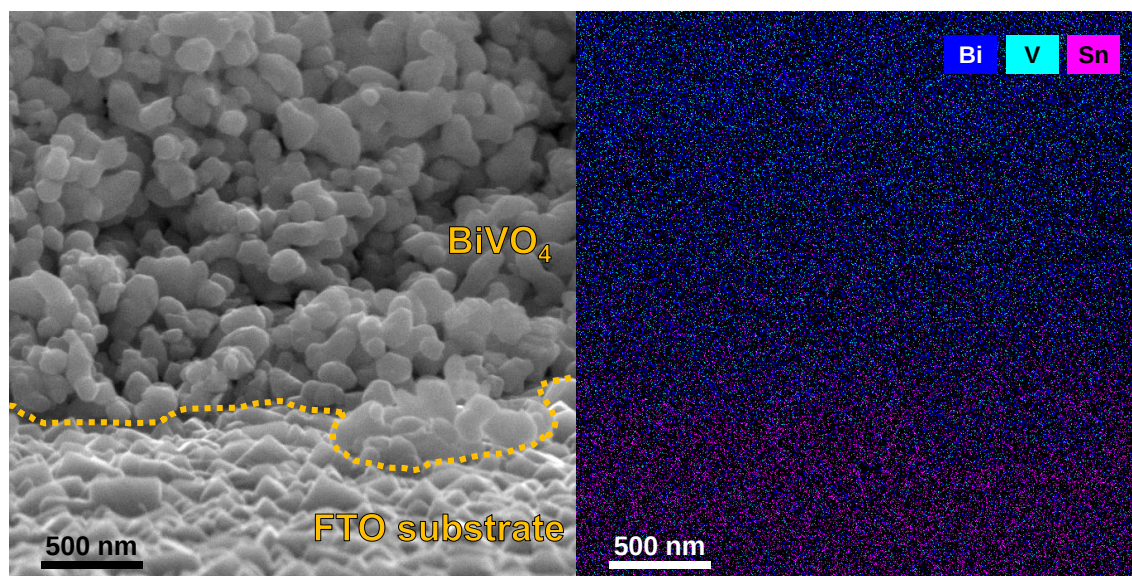


Figure 6.7. SEM image of the cross-section of BiVO₄ particles (sample C) on the FTO substrate and the corresponding EDS mapping of the Bi, V and Sn elements. The interface of BiVO₄ and FTO can be clearly identified as the FTO substrate is Sn-rich, while the BiVO₄ particles are recognized as the area rich in Bi and V elements.

6.3.5. Photocatalytic O₂ Evolution

To delve into the reactivity of the three BiVO₄ samples with different particle sizes in PS system, we carried out a separate activity test was carried out for water oxidation from aqueous silver nitrate (AgNO₃) solution under visible light (of wavelength, $\lambda > 420$ nm) illumination, in which Ag⁺ ions were the electron scavenger. Figure 6.8 illustrates the amount of O₂ generated as a function of time for each sample normalized in relation to per m² of surface area. Sample A unambiguously exhibits the highest activity with the fastest O₂ evolution rate followed by sample B and C. Substantial amount of O₂ was generated by sample A and B (925 $\mu\text{mol m}^{-2}$ and 268 $\mu\text{mol m}^{-2}$, respectively, over 3 h of illumination) except for sample C with an amount of merely 19 $\mu\text{mol m}^{-2}$, indicating larger BiVO₄ particles are beneficial for PS water oxidation activity. This observed trend of O₂ evolution activities of the suspended BiVO₄ particles

(sample C < sample B < sample A) is in stark contrast to their tendency in the PEC system (sample A < sample B < sample C).

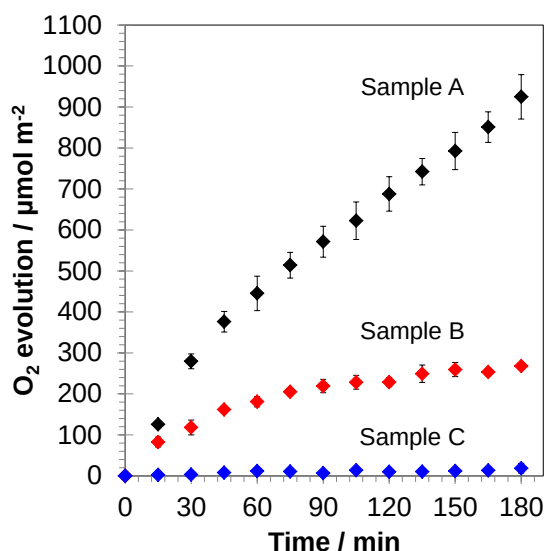


Figure 6.8. Time profiles of surface-specific O₂ evolution from aqueous AgNO₃ solution for sample A, B, and C, under visible light (of wavelength, $\lambda > 420$ nm) illumination. Every data point was an average of 3 experimental runs with the error bar corresponding to standard deviation.

6.3.6. Different Governing Factors in Powder Suspension and Photoelectrochemical Systems

The opposing behaviors of PEC and PS photoactivity dependence on the particle size of BiVO₄ indicate different governing factors in the two systems, as schematically depicted in Figure 6.9. Despite having more surface recombination centers arising from the higher density of surface defect sites, BiVO₄ particulate photoanode with smaller particles was shown to have better PEC performance. This is attributed to the presence of an externally applied potential to facilitate charge separation in the PEC system, in which the performance of the BiVO₄ photoanode is predominated by its charge transport properties. Smaller BiVO₄ particles immobilized on FTO substrate were found

to have shorter interparticle distance (i.e., enriched interparticle contacts) and better particle/FTO contact, allowing efficient interparticle charge transport and electron collection efficiency at the substrate to result in an enhanced PEC photocurrent. In contrast, the increased photocatalytic O₂ evolution activity for suspended BiVO₄ with larger particle size demonstrates charge separation as the key issue in the PS system rather than charge transport. The charge separation of a suspended photocatalyst is mainly dependent on the SCL formation. A thicker SCL is typically developed in larger particles to induce greater band bending beneficial for electron-hole pairs separation.⁴³ In nanoparticle where its size is smaller than the SCL thickness, the resulting SCL and band bending are negligible. In fact, significantly higher photocatalytic water oxidation activity of large rutile TiO₂ particles in comparison to that of small anatase particles has been attributed by Ohno et al. to the presence of band bending in the large particles.⁴⁴⁻⁴⁵ Additionally, the photogenerated electrons and holes have to be present on the surface of the same particle to conduct redox reactions on the suspended photocatalyst in the PS system. These electron-hole pairs are prone to recombination at the surface defects, which was shown to be particularly rich on the surfaces of small BiVO₄ particles with low crystallinity. The presence of band bending and fewer surface defects in large particle thus signifies enhanced charge separation to improve photocatalytic O₂ evolution.

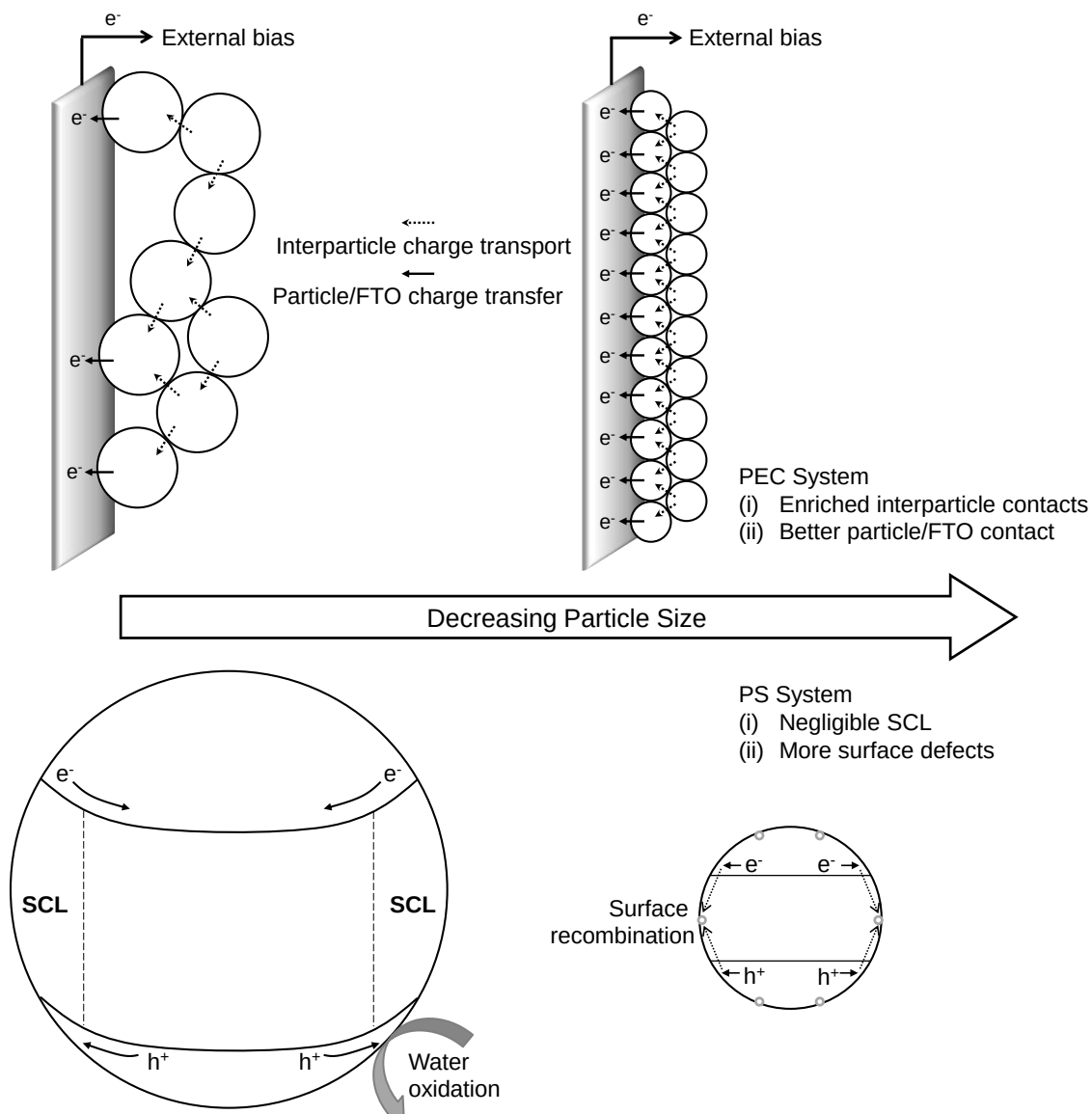


Figure 6.9. Schematic of the different roles of particle size in governing the photoactivity of BiVO_4 in PEC and PS systems, at which the former is predominated by charge transport properties and the latter is dominated by charge separation efficiency. SCL denotes the space charge layer.

6.4. Summary

Nanoscaling was demonstrated to render opposite effects in the water photooxidation activity of BiVO₄ particles via PEC and PS systems. Specifically, improved PEC photocurrent generation was observed as the size of the BiVO₄ particles immobilized on the photoanode decreased. SEM images illustrated enriched interparticle contacts and better contact between the particles and the FTO substrate in the presence of BiVO₄ with smaller particle size, resulting in better charge transport and charge collection efficiency that were supported by the EIS results. On the other hand, the photocatalytic O₂ evolution activity of the suspended BiVO₄ particles deteriorated with decreased particle size due to the loss of crystallinity and band bending necessary for charge separation. This work elucidates that the water oxidation efficiency in the PEC and PS systems relies on different key issues, namely, charge transport and charge separation. While particulate electrode composed of nanosized BiVO₄ particles is needed for improved PEC performance, faceted BiVO₄ microcrystals show better prospect for greater water oxidation activity in the PS system.

6.5. References

1. Sayama, K.; Mukasa, K.; Abe, R.; Abe, Y.; Arakawa, H., A New Photocatalytic Water Splitting System Under Visible Light Irradiation Mimicking a Z-Scheme Mechanism in Photosynthesis. *J. Photochem. Photobiol., A* **2002**, *148* (1), 71-77.
2. Kato, H.; Hori, M.; Kato, R.; Shimodaira, Y.; Kudo, A., Construction of Z-Scheme Type Heterogeneous Photocatalysis Systems for Water Splitting into H₂ and O₂ under Visible Light Irradiation. *Chem. Lett.* **2004**, *33* (10), 1348-1349.
3. Iwase, A.; Ng, Y. H.; Ishiguro, Y.; Kudo, A.; Amal, R., Reduced Graphene Oxide as a Solid-State Electron Mediator in Z-Scheme Photocatalytic Water Splitting under Visible Light. *J. Am. Chem. Soc.* **2011**, *133* (29), 11054-11057.
4. Maeda, K., Z-Scheme Water Splitting using Two Different Semiconductor Photocatalysts. *ACS Catal.* **2013**, *3* (7), 1486-1503.
5. Kudo, A.; Omori, K.; Kato, H., A Novel Aqueous Process for Preparation of Crystal Form-Controlled and Highly Crystalline BiVO₄ Powder from Layered Vanadates at Room Temperature and Its Photocatalytic and Photophysical Properties. *J. Am. Chem. Soc.* **1999**, *121* (49), 11459-11467.
6. Sayama, K.; Nomura, A.; Arai, T.; Sugita, T.; Abe, R.; Yanagida, M.; Oi, T.; Iwasaki, Y.; Abe, Y.; Sugihara, H., Photoelectrochemical Decomposition of Water into H₂ and O₂ on Porous BiVO₄ Thin-Film Electrodes under Visible Light and Significant Effect of Ag Ion Treatment. *J. Phys. Chem. B* **2006**, *110* (23), 11352-11360.
7. Kudo, A.; Ueda, K.; Kato, H.; Mikami, I., Photocatalytic O₂ Evolution under Visible Light Irradiation on BiVO₄ in Aqueous AgNO₃ Solution. *Catal. Lett.* **1998**, *53* (3-4), 229-230.

8. Tokunaga, S.; Kato, H.; Kudo, A., Selective Preparation of Monoclinic and Tetragonal BiVO₄ with Scheelite Structure and Their Photocatalytic Properties. *Chem. Mater.* **2001**, *13* (12), 4624-4628.
9. Sayama, K.; Nomura, A.; Zou, Z.; Abe, R.; Abe, Y.; Arakawa, H., Photoelectrochemical Decomposition of Water on Nanocrystalline BiVO₄ Film Electrodes under Visible Light. *Chem. Commun.* **2003**, (23), 2908-2909.
10. Liang, Y.; Tsubota, T.; Mooij, L. P.; van de Krol, R., Highly Improved Quantum Efficiencies for Thin Film BiVO₄ Photoanodes. *J. Phys. Chem. C* **2011**, *115* (35), 17594-17598.
11. Abdi, F. F.; Firet, N.; van de Krol, R., Efficient BiVO₄ Thin Film Photoanodes Modified With Cobalt Phosphate Catalyst and W - Doping. *ChemCatChem* **2013**, *5* (2), 490-496.
12. Kim, T. W.; Choi, K.-S., Nanoporous BiVO₄ Photoanodes with Dual-Layer Oxygen Evolution Catalysts for Solar Water Splitting. *Science* **2014**, *343* (6174), 990-994.
13. Luo, W.; Yang, Z.; Li, Z.; Zhang, J.; Liu, J.; Zhao, Z.; Wang, Z.; Yan, S.; Yu, T.; Zou, Z., Solar Hydrogen Generation from Seawater with a Modified BiVO₄ Photoanode. *Energy Environ. Sci.* **2011**, *4* (10), 4046-4051.
14. McDonald, K. J.; Choi, K.-S., A New Electrochemical Synthesis Route for a BiOI Electrode and its Conversion to a Highly Efficient Porous BiVO₄ Photoanode for Solar Water Oxidation. *Energy Environ. Sci.* **2012**, *5* (9), 8553-8557.
15. Seabold, J. A.; Zhu, K.; Neale, N. R., Efficient Solar Photoelectrolysis by Nanoporous Mo: BiVO₄ through Controlled Electron Transport. *Phys. Chem. Chem. Phys.* **2014**, *16* (3), 1121-1131.

16. Abdi, F. F.; van de Krol, R., Nature and Light Dependence of Bulk Recombination in Co-Pi-Catalyzed BiVO₄ Photoanodes. *J. Phys. Chem. C* **2012**, *116* (17), 9398-9404.
17. Wang, D.; Li, R.; Zhu, J.; Shi, J.; Han, J.; Zong, X.; Li, C., Photocatalytic Water Oxidation on BiVO₄ with the Electrocatalyst as an Oxidation Cocatalyst: Essential Relations between Electrocatalyst and Photocatalyst. *J. Phys. Chem. C* **2012**, *116* (8), 5082-5089.
18. Zhong, D. K.; Choi, S.; Gamelin, D. R., Near-Complete Suppression of Surface Recombination in Solar Photoelectrolysis by “Co-Pi” Catalyst-Modified W: BiVO₄. *J. Am. Chem. Soc.* **2011**, *133* (45), 18370-18377.
19. Pilli, S. K.; Furtak, T. E.; Brown, L. D.; Deutsch, T. G.; Turner, J. A.; Herring, A. M., Cobalt-Phosphate (Co-Pi) Catalyst Modified Mo-Doped BiVO₄ Photoelectrodes for Solar Water Oxidation. *Energy Environ. Sci.* **2011**, *4* (12), 5028-5034.
20. Seabold, J. A.; Choi, K.-S., Efficient and Stable Photo-Oxidation of Water by a Bismuth Vanadate Photoanode Coupled with an Iron Oxyhydroxide Oxygen Evolution Catalyst. *J. Am. Chem. Soc.* **2012**, *134* (4), 2186-2192.
21. Yao, W.; Iwai, H.; Ye, J., Effects of Molybdenum Substitution on the Photocatalytic Behavior of BiVO₄. *Dalton Trans.* **2008**, (11), 1426-1430.
22. Luo, W.; Li, Z.; Yu, T.; Zou, Z., Effects of Surface Electrochemical Pretreatment on the Photoelectrochemical Performance of Mo-Doped BiVO₄. *J. Phys. Chem. C* **2012**, *116* (8), 5076-5081.
23. Abdi, F. F.; Han, L.; Smets, A. H. M.; Zeman, M.; Dam, B.; van de Krol, R., Efficient Solar Water Splitting by Enhanced Charge Separation in a Bismuth Vanadate-Silicon Tandem Photoelectrode. *Nat. Commun.* **2013**, *4*, 2195.

24. Abdi, F. F.; Savenije, T. J.; May, M. M.; Dam, B.; van de Krol, R., The Origin of Slow Carrier Transport in BiVO₄ Thin Film Photoanodes: A Time-Resolved Microwave Conductivity Study. *J. Phys. Chem. Lett.* **2013**, 4 (16), 2752-2757.
25. Rao, P. M.; Cai, L.; Liu, C.; Cho, I. S.; Lee, C. H.; Weisse, J. M.; Yang, P.; Zheng, X., Simultaneously Efficient Light Absorption and Charge Separation in WO₃/BiVO₄ Core/Shell Nanowire Photoanode for Photoelectrochemical Water Oxidation. *Nano Lett.* **2014**, 14 (2), 1099-1105.
26. Osterloh, F. E., Nanoscale Effects in Water Splitting Photocatalysis. In *Solar Energy for Fuels*, Springer International Publishing: **2015**, pp 105-142.
27. Newton, K. A.; Osterloh, F. E., Size and Morphology of Suspended WO₃ Particles Control Photochemical Charge Carrier Extraction and Photocatalytic Water Oxidation Activity. *Top. Catal.* **2016**, 1-7.
28. Hong, S. J.; Jun, H.; Borse, P. H.; Lee, J. S., Size Effects of WO₃ Nanocrystals for Photooxidation of Water in Particulate Suspension and Photoelectrochemical Film Systems. *Int. J. Hydrogen Energy* **2009**, 34 (8), 3234-3242.
29. Kho, Y. K.; Teoh, W. Y.; Iwase, A.; Madler, L.; Kudo, A.; Amal, R., Flame Preparation of Visible-Light-Responsive BiVO₄ Oxygen Evolution Photocatalysts with Subsequent Activation via Aqueous Route. *ACS Appl. Mater. Interfaces* **2011**, 3 (6), 1997-2004.
30. Iwase, A.; Kudo, A., Photoelectrochemical Water Splitting using Visible-Light-Responsive BiVO₄ Fine Particles Prepared in an Aqueous Acetic Acid Solution. *J. Mater. Chem.* **2010**, 20 (35), 7536-7542.
31. Li, R.; Zhang, F.; Wang, D.; Yang, J.; Li, M.; Zhu, J.; Zhou, X.; Han, H.; Li, C., Spatial Separation of Photogenerated Electrons and Holes Among {010} and {110} Crystal Facets of BiVO₄. *Nat. Commun.* **2013**, 4, 1432.

32. Iwase, A.; Kato, H.; Kudo, A., A Simple Preparation Method of Visible-Light-Driven BiVO₄ Photocatalysts from Oxide Starting Materials (Bi₂O₃ and V₂O₅) and Their Photocatalytic Activities. *J. Sol. Energy Eng.* **2010**, *132* (2), 021106.
33. Ng, Y. H.; Iwase, A.; Kudo, A.; Amal, R., Reducing Graphene Oxide on a Visible-Light BiVO₄ Photocatalyst for an Enhanced Photoelectrochemical Water Splitting. *J. Phys. Chem. Lett* **2010**, *1* (17), 2607-2612.
34. Su, J.; Zou, X.-X.; Li, G.-D.; Wei, X.; Yan, C.; Wang, Y.-N.; Zhao, J.; Zhou, L.-J.; Chen, J.-S., Macroporous V₂O₅-BiVO₄ Composites: Effect of Heterojunction on the Behavior of Photogenerated Charges. *J. Phys. Chem. C* **2011**, *115* (16), 8064-8071.
35. Singh, A. P.; Kodan, N.; Dey, A.; Krishnamurthy, S.; Mehta, B. R., Improvement in the Structural, Optical, Electronic and Photoelectrochemical Properties of Hydrogen Treated Bismuth Vanadate Thin Films. *Int. J. Hydrogen Energy* **2015**, *40* (12), 4311-4319.
36. Citrin, P. H.; Wertheim, G.; Baer, Y., Core-level Binding Energy and Density of States from the Surface Atoms of Gold. *Phys. Rev. Lett.* **1978**, *41* (20), 1425.
37. McCafferty, E.; Wightman, J., Determination of the Concentration of Surface Hydroxyl Groups on Metal Oxide Films by a Quantitative XPS Method. *Surf. Interface Anal.* **1998**, *26* (8), 549-564.
38. Berglund, S. P.; Rettie, A. J.; Hoang, S.; Mullins, C. B., Incorporation of Mo and W into Nanostructured BiVO₄ Films for Efficient Photoelectrochemical Water Oxidation. *Phys. Chem. Chem. Phys.* **2012**, *14* (19), 7065-7075.
39. Bluhm, H., Photoelectron Spectroscopy of Surfaces under Humid Conditions. *J. Electron. Spectrosc. Relat. Phenom.* **2010**, *177* (2), 71-84.

40. Wang, G.; Wang, H.; Ling, Y.; Tang, Y.; Yang, X.; Fitzmorris, R. C.; Wang, C.; Zhang, J. Z.; Li, Y., Hydrogen-Treated TiO₂ Nanowire Arrays for Photoelectrochemical Water Splitting. *Nano Lett.* **2011**, *11* (7), 3026-3033.
41. Ng, C.; Iwase, A.; Ng, Y. H.; Amal, R., Transforming Anodized WO₃ Films into Visible-Light-Active Bi₂WO₆ Photoelectrodes by Hydrothermal Treatment. *J. Phys. Chem. Lett.* **2012**, *3* (7), 913-918.
42. Santato, C.; Ulmann, M.; Augustynski, J., Photoelectrochemical Properties of Nanostructured Tungsten Trioxide Films. *J. Phys. Chem. B* **2001**, *105* (5), 936-940.
43. Zhang, Z.; Yates Jr, J. T., Band Bending in Semiconductors: Chemical and Physical Consequences at Surfaces and Interfaces. *Chem. Rev.* **2012**, *112* (10), 5520-5551.
44. Fujihara, K.; Izumi, S.; Ohno, T.; Matsumura, M., Time-Resolved Photoluminescence of Particulate TiO₂ Photocatalysts Suspended in Aqueous Solutions. *J. Photochem. Photobiol., A* **2000**, *132* (1), 99-104.
45. Ohno, T.; Sarukawa, K.; Matsumura, M., Crystal Faces of Rutile and Anatase TiO₂ Particles and Their Roles in Photocatalytic Reactions. *New J. Chem.* **2002**, *26* (9), 1167-1170.

Chapter 7

Conclusion & Recommendations

7.1. Conclusion

The three key steps related to charge kinetics (i.e., charge separation, transport, and transfer) of BiVO_4 were determined to be reliant on the surface and bulk properties of the material. They include the exposed facets, crystallinity, introduction of mid gap states, and particle size. While strategies such as morphology control and post-synthesis treatment have been shown to be effective in improving the photocatalytic performance of BiVO_4 , they are often found to have limited capabilities in targeting simultaneous enhancement toward all three aspects of charge kinetics that are complementary. It is hereby demonstrated the potential concurrent optimization of all three steps via a combination of multiple strategies.

The influence of exposed crystal facets on the charge transfer efficiency of BiVO_4 was first probed using dual-faceted BiVO_4 particles with distinctly different relative exposure extents of $\{010\}$ and $\{110\}$ facets. The two facets have been proven to be the respective active reduction and oxidation functional facets of BiVO_4 due to spatial separation of photogenerated electrons and holes. However, the BiVO_4 with dominating $\{010\}$ reduction functional facets outperformed the $\{110\}$ -dominant BiVO_4 in photooxidation reactions (i.e., photocatalytic water oxidation and 2,4-dichlorophenoxyacetic acid degradation). Steady-state PL measurements (in the

presence of charge scavengers) revealed that the population of photogenerated electrons and holes on the surface are proportional to the respective surface areas of {010} and {110} exposed on BiVO₄; {010}-dominant BiVO₄ has relatively more electrons than holes available on the surface, while {110}-dominant BiVO₄ surface has more holes than electrons. On the other hand, time-resolved PL analysis and flat band potential estimation based on Mott-Schottky relationship suggested that a greater extent of electron trapping is present in the {110}-dominant BiVO₄. This was attributed to the longer distance electrons have to diffuse from the bulk of the thick {110}-dominant BiVO₄ particle to the {010} surface, increasing the probability of electrons being trapped in the defects along the way. With the restricted numbers of electrons on the small {010} surface and greater degree of electron trapping, the inefficient electron extraction led to increased charge recombination, which resulted in poor photooxidation activities of {110}-dominant BiVO₄ despite the presence of large oxidation functional surface. This study shows that enlargement of {010} facets is essential to facilitate electron transfer, not only for effective photoreduction reactions, but also to improve photooxidation efficiency.

The dual-faceted BiVO₄ particles with different relative exposure extents of {010}/{110} facets were subsequently coupled with RGO to examine the crystal facet dependence of charge transfer between BiVO₄ and RGO. RGO has been widely reported as a good electron mediator to suppress charge recombination in photocatalysts. In the present thesis, the PEC photocurrents of all BiVO₄ samples were observed to be enhanced after incorporation of RGO, consistent with literature findings. Although the overall photocurrents of the RGO-BiVO₄ samples were lower than that reported in the literature due to the significantly larger BiVO₄ microcrystals, the extent of enhancement was

found to correlate with the exposure extent of {010} on BiVO₄. EIS measurements indicated that the greater extent of enhancement in RGO-BiVO₄ is aroused from the decrease in charge transfer resistance, indicating the beneficial role of {010} facets to expedite electron transfer from BiVO₄ to RGO. DFT calculations were also performed to determine the difference in electronic properties between graphene/BiVO₄{010} and graphene/BiVO₄{110} interfaces. It was predicted that the former interface has metallic characteristics with smaller Schottky barrier and higher binding energy than the latter semiconductive interface, supporting that electron transfer between BiVO₄ and RGO is favorable through the {010} facets of BiVO₄.

Although the charge transfer efficiency of the dual-faceted BiVO₄ can be controlled by manipulating the relative exposure extent of {010}/{110}, the charge transport aspect of the material remained unaltered. The ability of annealing, particularly in oxygen-deficient Ar environment, as post-synthesis treatment to overcome the charge transport limitation and optimize the charge separation efficiency of the faceted BiVO₄ was then investigated. The photoactivities of the faceted BiVO₄ for photocatalytic O₂ evolution and PEC photocurrent were shown to be affected by Ar annealing in the temperature range of 300 – 700 °C. SPS measurements showed that the higher temperature treatment (both 500 and 700 °C) favor formation of new sub gap states, which were confirmed to be oxygen vacancies (i.e., shallow donors that have been widely reported to effectively improve electron transport in BiVO₄) using EPR analysis. Additionally, XRD, Raman, and UV-vis spectroscopy analyses revealed that while treatment at 300 °C has little to no effect, higher temperatures of 500 and 700 °C also enhance the crystallinity, induce greater local structure distortion, and reduce the band gap energy, all of which are advantageous for charge separation in the treated BiVO₄. However, it was shown here

that the charge separation, transport, and photoactivity of the faceted BiVO_4 are optimized by Ar treatment at 500 °C. Further increase of the temperature to 700 °C was found to be undesirable due to diminution of well-developed facets and creation of surface bismuth vacancies, which are detrimental for charge separation.

Lastly, the effect of particle size on the water oxidation activity of BiVO_4 in powder suspension (PS) and PEC systems, which are the two approaches commonly employed for water splitting reaction, was explored by comparing the performance of the faceted BiVO_4 microcrystal with two other BiVO_4 particles of smaller size. While water oxidation in PS system (known as photocatalytic O_2 evolution) was quantified by the amount of O_2 being produced, the performance of water oxidation at the photoanode in the PEC system was evaluated by the magnitude of the photocurrent being generated. Particle size of BiVO_4 was shown to have opposing effect on its photoactivity in the PS and PEC systems. Large BiVO_4 particles were found to improve O_2 generation owing to the higher crystallinity and the presence of band bending to render a built-in electric field, both of which are essential for efficient charge separation in the PS system (without the assistance from an externally applied potential). In contrast, small BiVO_4 particles were shown to generate higher photocurrent, attributing the shorter interparticle distance to facilitate charge transport and better particle/FTO contact for improved electron collection efficiency of the particulate electrode.

In summary, this thesis reveals that while the charge transfer efficiency of dual-faceted BiVO_4 can be facilitated by the enlargement of $\{010\}$ facets, simultaneous improvements of the charge transport and separation aspects of the material can be achieved via Ar annealing. The water oxidation performance of the micro-sized faceted BiVO_4 was also found to surpass those of smaller BiVO_4 particles in the PS system.

Despite the microscale particle size which could have been envisaged as the major limitation of the charge transport and transfer efficiencies of the faceted BiVO_4 , it is hereby shown to have the best performance for water oxidation in the PS system due to effective charge separation.

7.2. Recommendations

7.2.1. Dual-Faceted BiVO_4 : Further Studies, Material Optimization and Potential Application

The results of this work demonstrated the potential of crystal facet engineering to enhance the charge transfer efficiency of BiVO_4 . While manipulation of the relative exposure extent of $\{010\}$ and $\{110\}$ facets exposed on BiVO_4 was found to affect the surface population of photogenerated charge carriers, enlargement of $\{010\}$ surface was revealed to be advantageous for facilitating electron transfer that is essential for both photoreduction and photooxidation reactions. The exposure extent of $\{010\}/\{110\}$ facets on BiVO_4 was also shown to impact on its interfacial charge interactions with RGO, in which electron transfer from BiVO_4 to RGO is favorable through the $\{010\}$ surface relative to the $\{110\}$. These intriguing results thus warrant further investigation on this material with potential optimization and applications as elaborated as follows.

Comparison of the time-resolved fluorescence lifetimes and fermi levels (based on flat band potentials) between $\{110\}$ -dominant BiVO_4 and $\{010\}$ -dominant BiVO_4 in Chapter 3 suggested that a greater extent of electron trapping is present in the former. The difference in carrier dynamics between the two BiVO_4 samples could be further verified using other techniques. Electron trapping affects the charge separation, charge carrier mobility and charge lifetime of the material. Surface photovoltage spectroscopy

(SPS) that was employed in Chapter 5 can potentially be used to reveal the charge transfer direction associated with charge trapping and the difference in charge separation efficiency of the two BiVO_4 's. In terms of carrier mobility and lifetime quantifications, time-resolved microwave conductivity (TRMC) study that has been previously demonstrated by Abdi et al. on BiVO_4 can be conducted.¹ For better sensitivity however, optical-pump-terahertz (THz)-probe (OPTP) spectroscopy, which is a higher-frequency technique, is preferable. OPTP is not only capable of determining carrier mobility down to sub-picosecond timescales, it is also well-suited to probe the ultrafast charge trapping effect in photocatalysts.²

Given that $\{010\}$ surface was demonstrated to be beneficial for enhancing the photoactivity of BiVO_4 and its interfacial electron transfer ability with RGO, further study on faceted BiVO_4 is recommended to be focused on fabrication of BiVO_4 with extended $\{010\}$ exposed surface. To this end, the solid-liquid state reaction employed in this work for the synthesis of dual-faceted BiVO_4 with controllable $\{010\}/\{110\}$ relative exposure extent could potentially be explored to obtain thin BiVO_4 with highly exposed $\{010\}$ facets. Apart from being a green approach that produces zero byproducts, the solid-liquid state reaction is a favorable method because it is free of template and surfactant, both of which are generally needed to produce facet-controlled photocatalysts.³⁻⁷ For this purpose, understanding of the formation mechanisms of the BiVO_4 particles with respect to nitric acid concentration in the solid-liquid state reaction is needed. While the acid concentration may influence the dissolution and precipitation rate to govern the exposure extent of $\{010\}$ and $\{110\}$ facets on the resulting BiVO_4 particles, examination of the roles of NO_3^- anions in the crystal growth process of BiVO_4 may also be useful.

In Chapter 4, the RGO-BiVO₄ composite fabricated from photocatalytic reduction of GO using dual-faceted BiVO₄ was shown to have the RGO sheets randomly attached to the {010} and {110} facets of BiVO₄. Such random orientation of BiVO₄ particles on the RGO sheets would have undermined the interfacial charge transfer efficiency between the two components since electron transfer from BiVO₄ to graphene was revealed to be more effective from the {010} facets compared to from the {110} facets. Optimization of the RGO-BiVO₄ composite structure could thus be considered by selective attachment of RGO sheet to the {010} facets of BiVO₄. By exploiting the functionality of {010} facets as the electron accumulating sites of BiVO₄, the surface could be functionalized with functional groups via photoreduction approach. These functional groups are aimed to react with the various oxygen groups on GO such that the GO sheet is mainly attracted to the {010} surface of BiVO₄ prior to light illumination for RGO-BiVO₄ composite formation.

The demonstration of Ar annealing as a post-synthesis treatment to effectively improve the photoactivity of dual-faceted BiVO₄ in Chapter 5 highlighted the needs of using a combination of multiple strategies to optimize the performance of a photocatalyst. While crystal facet engineering is effective to improve the charge separation and transfer aspects of BiVO₄, charge transport remains as the major limitation of this material. Despite the proven efficacy of Ar annealing to enhance electron transport in dual-faceted BiVO₄ via oxygen vacancy formation, it is still necessary to explore other approaches to circumvent this limitation. One potential approach would be to introduce n-type dopants in the faceted BiVO₄. In this regards, W and Mo are recommended as the dopant candidates since they have been widely reported to be efficient in promoting electron transport in BiVO₄.⁸⁻¹²

Comparison of the water oxidation performances of dual-faceted BiVO₄ microcrystals and smaller BiVO₄ particles in the powder suspension system has also validated the superiority of the faceted BiVO₄ particles (Chapter 6). As mentioned in Chapter 2 (Literature Review), the functionality of BiVO₄ as the O₂-evolving photocatalyst in combination with Rh-doped SrTiO₃ or metal sulfides as the H₂-evolving photocatalyst has been demonstrated to achieve Z-scheme overall water splitting.¹³⁻¹⁸ Extending the application of the faceted BiVO₄ particles into Z-scheme system would be beneficial. One possible research area is to combine a selected H₂-evolving photocatalyst with BiVO₄ particles of different {010}/{110} relative exposure extents to gain insights into the crystal facet dependence of the charge interactions between the two photocatalysts. On the other hand, given that RGO can be used as a solid-state electron mediator, the functionality of the RGO-BiVO₄ composite with optimized structure as previously proposed can be compared with the RGO-BiVO₄ composite of randomly oriented BiVO₄ particles using the Z-scheme system.

7.3. References

1. Abdi, F. F.; Savenije, T. J.; May, M. M.; Dam, B.; van de Krol, R., The Origin of Slow Carrier Transport in BiVO₄ Thin Film Photoanodes: A Time-Resolved Microwave Conductivity Study. *J. Phys. Chem. Lett.* **2013**, *4* (16), 2752-2757.
2. Wang, F.; Jin, Z.; Jiang, Y.; Backus, E. H.; Bonn, M.; Lou, S. N.; Turchinovich, D.; Amal, R., Probing the Charge Separation Process on In₂S₃/Pt-TiO₂ Nanocomposites for Boosted Visible-Light Photocatalytic Hydrogen Production. *Appl. Catal., B* **2016**, *198*, 25-31.
3. Iwase, A.; Kato, H.; Kudo, A., A Simple Preparation Method of Visible-Light-Driven BiVO₄ Photocatalysts from Oxide Starting Materials (Bi₂O₃ and V₂O₅) and Their Photocatalytic Activities. *J. Sol. Energy Eng.* **2010**, *132* (2), 021106.
4. Zhang, L.; Chen, D.; Jiao, X., Monoclinic Structured BiVO₄ Nanosheets: Hydrothermal Preparation, Formation Mechanism, and Coloristic and Photocatalytic Properties. *J. Phys. Chem. B* **2006**, *110* (6), 2668-2673.
5. Yang, H. G.; Sun, C. H.; Qiao, S. Z.; Zou, J.; Liu, G.; Smith, S. C.; Cheng, H. M.; Lu, G. Q., Anatase TiO₂ Single Crystals with a Large Percentage of Reactive Facets. *Nature* **2008**, *453* (7195), 638-641.
6. Wang, D.; Jiang, H.; Zong, X.; Xu, Q.; Ma, Y.; Li, G.; Li, C., Crystal Facet Dependence of Water Oxidation on BiVO₄ Sheets under Visible Light Irradiation. *Chem. Eur. J.* **2011**, *17* (4), 1275-1282.
7. Pan, J.; Liu, G.; Lu, G. Q. M.; Cheng, H. M., On the True Photoreactivity Order of {001},{010}, and {101} Facets of Anatase TiO₂ Crystals. *Angew. Chem. Int. Ed.* **2011**, *50* (9), 2133-2137.

8. Zhong, D. K.; Choi, S.; Gamelin, D. R., Near-Complete Suppression of Surface Recombination in Solar Photoelectrolysis by “Co-Pi” Catalyst-Modified W: BiVO₄. *J. Am. Chem. Soc.* **2011**, *133* (45), 18370-18377.
9. Abdi, F. F.; Firet, N.; van de Krol, R., Efficient BiVO₄ Thin Film Photoanodes Modified With Cobalt Phosphate Catalyst and W - Doping. *ChemCatChem* **2013**, *5* (2), 490-496.
10. Abdi, F. F.; Han, L.; Smets, A. H. M.; Zeman, M.; Dam, B.; van de Krol, R., Efficient Solar Water Splitting by Enhanced Charge Separation in a Bismuth Vanadate-Silicon Tandem Photoelectrode. *Nat. Commun.* **2013**, *4*, 2195.
11. Luo, W.; Yang, Z.; Li, Z.; Zhang, J.; Liu, J.; Zhao, Z.; Wang, Z.; Yan, S.; Yu, T.; Zou, Z., Solar Hydrogen Generation from Seawater with a Modified BiVO₄ Photoanode. *Energy Environ. Sci.* **2011**, *4* (10), 4046-4051.
12. Pilli, S. K.; Furtak, T. E.; Brown, L. D.; Deutsch, T. G.; Turner, J. A.; Herring, A. M., Cobalt-Phosphate (Co-Pi) Catalyst Modified Mo-Doped BiVO₄ Photoelectrodes for Solar Water Oxidation. *Energy Environ. Sci.* **2011**, *4* (12), 5028-5034.
13. Kato, H.; Hori, M.; Kato, R.; Shimodaira, Y.; Kudo, A., Construction of Z-Scheme Type Heterogeneous Photocatalysis Systems for Water Splitting into H₂ and O₂ under Visible Light Irradiation. *Chem. Lett.* **2004**, *33* (10), 1348-1349.
14. Sasaki, Y.; Iwase, A.; Kato, H.; Kudo, A., The Effect of Co-Catalyst for Z-Scheme Photocatalysis Systems with an Fe³⁺/Fe²⁺ Electron Mediator on Overall Water Splitting under Visible Light Irradiation. *J. Catal.* **2008**, *259* (1), 133-137.
15. Sasaki, Y.; Kato, H.; Kudo, A., [Co(bpy)₃]^{3+/2+} and [Co(phen)₃]^{3+/2+} Electron Mediators for Overall Water Splitting under Sunlight Irradiation using Z-Scheme Photocatalyst System. *J. Am. Chem. Soc.* **2013**, *135* (14), 5441-5449.

16. Iwase, A.; Ng, Y. H.; Ishiguro, Y.; Kudo, A.; Amal, R., Reduced Graphene Oxide as a Solid-State Electron Mediator in Z-Scheme Photocatalytic Water Splitting under Visible Light. *J. Am. Chem. Soc.* **2011**, *133* (29), 11054-11057.
17. Sasaki, Y.; Nemoto, H.; Saito, K.; Kudo, A., Solar Water Splitting using Powdered Photocatalysts Driven by Z-Schematic Interparticle Electron Transfer without an Electron Mediator. *J. Phys. Chem. C* **2009**, *113* (40), 17536-17542.
18. Iwase, A.; Yoshino, S.; Takayama, T.; Ng, Y. H.; Amal, R.; Kudo, A., Water Splitting and CO₂ Reduction under Visible Light Irradiation Using Z-Scheme Systems Consisting of Metal Sulfides, CoOx-Loaded BiVO₄, and a Reduced Graphene Oxide Electron Mediator. *J. Am. Chem. Soc.* **2016**, *138* (32), 10260-10264.