

**Metal Oxide Based Thin Film Photoelectrodes
for Water Splitting**

BY

Amar Kamal Mohamedkhair Salih

A Dissertation Presented to the
DEANSHIP OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

DOCTOR OF PHILOSOPHY

In

PHYSICS

December, 2021

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

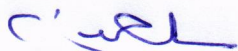
DHAHRAN- 31261, SAUDI ARABIA

DEANSHIP OF GRADUATE STUDIES

This thesis, written by **AMAR KAMAL MOHAMEDKHAIR SALIH** the direction of his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **DOCTOR OF PHILOSOPHY IN PHYSICS**.



Dr. Abdulaziz Husain M. Al-Aswad
Department Chairman

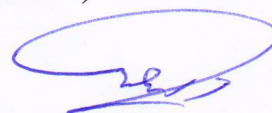


Prof. Suliman Saleh Al-Homidan
Dean of Graduate Studies

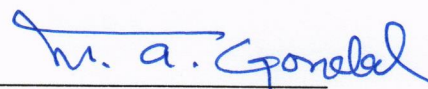
Date



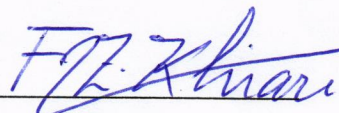
Prof. Zain H. Yamani
(Advisor)



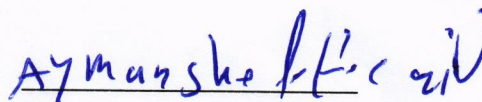
Dr. Qasem A. Drmosh
(Co. Advisor)



Prof. Mohamed A. Gondal
(Member)



Dr. Fatah Z. Khiari
(Member)



Dr. Ayman S. El-Said
(Member)

© Amar Kamal Mohamedkhair Salih

2021

This work is dedicated to my family

ACKNOWLEDGEMENTS

It has been a terrific four and a half years at KFUPM for me, and I have several people to thank for that. First of all, I would like to express my sincere gratitude to my advisor Prof. Zain H. Yamani, and Co-advisor, Dr. Qasem Drmash, for their guidance, enthusiasm, encouragement, and imparting their knowledge and expertise.

I would like to thank my committee members Prof. Mohammad A. Gondal, Dr. Ayman S. El-Said, and Dr. Fatah Z. Khiari, for their valuable assistance, guidance, and constructive feedback.

I want to express my sincere appreciation to Dr. Tarek Kandiel for his support.

I acknowledge King Fahd University of Petroleum and Minerals (KFUPM) and the Physics department for offering me this opportunity to accomplish my Ph.D. in physics and providing me the environment to achieve this level of study.

My appreciations also extend to the Interdisciplinary Research Centers for Hydrogen & Energy Storage (IRC-HES/previously CENT) team for their support and help.

Finally, I express my gratefulness to my parents, family, and friends for their endless love and supplication.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS.....	IV
TABLE OF CONTENTS.....	V
LIST OF FIGURES	VIII
ABSTRACT.....	XII
ملخص الرسالة.....	XIV
CHAPTER 1	1
INTRODUCTION	1
1.1 The Energy demand and global warming	1
1.2 Photoelectrochemical water splitting.....	2
1.2.1 Electron-hole recombination in semiconductor's photoanodes.....	5
1.2.2 The interface between semiconductor photoanode and electrolyte	5
1.2.3 The applied potential effects	6
1.2.4 The photocurrent at a semiconductor-electrolyte junction.....	8
1.2.5 Metal oxide semiconductors as photoanodes for photoelectron-chemical water splitting.....	11
CHAPTER 2	13
LITERATURE REVIEW	13
2.1 Tungsten oxide photoanodes.....	13
2.2 Bismuth vanadate photoanode	18
2.3 BiVO ₄ /WO ₃ heterostructure photoanode	21
2.4 The addition of oxygen evolution co-catalyst.....	22
2.5 Thesis outlines	24
CHAPTER 3	27
EXPERIMENTAL METHODS AND CHARACTERIZATION.....	27
3.1 Synthesis of the thin film photoanode.....	27
3.1.1 Sputtering Techniques.....	27
3.1.2 Preparation of W ₁₈ O ₄₉ Thin-Film Electrodes.....	29
3.1.3 Preparation of WO ₃ Thin-Film Electrodes.....	29
3.1.4 Preparation of Co–Pi/BiVO ₄ Thin-Film Electrodes.....	30
3.1.5 Preparation of Co–Pi/BiVO ₄ /WO ₃ Thin-Film Electrodes.....	31
3.2 Structural Characterization Techniques	33

3.2.1	X-ray Diffraction Analysis (XRD)	33
3.2.2	Field emission scanning electron microscopy and energy-dispersive X-ray spectroscopy (FE-SEM and EDS).....	34
3.2.3	X-ray photoelectron spectroscopy	36
3.2.4	Ultraviolet-visible spectroscopy (UV-Vis)	39
3.3	Photoelectrochemical measurements	42
3.3.1	Potentiostat.....	42
3.3.2	Photoelectrochemical measurements for $W_{18}O_{49}$ and WO_3 photoanodes.....	44
3.3.3	Photoelectrochemical measurements for Co–Pi/BiVO ₄ and Co–Pi/BiVO ₄ /WO ₃ photoanodes.	44
3.4	Theoretical calculation.....	46
3.4.1	Theoretical calculation of WO_x	48
3.4.2	Theoretical calculation of BiVO ₄	49
CHAPTER 4		50
	TUNGSTEN OXIDE PHOTOANODES.....	50
4.1	Structural, morphological, compositional, and optical analysis of $W_{18}O_{49}$ photoanode's films.....	51
4.1.1	XRD results of $W_{18}O_{49}$ photoanode's films	51
4.1.2	FE-SEM results of $W_{18}O_{49}$ photoanode's films	53
4.1.3	UV-Vis results of $W_{18}O_{49}$ photoanode's films.....	56
4.1.4	XPS results of $W_{18}O_{49}$ photoanode's films	58
4.2	Structural, morphological, compositional, and optical analysis of WO_3 photoanode's films.....	61
4.2.1	XRD results of WO_3 photoanode's films.....	61
4.2.2	FE-SEM results of WO_3 photoanode's films	64
4.2.3	UV-Vis results of WO_3 photoanode's films.....	68
4.2.4	XPS results of WO_3 photoanode's films.....	71
4.3	Band structure calculations of $W_{18}O_{49}$	73
4.4	Band structure calculations of WO_3	75
4.5	Photoelectrochemical measurements of $W_{18}O_{49}$ photoanode's films.	77
4.6	Photoelectrochemical measurements of WO_3 photoanode's films.	82
CHAPTER 5		88
	Co–Pi/BiVO ₄ PHOTOANODES	88
5.1	Structural, morphological, compositional, and optical analysis of Co–Pi/BiVO ₄ photoanode's films.....	88
5.1.1	XRD results of Co–Pi/BiVO ₄ photoanode's films.....	88

5.1.2	FE-SEM results of Co–Pi/BiVO ₄ photoanode’s films	91
5.1.3	UV-Vis results of Co–Pi/BiVO ₄ photoanode’s films.....	93
5.1.4	XPS results of Co–Pi/BiVO ₄ photoanode’s films	94
5.2	Band structure calculations of BiVO ₄	95
5.3	Photoelectrochemical measurements of Co–Pi/BiVO ₄ photoanode	96
5.4	Charge transfer mechanism of photo-induced charge carriers in Co–Pi/BiVO ₄ photoanodes	104
CHAPTER 6		106
Co–Pi/BiVO ₄ /WO ₃ PHOTOANODES		106
6.1	Structural, morphological, compositional, and optical analysis of Co–Pi/BiVO ₄ /WO ₃ photoanode’s films.....	106
6.1.1	XRD results of Co–Pi/BiVO ₄ /WO ₃ photoanode’s films.....	106
6.1.2	FE-SEM results of Co–Pi/BiVO ₄ /WO ₃ photoanode’s films	107
6.1.3	UV-Vis results of Co–Pi/BiVO ₄ /WO ₃ photoanode’s films.....	110
6.1.4	XPS results of Co–Pi/BiVO ₄ /WO ₃ photoanode’s films	111
6.2	Photoelectrochemical measurements of Co–Pi/BiVO ₄ /WO ₃ photoanode	113
6.3	Charge transfer mechanism of photo-induced charge carriers in Co–Pi/BiVO ₄ /WO ₃ photoanode.....	120
6.4	Theoretical calculation on charge transfer mechanism of photo-induced charge carriers in Co–Pi/BiVO ₄ /WO ₃ photoanode.....	122
CHAPTER 7		124
CONCLUSION.....		124
References.....		129
Vitae.....		149

LIST OF FIGURES

Figure 1.1. Photocurrent as a function of applied potential (J – V curves).	8
Figure 1.2. Band edges of some metal oxides materials are used as photoanodes for photoelectrochemical water splitting (adapted from [44])......	12
Figure 2.1. (a) An ideal cubic and (b) monoclinic structures of tungsten oxide crystal.	14
Figure 2.2. Monoclinic structure of bismuth vanadate.	19
Figure 2.3. Scanning electron microscopy images of BiVO ₄ films prepared via different fabrication methods [96].	20
28	
Figure 3.1 Photograph of the sputtering system (IRC-HES / KFUPM)	28
Figure 3.2. Photograph of the XRD unit (IRC-HES lab / KFUPM).....	34
Figure 3.3. A photograph of the FE-SEM instrument, IRC-HES imaging lab, KFUPM.	36
Figure 3.4. XPS photograph (Physics department / KFUPM).....	39
Figure 3.5. A photograph of the UV-Vis instrument located at IRC-HES lab, KFUPM.	41
Figure 4.0. Chopped-light stability test for tungsten oxide films prepared by (a) PLD and (b) sputtering deposition methods.	50
Figure 4.1. XRD patterns of the (a) W ₁₈ O ₄₉ films with varies thickness fabricated by post annealing of sputtered W film at 500 °C in air (b) metallic W film to W ₁₈ O ₄₉ phase transformation as a function of post annealing treatment.	53
Figure 4.2. FE-SEM images of W ₁₈ O ₄₉ films deposited for (a) 1, (b) 5, (c) 10, and (d) 20 min. and FE-SEM cross-section images of W ₁₈ O ₄₉ films deposited for (e) 1, (f) 5, (g) 10, and (h) 20 min. All the films were annealed at 500 °C in air.	55
Figure 4.3. Low and high magnification FE-SEM images of the W films annealed at (a) 100, (b) 200, (c) 300, (d) 400, (e) 500, and (f) 600 oC in air.	56
Figure 4.4. UV-Vis absorption spectra and band gap of W ₁₈ O ₄₉ films as a function of deposition time (a and b), and UV-Vis absorption spectra and Tacu's plot of W ₁₈ O ₄₉ films (c and d) fabricated by post-annealing of sputtered W films at 500 and 600 °C in air.	58
Figure 4.5. XPS spectra of: (a, b) the survey spectra, (c,d) W4f, and (e,f) O1s of the as-deposited and W ₁₈ O ₄₉ film fabricated by post annealing of sputtered W film at 500 °C in air.	60
Figure 4.6. XRD patterns of WO ₃ films: (a) annealed at different temperatures in air, the deposition time was 10 min, (b) prepared with different deposition times, annealed at 500 °C in air, and (c) annealed in vacuum and air, deposition time = 10 min and annealing temperature = 500 °C.	63

Figure 4.7. FESEM images of WO ₃ films: (a) as-deposited, and annealed at (b) 100, (c) 200, (d) 300, (e) 400, (f) 500, and (g) 600 °C in air, and (h) the film annealed at 500 °C in vacuum. All samples are deposited for 10 min.	66
Figure 4.8. FESEM images of WO ₃ films deposited for (a) 5, (b) 10, (c) 15, (d) 20 min, and their corresponding cross-section images (e) 5, (f) 10, (g) 15, (h) 20 min. All the films were annealed at 500 °C in air.....	67
Figure 4.9. UV-Vis absorption spectra of WO ₃ films as a function of (a) air annealing temperature, (c) deposition time, and (e) annealing atmosphere. Tauc's plot of WO ₃ films as (b) air annealing temperature, (d) deposition time, and (f) annealing atmosphere.	70
Figure 4.10. XPS spectra of (a, b, and c) survey scan, (d, e, and f) W 4f, and (g, h, and i) O 1s of the as-deposited, air-annealed (500 °C), and vacuum-annealed (500 °C) of WO ₃ films, respectively.....	72
Figure 4.11. (a) W ₁₈ O ₄₉ optimized structure, (b) W ₁₈ O ₄₉ band structure and DOS calculations using GGA-PBE functional, and (c) W ₁₈ O ₄₉ band structure calculation corrected by hybrid functional DFT.	74
Figure 4.12. (a) WO ₃ optimized structure, (b) WO ₃ band structure and DOS calculations using GGA-PBE functional, and (c) WO ₃ band structure calculation corrected by hybrid functional DFT.	76
Figure 4.13. PEC performance measurements: Potentiostatic (a and d) and potentiodynamic (b and d) response of the films obtained at different deposition time and annealing temperatures. Measurements were carried out under intermittent light illumination.	79
Figure 4.14. (a) Nyquist plots of W films annealed at 300, 400, 500, and 600 °C under light. (b) Nyquist plots of W ₁₈ O ₄₉ films deposited for 1, 5, 10, and 20 min. under light. (c) Nyquist plots of W ₁₈ O ₄₉ films deposited for 10 min and annealed at 500 °C under dark and light. (d) Stability test of W ₁₈ O ₄₉ films deposited for 10 min and annealed at 500 °C under light for 7200 sec.....	81
Figure 4.15. PEC performance measurements; light on/off chronoamperometry and LSV measurements for WO ₃ films (a, b) annealed at different temperatures in air, (c, d) different deposition time, and (e, f) in air and vacuum, annealed at 500 °C. (f) Stability test of WO ₃ films deposited for 10 min and annealed at 500 °C under light for 120 minutes.	85
Figure 4.16. Nyquist plots of the WO ₃ films: (a) annealed in air at different temperature, (b) deposited for different time, (c) comparison under dark and light conditions. Nyquist plots of WO ₃ films deposited for 10 min and annealed in air at 500 °C under dark and light.	87
Figure 5.1. X-ray diffractions of (a) Bi ₂ O ₃ , BiVO ₄ , and Co–Pi/BiVO ₄ films. Deposition time = 5 min, annealing temperature = 450 °C. (b) Bi ₂ O ₃ and BiVO ₄ films fabricated at 1, 5-, 10-, 15-, and 20-min. deposition time, and annealed at 450 °C.....	90

Figure 5.2. FESEM images of (a) Bi ₂ O ₃ , (c) BiVO ₄ , (e) Co–Pi/BiVO ₄ films. FESEM cross-section images of (b) Bi ₂ O ₃ , (d) BiVO ₄ films. EDS spectrum (f) of Co–Pi/BiVO ₄ films.	92
Figure 5.2.1. Low magnification FE-SEM images of BiVO ₄ film	93
Figure 5.3. (a) UV-Vis absorption spectra of Bi ₂ O ₃ , BiVO ₄ , and Co–Pi/BiVO ₄ films and (b) Tauc's plots of Bi ₂ O ₃ , BiVO ₄ and Co–Pi/BiVO ₄ films.....	94
Figure 5.4. XPS spectra of of Co–Pi /BiVO ₄ : (a) survey scan, (b) Bi 4f, (c), V 2p, (d) O 1s, (e) Co 2p, and (f) P 2p.	95
Figure 5.5. Band structure and pDOS of BiVO ₄ structure.....	96
Figure 5.6. (a) LSVs of BiVO ₄ samples with different thicknesses, (b) LSVs recorded in the presence of hole scavenger (Na ₂ SO ₃), (c) comparative LSVs of BiVO ₄ and Co–Pi/BiVO ₄ , (d) IPCE of BiVO ₄ and Co–Pi/BiVO ₄ , (e) photocurrent under intermittent illumination for 600 s, (f) stability test for 2 h.....	99
Figure 5.6.1. (a) I–V curves for photoelectrochemical water oxidation of BiVO ₄ and Bi ₂ O ₃ photoanodes measured in 0.5 M PBS under simulated solar light (1 sun, AM 1.5G). (b) I–V curves for photoelectrochemical water oxidation of Co–Pi deposited on BiVO ₄ photoanodes at different deposition times.	100
Figure 5.7. (a) Transient photocurrent (TPC) response, and (b) transient decay time for BiVO ₄ and Co–Pi/BiVO ₄ electrodes at 1.23 V _{RHE} under standard illumination conditions in 0.5 M PBS.....	102
Figure 5.8. (a) Mott-Schottky plots (b) Nyquist plot of BiVO ₄ and Co–Pi/BiVO ₄ photoanodes under standard illumination conditions (AM 1.5 G, 1.0 sun), measured in 0.5 M PBS.....	104
Figure 6.1. X-ray diffractions of WO ₃ , BiVO ₄ , and BiVO ₄ /WO ₃ films photoanode. ..	107
Figure 6.2. FESEM images of (a) WO ₃ , (b) BiVO ₄ , (c) BiVO ₄ /WO ₃ , and (d) Co–P/BiVO ₄ /WO ₃ films. (e) EDS spectrum of Co–Pi/BiVO ₄ films. ...	109
Figure 6.3. (a) UV-Vis absorption spectra and (b) Tauc's plots of WO ₃ , BiVO ₄ , BiVO ₄ /WO ₃ , and Co–Pi/BiVO ₄ /WO ₃ films.	111
Figure 6.4. XPS spectra of Co–Pi /BiVO ₄ /WO ₃ : (a) survey scan, (b) Bi 4f, (c), V 2p, (d) O 1s, (e) W 4f, (g) P 2p, and (f) Co 2p.....	112
Figure 6.5. (a) LSVs of BiVO ₄ /WO ₃ samples with different WO ₃ thicknesses, (b) LSV of BiVO ₄ /WO ₃ recorded in the presence of hole scavenger (Na ₂ SO ₃), (c) comparative LSVs of Co–Pi/BiVO ₄ /WO ₃ , BiVO ₄ /WO ₃ , BiVO ₄ , and WO ₃ , (d) photocurrent under intermittent illumination for 600 s, (e) stability test for 2 h, (f) IPCE of Co–Pi/BiVO ₄ /WO ₃ , BiVO ₄ /WO ₃ , BiVO ₄ , and WO ₃	116
Figure 6.5.1. Co–Pi disposition optimization onto the surface of BiVO ₄ /WO ₃ photoanode films at (a) various potentials and (b) time intervals.....	117
Figure 6.6. (a) Transient photocurrent (TPC) response, and (b) transient decay time for WO ₃ , BiVO ₄ , BiVO ₄ /WO ₃ , and Co–Pi/BiVO ₄ /WO ₃ photoanodes at 0.9 V _{RHE} under standard illumination conditions.....	118

Figure 6.7. (a) Mott-Schottky plots, and (b) Nyquist plots of the Co–Pi/BiVO ₄ /WO ₃ , BiVO ₄ /WO ₃ , BiVO ₄ , and WO ₃ photoanodes under standard illumination conditions.	120
Figure 6.8. Conduction and valance band edges of (a) WO ₃ , (b) BiVO ₄ . Work function calculation of (c) WO ₃ and (d) BiVO ₄	123

ABSTRACT

Full Name : Amar Kamal Mohamedkhair Salih
Thesis Title : Metal Oxide Based Thin Film Photoelectrodes for Water Splitting
Major Field : Physics
Date of Degree : December 2021

Solar radiation is an enormous and continuous resource that can provide our planet with all of the energy it requires. Semiconductor nanomaterials can be utilized as photocatalysts to separate hydrogen from water and use it as a green and sustainable fuel using photo-electrochemical cells. In this study, we developed, modified, and functionalized tungsten oxide (WO_x), bismuth vanadate (BiVO_4), and double-layered tungsten oxide/bismuth vanadate thin films ($\text{BiVO}_4/\text{WO}_3$) as photo-anodes for photo-electrochemical water splitting. The DC and DC reactive sputtering techniques were used to fabricate and control the properties of the deposited tungsten oxide films. Characteristics such as crystallinity phase, oxidation phase, annealing temperature, annealing environment, and thickness have a significant effect on achieving the appropriate bandgap that can absorb a wide range of the visible light spectrum and improve the charge transport parameters of the active photoanode. A novel method for producing a pinhole-free BiVO_4 thin film was developed using a combination of sputtering and drop-casting techniques. Using this method enabled us to fabricate continuous, stable, and porous structured BiVO_4 films. Additionally, heterostructure photoanodes with double layers of BiVO_4 and WO_3 films were synthesized and tuned to enhance the oxygen evolution reaction efficiency of

the PEC. Besides, a photo-assisted electrodeposition approach was used to deposit Co–Pi with optimum thickness onto the surface of BiVO₄ and BiVO₄/WO₃ films. The structural, morphological, optical, and compositional characteristics of the developed photoanode films were studied using XRD, FE-SEM, UV-Vis, and XPS, respectively. The photocatalytic performance, such as photocurrent, photocurrent efficiency, and charge transfer rate of the prepared photoanodes, were evaluated in dark and light using an electrochemical workstation and solar simulator. DFT computations helped to investigate the electronic nanostructure of WO_x and BiVO₄ photoanode films.

ملخص الرسالة

الأسم الكامل : عمار كمال محمد خير صالح.
عنوان الرسالة : الأنودات الضوئية ذات الأفلام الرقيقة المصنوعة من أكاسيد المعادن و المستخدمة في التحليل الكهروضوئي للماء.
التخصص : الفيزياء.
تاريخ الدرجة العلمية : ديسمبر، 2021م.

الإشعاع الشمسي هو مورد هائل ومستمر يمكنه أن يزود كوكبنا بكل الطاقة التي يحتاجها. يمكن استخدام المواد النانوية شبه الموصلة كمحفزات ضوئية لفصل الهيدروجين عن الماء وإستخدامه كوقود أخضر ومستدام بإستخدام الخلايا الكهروكيميائية الضوئية. في هذه الدراسة ، قمنا بتطوير وتحسين وتشغيل أكسيد التنجستن (WO_x) وفانادات البزموت ($BiVO_4$) والأغشية الرقيقة من أكسيد التنجستن /فانادات البزموت ذات الطبقات المزدوجة ($BiVO_4/WO_3$) كأقطاب ضوئية و إستخدامها للتحليل الكهروكيميائي للمياه. تم إستخدام تقنية ترسيب الأفلام الرقيقة (DC and DC relative sputtering) لتصنيع والتحكم في درجة أكسدة وسماكة فيلم أكسيد التنجستن من أجل تحقيق فجوة النطاق المناسبة ومعاملات نقل الشحن الضوئية النشطة. بالإضافة إلى ذلك ، تم تطوير طريقة جديدة لإنتاج أفلام رقيقة و خالية من الفجوات،مصنوعة من $BiVO_4$ بإستخدام مزيج من تقنيات الترسيب والتقطير. مكننا إستخدام هذه الطريقة من تصنيع أفلام $BiVO_4$ متصله و بدون تشقق ،و مستقرة ،و مسامية. بالإضافة إلى ذلك ، تم تصنيع الأقطاب الضوئية ذات البنية غير المتجانسة من أفلام $BiVO_4$ و WO_3 وتعديلها لتعزيز كفاءة تفاعل تطور الأكسجين في الخلية الكهروضوئية. علاوة على ذلك ، تم إستخدام طريقة الترسيب الكهربائي بمساعدة الضوء لترسيب مادة الCo-Pi على سطح أفلام $BiVO_4$ و $BiVO_4/WO_3$. تمت دراسة الخصائص التركيبية والمورفولوجية والبصرية لرقائق الأنود الضوئي المطورة بإستخدام إختبارات XRD و FE-SEM و UV-Vis و XPS على الترتيب. تم تقييم أداء

التحفيز الضوئي ، مثل التيار الضوئي ، وشدة كفاءة التيار الضوئي ، ومعدل نقل الشحنة للأنودات الضوئية المعدة في الظلام و في وجود الضوء باستخدام جهاز الفحص الكهروكيميائي. تم استخدام محاكاة DFT لدراسة البنية النانوية الإلكترونية لرقائق WO_3 و $BiVO_4$ المستخدمة كأنودات (مساعد كيميائي) ضوئية.

CHAPTER 1

INTRODUCTION

1.1 The Energy demand and global warming

The theoretical capacity of renewable energy exceeds present and forecast world energy demands, opening the door to climate change mitigation and a foundation for long-term economic prosperity [1]. As a result, renewable energy generation has received much attention to reduce greenhouse gas (GHG) emissions. In 2018, electricity generation from renewable sources climbed by 7%, with nuclear energy playing a more significant role. In addition, renewable energy accounted for 25% of global power generation [2]. However, the increase in renewable energy generation has not kept pace with the rise in energy consumption [2]. Renewable energy must account for two-thirds of energy generation by 2040 in order to satisfy the IEA's (International Energy Agency) worldwide targets as part of its sustainable development scenario, which involves the use of renewable energy in all areas, including transportation, energy production, and heating [2,3].

A hydrogen economy could be a viable alternative to a carbon-based fuel system. Hydrogen has the potential to be a "clean" chemical fuel because the only byproduct produced when energy is released through combustion or in fuel cells to produce electricity is water vapor. The American scientist Craig A. Grimes mentioned in his book that hydrogen could be used as fuel in the future as a replacement of the fossil fuel for a few reasons [4]:

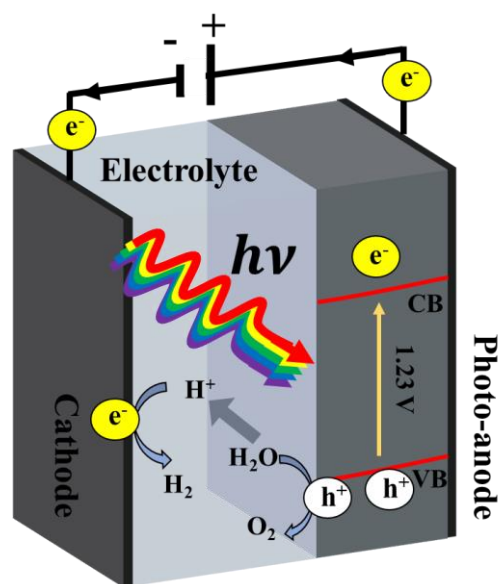
- 1- Hydrogen can be produced from water, and hence it can be considered a renewable energy source.
- 2- Hydrogen can store around 2.7 times the energy that can be stored in gasoline by weight. Gasoline can store about 45 MJ/kg of fuel, while hydrogen can store around 120 MJ/kg of its fuel.
- 3- Hydrogen can be extracted from water through the photoelectrochemical water-splitting process.
- 4- Electricity can be generated from hydrogen in fuel cells.
- 5- Hydrogen can be transported through tankers or pipelines for large distances.
- 6- Hydrogen is a clean energy carrier as its use, production, transportation, and storage do not cause air pollution and generate harmful gases.

However, current hydrogen generation methods, such as steam reforming of methane, which accounts for around 90% of hydrogen output, are CO₂ intensive (accounting for 3% of annual global CO₂ emissions) [5], and thus are not an ideal decarbonization pathway for a low-GHG emission energy carrier system at this time. Nonetheless, hydrogen can be produced in a renewable manner by combining photovoltaics with electrolyzers for water electrolysis or by using photocatalytic solar water-splitting [6-8]. The hydrogen produced can then be used as an energy-carrying medium in sectors such as electricity generation via fuel cells, transportation via electric vehicles, and home heating via hydrogen-powered boilers.

1.2 Photoelectrochemical water splitting

The photoelectrochemical process is a process of splitting water into its two components, oxygen and hydrogen, using solar power [9-11]. It was first demonstrated

by Honda and Funishima [12], whose photoelectrochemical cell (PEC) was formed of a platinum electrode that functioned as a cathode, and TiO_2 (n-type semiconductor) electrode utilized as photo-anode. Principally, in PEC, electrons and holes are generated due to the illumination that drives an electrolysis reaction at the interface between the electrolyte and the surface of the semiconductor [12-14]. By inserting semiconductor electrodes inside the electrolyte, an energy band pending will accrue due to charge transfer between the semiconductor and electrolyte, creating a depletion region at the semiconductor/electrolyte interface [13]. Upon illumination, the electron/hole pairs will be generated. The holes will be attracted to the semiconductor/electrolyte interface to oxidize the water. At the same time, the electrons will be transferred to the cathode by the external biased voltage to reduce the hydrogen [13,15]. Scheme 1.1 describes the photoelectrochemical water-splitting process.



Scheme 1.1. Photoelectrochemical water splitting process.

At the semiconductor photo-anode, the generated holes in the valance band (VB) and the excited electrons in the conduction band (CB) contribute to the water splitting process at the cathode and photo-anode as follows [16]:

Anodic Oxidation:



Cathodic Reduction:



Overall water splitting process reaction:



As can be seen from Eq. (1.1), four equivalents of holes are required per one mole of O_2 , making this half-reaction kinetically slow. As a result, oxygen evolution is generally seen as the kinetic bottleneck for the complete water splitting process, and improving the kinetics of this reaction is a critical challenge [17].

The minimum energy required to break the water into H_2 and O_2 is 1.23 eV. Hence, the ideal photocatalytic materials should have a high ability to absorb and generate electron/hole pairs under visible light radiation (400-700 nm) [18]. In addition, the valance band edge of the material should be at potential energy more positive than 1.23 eV for water oxidation, and the conduction band at potential energy more negative than 0 eV for hydrogen reduction [18]. Moreover, the ideal photocatalytic material should have high chemical stability, efficient charge transport, and relatively low cost

[19]. The efficiency achieved by solar radiation is not high due to the presence of some inhibiting factors such as electron-hole recombination and reaction cell potential [16,20,21].

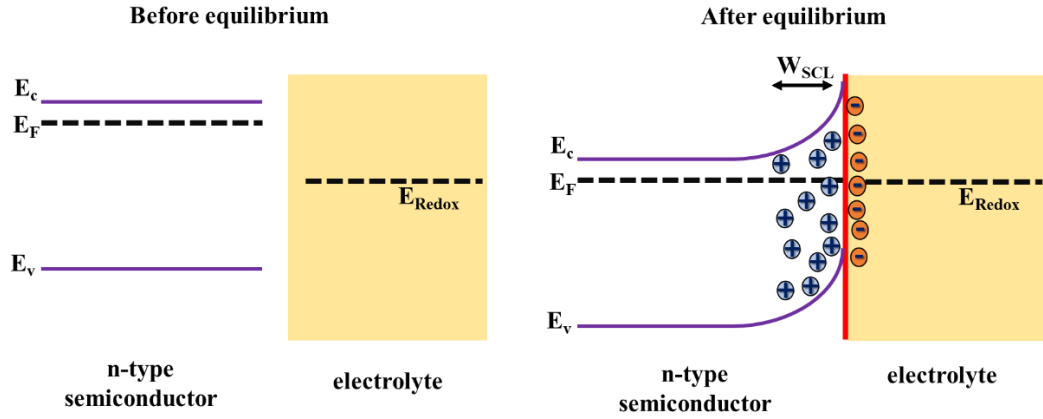
1.2.1 Electron-hole recombination in semiconductor's photoanodes

The bandgap of semiconductors is a critical consideration when using them as a photoanode in photoelectrochemical water splitting. Having a proper bandgap facilitates and maximizes the generation of the charge carriers required for the water-splitting process. However, following charge generation, electron-hole recombination losses (for a given material bandgap) constrain the efficiency of the photoanode due to the poor charge collection by water molecules [22]. For photoanodes, in order to drive redox reactions after the photoexcitation, electrons in the conduction band must reach the back contact and be extracted into the external circuit; meanwhile, holes in the valence band must be transferred to reach the semiconductor/electrolyte interface to oxidize the water. This process is based on the speed at which charges flow through the semiconductor material [23]. Therefore, higher recombination losses and hence lower efficiencies can be caused by poor charge transport properties of the photoanode's material [23]. Furthermore, sluggish interfacial reaction kinetics can result in charge accumulation, which can cause surface recombination losses, as is commonly the case with a kinetically slow water oxidation process [24].

1.2.2 The interface between semiconductor photoanode and electrolyte

The Fermi level of a semiconductor equilibrates with the redox potential of the electrolyte when it comes into contact with an electrolyte [24]. The majority of the charge carriers in the n-type semiconductor (electrons) diffuse from the bulk to the

interface and then transfer to the electrolyte until equilibrium is reached [24], as shown in scheme (1.2). The flow of electrons from the semiconductor to the electrolyte depletes the region near the semiconductor's surface [25]. The space-charge layer (SCL), with a width of W_{SCL} , is known as the depleted zone. Electric field build-up occurs across the SCL, resulting in band-bending, which is critical for separating the photogenerated charge [24]. The adsorption of negative ions in the electrolyte to the semiconductor surface field, which is mainly located within the Helmholtz layer of the electrolyte, counteracts the space-charge field [26].



Scheme 1.2. Band diagram for semiconductor/electrolyte interface.

1.2.3 The applied potential effects

Typically, photoanodes' performance is determined by plotting the photocurrent as a function of applied potential ($J - V$ curves), as shown in Fig. (1.1). The dark current is associated with the electrochemical water oxidation catalysis ability of the semiconductor [27]. On the other hand, when the photoanode is irradiated with light, photogenerated holes in its valence band are capable of oxidizing water (if the valence band has sufficient potential energy to drive this reaction). The photocurrent onset is

constrained by the photoanode's flat band potential (V_{FB}) [28], which is the potential at which no band bending or charge depletion occurs [29]. However, experimental evidence indicates that the overpotentials related to water oxidation, bulk recombination losses, and surface recombination processes cause a non-ideal behavior on photocurrent generation.

Positive applied potentials are crucial to get high photocurrents in photoelectrodes. When a photoanode is charged positively, a potential drop across the space charge layer occurs at the semiconductor/electrolyte interface, whereas a larger potential increases the space charge layer field and the W_{SCL} [30]. The band-bending in the SCL reduces loss processes such as back-electron hole recombination [24], which is usually observed to dominate at photocurrent onset potentials. Additionally, as a positive bias increases, the charge separation rates improve, resulting in a bigger number of holes migration to the semiconductor/electrolyte interface. At applied potentials just above the V_{FB} , the band bending within the SCL is commonly inadequate to cause charge separation, resulting in the dominance of recombination processes and the absence of photocurrent [25]. When applied at moderately positive potentials, the width of the space charge layer expands, which promotes charge separation and pushes holes to the surface [25]. These holes aggregate near the surface and are capable of accelerating the oxidation of water. However, the accumulating holes at the surface are coulombically attracted to the bulk electrons, resulting in back electron-hole recombination (BER) processes that compete kinetically with water oxidation [24]. This causes an electron backflow from the external circuit, which usually manifests as negative spikes on transient photocurrent measurements [31]. When the photoanode is charged to a high positive potential, the

increased band bending across the space charge layer suppresses back electron-hole recombination, allowing the holes stored at the surface to accelerate water oxidation [31]. The amount of bias required to eliminate back electron-hole recombination losses varies based on the photoanode's material; for bismuth vanadate (BiVO_4), this value has been reported to be 1.2 V more positive than the V_{FB} [32], while for hematite (Fe_2O_3), the value has been reported to be 0.8 V [31].

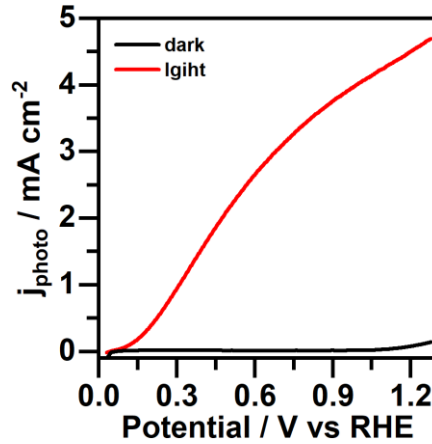
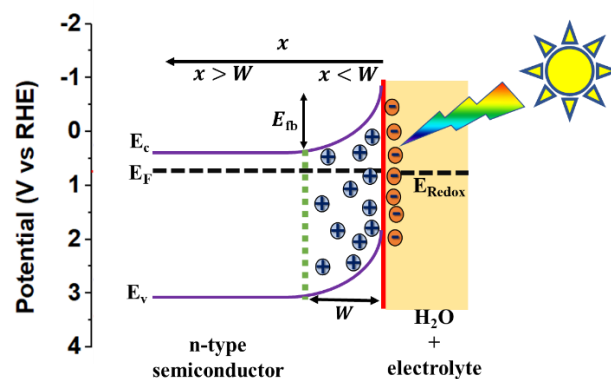


Figure 1.1. Photocurrent as a function of applied potential (J – V curves).

1.2.4 The photocurrent at a semiconductor-electrolyte junction

The physical parameters of the semiconductor material used as the photoanode in the photoelectrochemical water splitting cell are critical in determining the PEC's effectiveness. By identifying these features, we can optimize and change them to increase their photocatalytic activity. To conclude the photocurrent created at the PEC, incoming light with photon energy greater than the band gap of the photoanode material will result in the formation of electron-hole pairs. This pair is separated by the electric field generated by the electron transfer between the semiconductor fermi level and the electrolyte's redox

potential [33]. The photoexcited holes are then trapped on the surface of the photoanode, while the electrons are transported to the cathode for water reduction. The Schottky barrier between a metal and a semiconductor can be used to simulate the junction between the semiconductor and the electrolyte [34,35]. Moreover, the photocurrent is dependent on additional characteristics such as the semiconductor's conductivity and the applied bias potential [36]. Scheme 1.3 illustrates the photoelectrochemical water oxidation process by n-type semiconductor film.



Scheme 1.3. Illustration of the photoelectrochemical water oxidation process by n-type semiconductor film.

In general, the total photocurrent density, J_{tot} , generated within the biased depletion layer is given by the following equation, Eq. (1.4) [37]:

$$J_{tot} = J_{drf} + J_{diff} \quad \text{Eq. (1.4)}$$

Where J_{drf} represent the drift current density caused by the charge charier generated inside the depletion region, and J_{diff} is the diffusion current density outside the depletion region (in bulk) caused by the minority charge carrier.

The J_{drf} is mainly influenced by the number of electron-hole pairs generated by the incident photon flux Φ . Hence, the J_{drf} can be represented by Eq. (1.5) as follows [38]:

$$J_{drf} = q \int_0^w g(x) dx = q\Phi(e^{-\alpha w} - 1) \quad \text{Eq. (1.5)}$$

Where $g(x)$ is the charge carrier generation rate $= \Phi\alpha e^{-\alpha x}$, w is the depletion region width, α is the light absorption coefficient, and q is the electronic charge.

By considering the electron-hole pair recombination occurs at the semiconductor bulk, the one dimension n-type minority carrier diffusion equation at steady-state could be expressed by Eq. (1.6) [39]:

$$D_p \frac{d^2 p}{dx^2} - \frac{(p-p_o)}{\tau} + g(x) = 0 \quad \text{Eq. (1.6)}$$

Where D_p is the hole diffusion coefficient, p is the hole density, p_o is the equilibrium hole density (under illumination), τ is the charge carrier's lifetime.

By using the following boundary conditions:

$$\begin{aligned} \text{for } x = \infty, \quad p &= p_o \\ \text{for } x = w, \quad p &= 0 \end{aligned}$$

Then, the solution of the one dimension minority carrier diffusion equation is given by Eq. (1.7):

$$p = p_o - (p_o + A e^{-\alpha w})e^{(w-x)/L_p} + A e^{-\alpha x} \quad \text{Eq. (1.7)}$$

Where L_p is the hole diffusion length [40] ($L_p = \sqrt{D_p \tau}$), and $A = \frac{\Phi}{D_p} \frac{\alpha^2 L_p^2}{\alpha(1-\alpha^2 L_p^2)}$.

The diffusion current is given by Eq. (1.8) [40]:

$$J_{diff} = qD_p \frac{dp}{dx} \quad \text{Eq. (1.8)}$$

So, at $x = w$

$$J_{diff} = q\phi \frac{\alpha L_p}{(1+\alpha L_p)} e^{-\alpha w} + qp_o \frac{D_p}{L_p} \quad \text{Eq. (1.9)}$$

By combining Eq. (1.5) and Eq. (1.9), the total current density is given by Eq. (1.10) [41]:

$$J_{tot} = q\phi \left[1 - \frac{e^{-\alpha w}}{1+\alpha L_p} \right] + qp_o \frac{D_p}{L_p} \quad \text{Eq. (1.10)}$$

The depletion layer width w is given by the following equation, Eq. (1.11) [42]:

$$w(cm) = \sqrt{\frac{2\epsilon\epsilon_o(E-E_{fb})}{qN_d}} \quad \text{Eq. (1.11)}$$

Where ϵ is the relative dielectric constant, ϵ_o is the permittivity of vacuum, N_d is the doping density (cm^{-3}), E is the applied bias potential, and E_{fb} is the flat band potential.

1.2.5 Metal oxide semiconductors as photoanodes for photoelectron-chemical water splitting

Metal oxide-based photoanodes have triggered a lot of interest due to their chemical stability in aqueous media, appropriate valence bands for driving water oxidation, and for some materials, visible light absorption [43]. They are also non-toxic and can be manufactured using low-cost methods that are generally up-scalable. Fig. (1.2) depicts the band positions and bandgaps of some studied metal oxides.

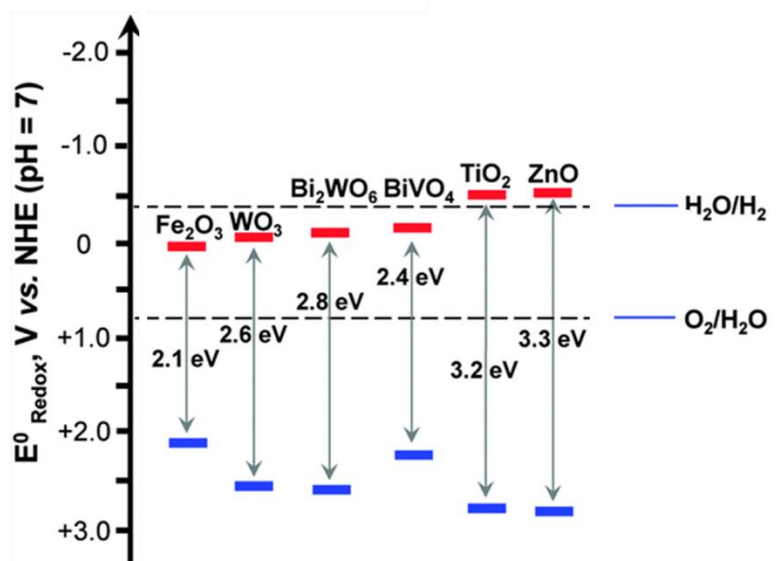


Figure 1.2. Band edges of some metal oxides materials are used as photoanodes for photoelectrochemical water splitting (adapted from [44]).

As an example of these materials, TiO₂ is one of the most extensively investigated photoanode materials; it is a promising material for performing both hydrogen and oxygen evolution half processes [45]. However, due to the high bandgap (~3.1 eV), TiO₂ can absorb only a small portion of the solar spectrum [45]. On the other hand, WO₃ has a relatively wide bandgap (~2.9 eV) and is frequently used as a photoanode in oxygen evolution reactions [46]. BiVO₄ and Fe₂O₃, having bandgaps of 2.4 eV and 2.1 eV, respectively [47,48], are also common photoelectrochemical photoanodes. BiVO₄, in particular, has shown considerable potential in recent literature [49].

CHAPTER 2

LITERATURE REVIEW

Photo-electrochemistry of semiconductors is a field that builds on the fundamentals of electronics, chemistry, physics, and optics. It is a fascinating scientific research field that comprises the electrochemical systems that contain light exposed semiconductor materials.

Becquerel is a pioneer in the photoelectrochemical research area. In 1839, he demonstrated the photovoltaic effect when he used a silver chloride electrode connected to a platinum electrode in an acidic solution [50,51]. Garrett and Brattain researched the p-/n-type germanium electrodes in several electrolyte solutions in 1954. They were able to show the effect of light intensity on the cathodic and anodic reactions [52]. For water splitting, the TiO_2 photo-anode, prepared by Fujishima and Honda in 1972, pioneered the area of the photoelectrochemical water splitting process [12].

2.1 Tungsten oxide photoanodes

Tungsten oxide (WO_3) is generally described as a cubical structure with WO_6 octahedra sharing corners [53,54]. However, in reality, and as a result of the aggressive distortion of the ideal structure, several WO_3 formations have been observed. The crystal structures of WO_3 phases are commonly described as tetragonal ($\alpha\text{-WO}_3$), orthorhombic ($\beta\text{-WO}_3$), monoclinic I ($\Gamma\text{-WO}_3$), monoclinic II ($\varepsilon\text{-WO}_3$), and triclinic ($\Delta\text{-WO}_3$) [55]. The stability of these structures varies according to the temperature of the surrounding environment. For example, at room temperature, the most stable phase is monoclinic I ($\Gamma\text{-}$

WO₃) [55]. Figure (2.1a-b) shows the ideal cubic and monoclinic structures of the WO₃, respectively.

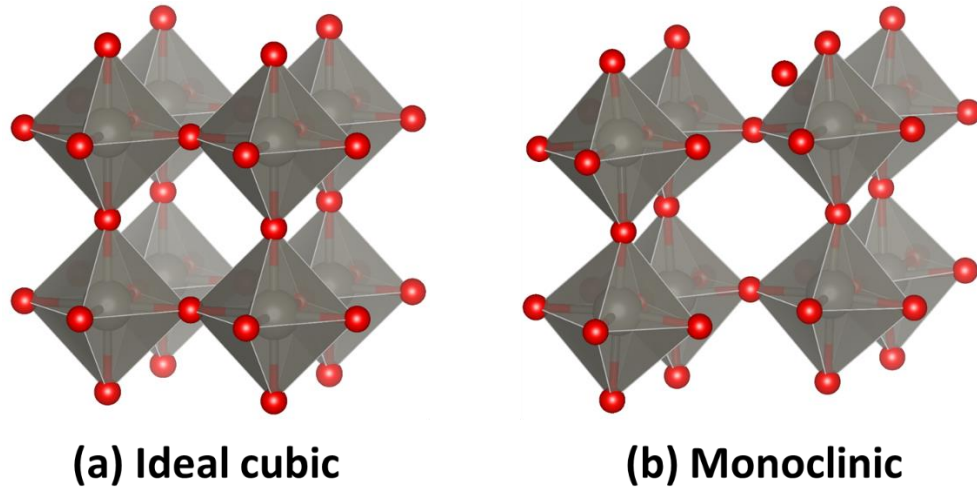


Figure 2.1. (a) An ideal cubic and (b) monoclinic structures of tungsten oxide crystal.

Under certain conditions, an oxygen vacancy forms in the crystal of tungsten oxide, resulting in the formation of substoichiometric structures such as W₂₄O₆₈, W₂₀O₅₈, and W₁₈O₄₉ [56]. These sub-stoichiometric phases emerge as a result of the sharing of the edges or faces of WO₆ octahedra [56]. Additionally, the existence of a sufficient amount of oxygen vacancies in tungsten oxide influences its bandgap, which may improve its photocatalytic activity as a photoanode [57]. Moreover, the appropriate oxygen vacancies can behave as electron donors, resulting in a rise in donor density and thus the photoanode's charge transport properties [58]. On the other hand, while oxygen vacancies provide a lot of advantages, an excessive number of them may act as electron/hole recombination centers, reducing the photocatalytic activity of this material [59]. The generation of oxygen vacancies has been widely employed to enhance the photocatalytic activity of the WO₃ photoanode. For example, Yihan Liu et al. [60] synthesized an oxygen vacancy in a WO₃

photoanode film using hydrothermal synthesis. The oxygen vacancies were formed by etching the surface of the WO_3 layer with Ar plasma. The XPS study demonstrated a reduction of tungsten W^{6+} to $\text{W}^{4+}/\text{W}^{5+}$. Additionally, the etched sample's visible light absorption increased due to the narrowing of the WO_3 bandgap. As a result, the photocurrent of the WO_3 samples was enhanced from 0.9 mA/cm^2 , in the case of as-prepared samples, to 1.32 mA/cm^2 for the etched samples at $1.23 \text{ V}_{\text{RHE}}$. Another example was obtained by Xuefeng Liu et al. Through hydrogen surface reduction, they synthesized WO_{3-x} films. Both WO_3 and WO_{3-x} exhibit comparable UV-Vis light absorption and optical bandgap properties. WO_{3-x} , on the other hand, generated a photocurrent 7.3 times that of WO_3 . They concluded that the oxygen vacancies significantly enhanced the photocatalytic activity of the WO_{3-x} photoanode by mitigating electron/hole recombination and improving interfacial charge transfer properties. Magnéli-phase ($\text{W}_{18}\text{O}_{49}$) [61], which is attracting considerable interest in different applications, such as solar cells, photocatalysis, and sensors, is a non-stoichiometric tungsten oxide phase that possesses abundant oxygen vacancies [62,63]. The oxygen vacancies present in $\text{W}_{18}\text{O}_{49}$ work as active sites and enhance the adsorption of oxygen molecules from the water [62]. Moreover, the $\text{W}_{18}\text{O}_{49}$ phase is capable of absorbing visible light illumination without the addition of other dopant materials [64,65]. The photocatalytic activity of Magnéli-phase $\text{W}_{18}\text{O}_{49}$ is dictated by several factors, such as morphology, particle size, surface area, which are ultimately controlled by the fabrication method. For example, Chongshen et al. [66] demonstrated that the light absorption properties of the $\text{W}_{18}\text{O}_{49}$ changed with changing the bulk $\text{W}_{18}\text{O}_{49}$ to nanorods, nanograins, nanofibers, and nanoparticles. Guojuan et al. [67] found that

directional growth of $\text{W}_{18}\text{O}_{49}$ significantly affected oxygen vacancies, bandgap width, electron/hole separation, and optical attributes.

The morphology of the WO_3 photoanode film has been found to be one of the practical techniques for increasing its photocatalytic activity. Multiple morphologies of WO_3 have been reported with controlled characteristics, including quantum dots [68], exposed facets [69], shaped nanostructures [70], hierarchical nanostructures [71], and thin films [72]. The development of distinct morphologies is mainly determined by fabrication techniques like sol-gel [73], anodization [74], hydrothermal processes [75], spray pyrolysis [76], and sputtering [77]. The photocatalytic activity of a WO_3 photoanode is strongly impacted by its optical bandgap and the specific area, which are influenced by the crystallinity and morphology of the material. For example, Hunge et al. [78] reported that the balance between the crystallinity and the specific surface area for a WO_3 film fabricated by spray pyrolysis is essential. The authors showed that the photocatalytic activity and the number of active sites are increased by increasing the photoanode film's surface area and decreasing its crystallinity. Mohamed et al. [79] investigated two distinct WO_3 photoanode morphologies. The researchers noted that the nanoflake structure was more thermally stable than the nanoporous structure at the elevated annealing temperature. Specifically, following 400 °C annealing, the nanoporous structure of the WO_3 film collapsed, resulting in a decrease in its specific surface area and photocatalytic activity.

The sputtering system is one of the effective deposition techniques that can enable tuning the thin film parameters by controlling the deposition power, gas atmosphere, working pressure, deposition angle, substrate temperature, and deposition time [80-82]. The deposition conditions during sputtering have a significant impact on the photocatalytic

activity of WO_3 films. For instance, Limwichean et al. [77] fabricated a WO_3 nanorods photoanode using DC reactive sputtering. They noted that the optical properties, morphology, and crystallinity of the WO_3 film are significantly affected by the deposition angle and the substrate-target distance. The annealing temperature and atmosphere can also have a significant effect on the WO_3 's characteristics and photocatalytic performance. For example, Siao Li et al. [83] observed that the morphological and optical properties of WO_3 films prepared using a DC reactive sputtering magnetron varied with post-annealing temperature. Specifically, at elevated annealing temperatures, UV-Vis absorption increased (350 °C and above). Additionally, the charge transfer properties and photocurrent density of the produced films changed significantly as a function of the annealing temperature. Zhao et al. [84] investigated the annealing atmosphere for sputtered WO_3 films. The results indicated that annealing in O_2 and N_2 surroundings might result in the formation of a physical defect within the WO_3 crystals. These imperfections have an effect on the charge transfer characteristics of the film and act as electron/hole pair recombination centers. As a result, the photocatalytic activity is lower than that of the film annealed in ambient air. Another essential parameter is the film thickness, which may be changed by adjusting the deposition time. Valerini et al. [85] noticed a photocurrent increase of approximately 50% (from 0.025 to 0.045 mA/cm^2 at 1.23 V_{RHE}) after optimizing the thickness of the WO_3 photoanode film created by RF sputtering magnetron. They disclosed that increasing the thickness of the WO_3 film increased the UV-Vis absorption (deposition time). However, it was determined that an optimal film thickness (200 nm) exhibited the highest photocatalytic activity when compared to the other thicknesses (100, 350, and 500 nm). They claimed that while the 350 and 500 nm thick films absorbed more light, their

thickness resulted in a longer transport path for charge carriers, resulting in a greater number of electron/hole recombination events during the charge transport process.

2.2 Bismuth vanadate photoanode

Bismuth vanadate is an n-type ternary metal-oxide semiconductor that contains the following ions: Bi^{3+} , V^{5+} , and O^{2-} [86]. Tetragonal zircon, tetragonal scheelite, and monoclinic scheelite are the three primary crystalline forms of BiVO_4 [87]. The monoclinic scheelite structure, shown in Fig. (2.2), exhibits the maximum photocatalytic activity for water oxidation reaction in PEC due to its ability to its narrower bandgap [88]. The valence band of BiVO_4 is typically O 2p, which is low-lying, resulting in deep valence band positions and relatively high bandgaps. However, in the case of monoclinic BiVO_4 , the existence of Bi^{3+} with filled 6s states enables hybridization with O 2p levels within the valence band edge, resulting in a reduction in the bandgap, as demonstrated by density functional theory (DFT) calculations [89,90] and experimentally [90,91] observed. The minimum conduction band edge is dominated by V 3d states. DFT calculations and experimental evidence previously published indicate that the bandgap of BiVO_4 is direct [89,91]. In comparison, some computational investigations have indicated an indirect bandgap for BiVO_4 , but at a little higher energy, a direct bandgap also exists [92,93].

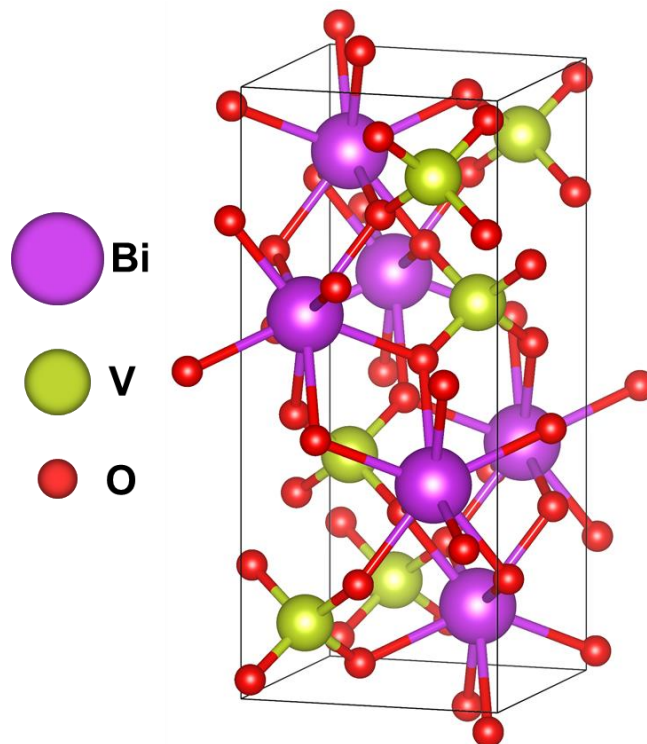


Figure 2.2. Monoclinic structure of bismuth vanadate.

Bismuth vanadate was firstly reported as a photocatalyst by Kudo et al. in 1998 [94,95]. They prepared BiVO_4 hydrothermally using a mixture of bismuth oxide and vanadium oxide precursors. Since then, various chemical methods such as metal-organic decomposition [96], spray pyrolysis of metal-organic precursors [97], spin coating cycles [98], reactive ballistic deposition [99], chemical vapor deposition [100], and electrodeposition [101] have been used to synthesize BiVO_4 with a variety of different properties. However, most of the chemical fabrication methods could cause a discontinuous film, in which the substrate layer is clearly exposed to the electrolyte solution [96], as shown in Fig. (2.3). The discontinuity of the photoanode film could cause solution-mediated recombination through back reduction [96].

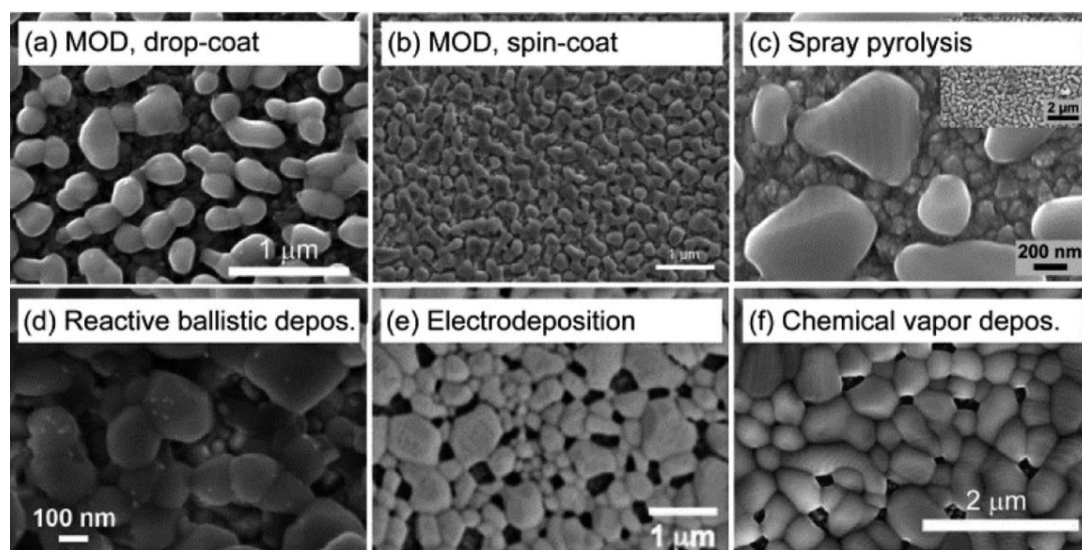


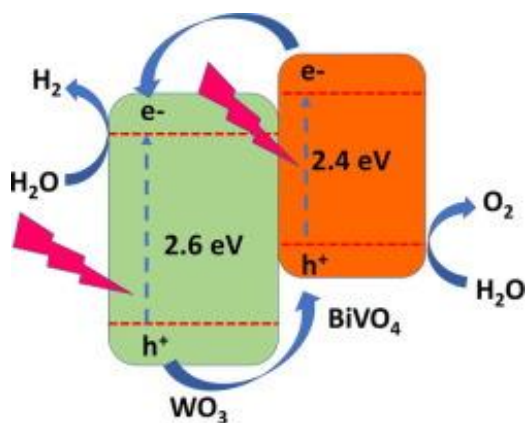
Figure 2.3. Scanning electron microscopy images of BiVO_4 films prepared via different fabrication methods [96].

In addition to the discontinuity problem mentioned above, it is difficult to find a chemical fabrication technique that is precisely controllable, stable, and suitable for mass production. Sputtering is a physical thin film deposition technique that allows the preparation of uniform, durable, tunable, and large dimensional area photoanode for photoelectrochemical water splitting cells. However, one disadvantage of employing such approaches may be the possibility of fabricating structure-less films with a limited surface area available for catalytic reactions. Recently, several attempts have been made to fabricate BiVO_4 photoanode using a sputtering deposition. For example, Madhavi et al. [102] sputtered BiVO_4 film using a powder target of $(\text{Bi}_2\text{O}_3)_{0.5}(\text{V}_2\text{O}_5)_{0.5}$. The photoanode generated 0.6 mA/cm^2 photocurrent at about $1.23 V_{\text{RHE}}$ reference electrode. Pedroni et al. [103] investigated the use of RF sputtering to fabricate BiVO_4 thin film photoanodes under a variety of deposition conditions. They discovered that BiVO_4 annealed at 600°C and illuminated from the backside produced the highest photocurrent density. According to

Kodan et al. [104], a BiVO_4 film fabricated via RF sputtering generated a current density of 0.04 mA/cm^2 at 0.6 V vs. an Ag/AgCl reference electrode. Additionally, they observed that doping the BiVO_4 with MoO_3 increased this current density by sixfold.

2.3 $\text{BiVO}_4/\text{WO}_3$ heterostructure photoanode

Separation of charges is critical for creating long-lived charges capable of performing kinetically slow reactions such as water oxidation, which requires about a millisecond [17]. In photosynthesis, a sequence of redox co-factors results in constructing an electron transport chain, which converts short-lived molecular excited states to long-lived charges as a result of charge carrier spatial separation. This increases the lifespan of photogenerated species from sub-nanoseconds to milliseconds, allowing them to drive sluggish redox processes [105]. In inorganic systems, semiconductor band offsets can be used to imitate the energy flows inherent in natural photosynthesis. This has been demonstrated most successfully with the $\text{WO}_3/\text{BiVO}_4$ heterojunction, shown in scheme (2.1).



Scheme 2.1. $\text{BiVO}_4/\text{WO}_3$ heterostructure for photocatalytic water splitting [106].

The $\text{WO}_3/\text{BiVO}_4$ heterojunction photoanodes have demonstrated considerable promise and have generated significant interest in photoelectrochemical water oxidation. For example, Jianqiao et al. [107] synthesized a $\text{BiVO}_4/\text{WO}_3$ heterostructure photoanode in two steps, using a hydrothermal technique for the WO_3 layer fabrication and dip-coating for the BiVO_4 layer fabrication. Additionally, they use thermal annealing in the presence of H_2 flow to form oxygen vacancies on the surface of the structured $\text{BiVO}_4/\text{WO}_3$ film. Their PEC results indicated that when the BiVO_4 top layer was added, the photogenerated current density of the pure WO_3 film (0.5 mA/cm^2 at $1.23 \text{ V}_{\text{RHE}}$) was doubled, resulting in a photocurrent density of 1 mA/cm^2 at $1.23 \text{ V}_{\text{RHE}}$. After thermal treatment, the photocurrent density was raised to 1.25 mA/cm^2 at $1.23 \text{ V}_{\text{RHE}}$ due to the presence of surface oxygen vacancies. Madhavi et al. [108] reported another example of a $\text{BiVO}_4/\text{WO}_3$ heterostructured photoanode. They synthesized 1D tungsten oxide nanorods using a DC reactive magnetron sputtering method. Further, they deposited the BiVO_4 layer on the surface of the WO_3 film using the RF magnetron sputtering technique. They observed that the individual films had photocurrent densities of around 0.50 and 0.75 mA/cm^2 at $1.23 \text{ V}_{\text{RHE}}$ for BiVO_4 and WO_3 , respectively. Additionally, when the two films were combined, the photocurrent density increased to 1.4 mA/cm^2 at $1.23 \text{ V}_{\text{RHE}}$.

2.4 The addition of oxygen evolution co-catalyst

Oxygen evolution catalysts are usually used to increase the rate of catalysis by transferring photogenerated holes from the semiconductor to the catalyst layer, which then drives water oxidation. For example, Co–Pi [109,110], CoFe – Prussian blue (PB) catalysts [111], and Ni/FeOOH metal oxyhydroxide-based catalysts [112] have all been used to

improve the performance of BiVO₄ photoanodes. Fang et al. [113] investigated the effect of Co–Pi loading on the BiVO₄ photoanode using the electrochemical deposition method. The Co–Pi presence enhanced the photocurrent density from ~0.25 mA/cm² at 1.23 V_{RHE}, for pure BiVO₄, to ~1.2 mA/cm² at 1.23 V_{RHE}. A similar Co–Pi deposition method was used by Jianqiao et al. [107]. They observed an increase in photocurrent density of approximately 65% after adding Co–Pi co-catalyst to their BiVO₄/WO₃ photoanode.

Nevertheless, there is considerable disagreement in the literature about the role of catalyst overlayers. For example, in the case of Co–Pi, there have been reports of water oxidation caused by Co–Pi. Forrest et al. [114] showed that the Co–Pi would have enough chemical potential to drive oxygen evolution reaction at a high applied potential. However, contradictory results have shown that Co–Pi acts as a surface passivation layer and increases band bending by forming a Schottky junction to improve charge carrier separation. For instance, in a recent article published by Krol et al. [109], the authors utilized the intensity-modulated photocurrent spectroscopy (IMPS) to investigate the Co–Pi enhancement effect on BiVO₄ photoanode. They found that the addition of Co–Pi passivates the BiVO₄ surface and reduces its surface recombination rate by a factor of 10–20, without a major change in the kinetics of the charge transfer. Furthermore, water oxidation on Co–Pi is several orders of magnitude slower than on BiVO₄, indicating that water oxidation on BiVO₄ may be more favorable kinetically.

2.5 Thesis outline

This work aimed to fabricate a highly active and stable thin-film photoanode for electrochemical water oxidation using tungsten oxide and bismuth vanadate. The specific objectives of this work are the following:

- 1- Prepare of metal oxide based photo-anode films, such as WO_3 and ZnO , using various preparation methods.
- 2- Computational modelling for optimal electro-photocatalytic splitting of water.
- 3- Study the structural, morphological, compositional properties, as well as charge carrier dynamics of the fabricated films using different characterization techniques such as XRD, XPS, UV-vis, AFM, FESEM, PL and FTA.
- 4- Investigate the photocatalytic activity of the prepared photo-electrodes.
- 5- Study the effect of the photo-electrode's oxidation state on the photocatalytic activity.
- 7- Investigate the effect of photo-electrode's thickness, oxygen vacancies, and the formation of heterostructure with other photoactive material on the electro-photocatalytic activity of the film.

This thesis is divided into seven chapters, which are as follows:

In Chapter 3, we show the detailed fabrication steps of $\text{W}_{18}\text{O}_{49}$, WO_3 , BiVO_4 , Co–Pi/ BiVO_4 , $\text{BiVO}_4/\text{WO}_3$, and Co–Pi/ $\text{BiVO}_4/\text{WO}_3$ photoanodes, along with their characterization methods and parameters.

In Chapter 4, we demonstrate the structural, optical, morphological, and compositional properties of two tungsten oxide phases ($W_{18}O_{49}$ and WO_3). Both phases are formed via sputtering deposition but with distinct deposition patterns. The influence of film thickness, annealing temperature, and environment on the film's properties is explored and correlated with their film's characteristics. We studied the PEC performance of the $W_{18}O_{49}$ and WO_3 photoanodes by monitoring their water oxidation process in the dark and light. Additionally, the theoretical bandgap and density of state of $W_{18}O_{49}$ and WO_3 films are estimated and compared to the observed values using DFT calculations.

In Chapter 5, we describe a novel approach for fabricating Co–Pi -modified $BiVO_4$ thin film for photoelectrochemical water oxidation by combining sputtering and drop-casting methods. Using these two approaches enabled us to fabricate a well-controlled, stable, and porous structured film. Thin-film of Bi_2O_3 is deposited on FTO glass using DC reactive sputtering. The Bi_2O_3 film is then modified by vanadium oxide precursor solution by the dropped cast. The film is annealed and etched to obtain $BiVO_4$ film. The thickness of the Bi_2O_3 film is optimized to maximize the diffusion of the vanadium oxide precursor solution into the film and thus complete transformation to $BiVO_4$. Co–Pi is loaded as a co-catalyst to enhance the $BiVO_4$ film's photoelectrochemical activity toward water oxidation under visible light radiation. The theoretical bandgap and the band edges values are calculated using DFT.

In Chapter 6, we fabricate a $BiVO_4/WO_3$ heterostructure photoanode in two stages. First, we deposit the WO_3 layer using DC reactive sputtering and subsequently annealing it to achieve its crystalline phase. Following that, we sputter the Bi_2O_3 film on top of the annealed WO_3 film and then modify it with the vanadium oxide precursor solution via

drop-casting followed by heat treatment. The thickness of the WO_3 -based layer is tuned to maximize the photoanode's PEC performance. The Co–Pi co-catalyst is electrochemically deposited and optimized on the surface of the $\text{BiVO}_4/\text{WO}_3$ film in order to get a higher photocurrent density when illuminated to visible light. The band structure alignment is confirmed using DFT calculation.

In Chapter 7, a comprehensive conclusion is obtained to summarize the overall thesis outcomes.

CHAPTER 3

EXPERIMENTAL METHODS AND CHARACTERIZATION

3.1 Synthesis of the thin film photoanode

3.1.1 Sputtering Techniques

Sputtering is a process for fabricating thin films that use accelerated heavy ions or atoms to bombard and extract particles from a solid surface [115]. The extracted atoms can subsequently be deposited on a substrate that has been positioned within one of the sputtering surrounding walls. Generally, this process is used to deposit a thin layer of a particular substance (thin film) onto a variety of different substrates. Sputtering has numerous advantages over other methods for producing thin films, including thickness control, surface smoothness, a fast rate of deposition, and film uniformity across a large area [115]. Sputtering techniques are classified into two types of deposition systems: direct current (DC) and radio frequency (RF) [115]. Atoms are ejected off their target material's surface in both disposition systems by exchanging momentum between the accelerated ions and the material's surface atom. However, DC sputtering is utilized to deposit an electrically conducting material, which does not accumulate charges as non-conductive materials do. In addition, when a reactive gas, such as oxygen, is introduced along with the inert argon gas, it is called reactive DC sputtering.

The RF sputtering technique, on the other hand, can be used to sputter insulators, semiconductors, and conductors. RF sputtering makes use of an alternating voltage power supply with a radio frequency of 13.56 MHz. Alternating current enables bombardment of the target material while preventing charge accumulation. The accumulated charges are removed as a result of the electrons responding to the RF frequency. Simultaneously, because of their high momentum, the accelerated ions will not be attracted. Different operational parameters affect the sputtering disposition process, such as vacuum level, substrate type, substrate temperature, substrate to target distance, target composition, gas pressure, and magnetron power. DC/RF sputtering machine (model NSC-4000, Nanomaster, USA), shown in Fig. (3.1).

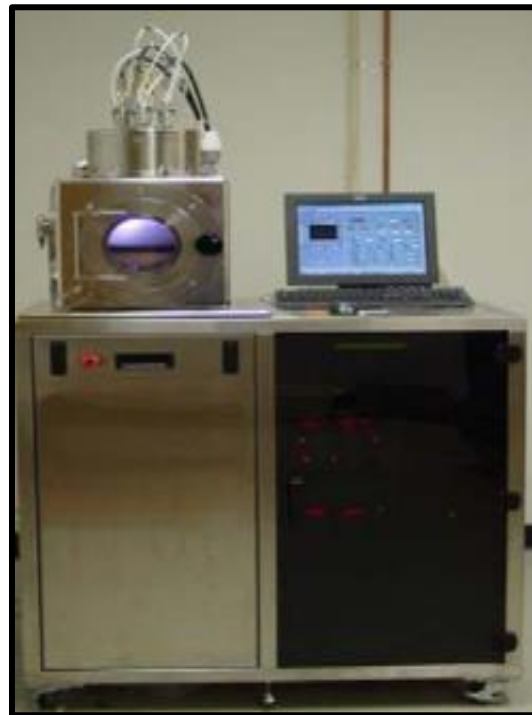


Figure 0.1 Photograph of the sputtering system (IRC-HES / KFUPM)

3.1.2 Preparation of $W_{18}O_{49}$ Thin-Film Electrodes

Tungsten oxide ($W_{18}O_{49}$) photo-anode films were fabricated by annealing the film of metallic tungsten prepared by the DC sputtering magnetron. Tungsten target (99.995% purity) was purchased from ACI alloys INC, (San Jose, CA, USA) and was used to deposit W films on FTO-coated glasses. The deposition was carried out in an argon atmosphere at a power of 100 watts. To investigate and reproduce the PEC performance of the $W_{18}O_{49}$, two films of each $W_{18}O_{49}$ were synthesized with varying thin-film thickness and post-annealing treatment. In both two parameters, the base and deposition pressure inside the sputtering chamber was fixed at 9×10^{-6} and 3.5×10^{-3} torr, respectively. To study the effect of the thin film thickness on the PEC activity of the $W_{18}O_{49}$, the sputtered W metallic films were deposited at varying thicknesses (1, 5, 10, and 20 min), while keeping all other parameters constant. To investigate the effect of post-annealing treatment on the performance of the $W_{18}O_{49}$, the sputtered W metallic films were annealed in a tube furnace (OTF-1200X from MTI corp.) at different temperatures in the ambient air. In detail, the deposited film was inserted in the middle of the tube furnace. Then, the furnace was adjusted to heat up at the rate of 20 °C/min. to reach the targeted temperature (100, 200, 300, 400, 500, and 600 °C). After 2 h annealing, the tube furnace was switched off, and the sample was left to cool down inside the furnace in order to reach room temperature.

3.1.3 Preparation of WO_3 Thin-Film Electrodes

The preparation of the WO_3 thin films was carried out using DC reactive sputtering techniques. A circular disk made from 99.995% of W (purchased from ACI alloys INC, San Jose, CA, USA) was used as the sputtering target. A conductive coated glass (FTO) was utilized as a substrate for the deposition of WO_3 films. In order to study the effect of

post-annealing temperature on the PEC performance, FTO substrates were cleaned, dried, and placed inside the sputtering chamber. The sputtering chamber was evacuated to an initial pressure of 8×10^{-6} torr. The deposition process was performed at 100 watts in a 70 sccm mixture of argon and oxygen (1:1) atmosphere with a working pressure of 3×10^{-3} torr. The deposited films were then post-annealed in air or vacuum at different temperatures for 2 h, and the substrate heater was sealed in an evacuated chamber. The thickness of the WO_3 films was controlled by changing the deposition time (5, 10, 15, 20 min) while keeping the other deposition parameters constant.

3.1.4 Preparation of Co–Pi/ BiVO_4 Thin-Film Electrodes

A combination of DC reactive sputtering and drop-casting was used to create BiVO_4 photoanode films. Firstly, a metallic bismuth target (99.995% purity, purchased from ACI alloys INC-San Jose, CA, USA) was used to deposit a thin layer of Bi_2O_3 on FTO glass using a DC reactive sputtering magnetron. The deposition was carried out in oxygen and argon atmosphere (total flow of 40 sccm, 1:1 oxygen/argon ratio) at a power of 30 watts. The sputtering chamber was evacuated to a base pressure of 9×10^{-6} torr before starting the deposition process, which was carried out at a working pressure of 3×10^{-3} torr. The thickness of the Bi_2O_3 films was controlled by varying the deposition time (1, 2.5, 5, 10, 15, and 20 min) by keeping other deposition parameters constant. After that, 30 μL of 0.15 M vanadyl acetylacetonate dissolved in dimethylsulfoxide was dropped on the surface of the Bi_2O_3 films. The films were then thermally treated in ambient air using a muffle furnace at 450 $^\circ\text{C}$ with a ramping rate of 2° min^{-1} for 2 hours. The excess vanadium oxide layer was removed by immersing the electrodes in 1.0 M NaOH solution for 10 min. The as-prepared BiVO_4 films were modified with a Co–Pi co-catalyst using photo-assisted

electrochemical deposition. The deposition was conducted at around 1.6 V_{RHE} for various deposition times (1, 3, and 5 min.) using a 0.5 M Co(NO₃)₂ in 0.1 M phosphate buffer (pH 7).

3.1.5 Preparation of Co–Pi/BiVO₄/WO₃ Thin-Film Electrodes

The DC reactive sputtering system was used to fabricate WO₃ thin film photoanode. A metallic W disk (99.995% purity, purchased from ACI alloys INC, San Jose, CA, USA) was used as a sputtering target. First, F: SnO₂ (FTO) glasses with a dimension of 2 × 1 cm were used as photoanode substrates. To eliminate surface contaminants from these substrates, they were sonicated in isopropanol for 30 minutes and then rinsed in DI water for 10 minutes. Following that, the FTO substrates were placed 12 cm away from the sputtering target inside the sputtering chamber. A variety of deposition periods (1, 2.5, 5, 10, and 15 minutes) were applied to change the WO₃ films' thickness. The deposition chamber was evacuated to an initial pressure of 9 × 10⁻⁶ Torr while maintaining the deposition pressure at 3 × 10⁻³ Torr. For all samples, the deposition process was carried out in a 70 sccm mixture of oxygen and argon (35 sccm each) at a power output of 100 W. Finally, the fabricated WO₃ were annealed in ambient air for 2 hours using a muffle furnace at 500 °C with 10° ramping rate.

As a post-processing step, the BiVO₄ layer was placed on the WO₃ films. As a first stage, separate WO₃ films of varying thicknesses were deposited inside the deposition chamber. A circular disk of metallic Bi (99.995% purity; purchased from ACI alloys INC, San Jose, CA, USA) was utilized as a sputtering target to deposit a thin layer of Bi₂O₃ using a DC reactive sputtering system. The Bi₂O₃ layer was deposited using a 30 W deposition power and a 40 sccm mixture of oxygen and argon (20 sccm each). The initial and

deposition pressures were kept consistent with those applied in the deposition of WO_3 thin films. Following that, 30 μL of vanadyl acetylacetonate solution in 0.15 M dimethylsulfoxide was placed on the surface of the $\text{Bi}_2\text{O}_3/\text{WO}_3$ films to convert it to a BiVO_4 layer. The drop cast films were subsequently heat-treated for 2 hours at 450 $^\circ\text{C}$ with a 2 $^\circ/\text{min}$ ramping rate in a muffle furnace. Finally, the extra V_2O_3 layer on the $\text{BiVO}_4/\text{WO}_3$ films was removed using 1.0 M NaOH.

The photo-assisted electrochemical deposition was used to deposit the Co–Pi on the surface of $\text{BiVO}_4/\text{WO}_3$ films. The deposition was carried out with a 0.5 M solution of $\text{Co}(\text{NO}_3)_2$ in 0.1 M phosphate buffer (pH 7). Several protentional (0.1, 0.2, 0.3, and 0.4 V_{RHE}) and deposition times were used (30, 60, 90, and 120 sec) to optimize the amount of Co–Pi deposition.

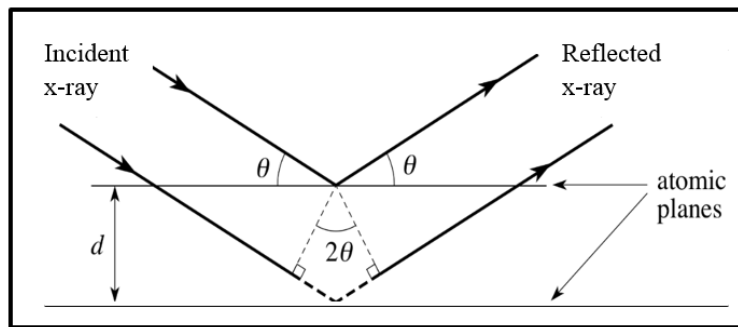
3.2 Structural Characterization Techniques

3.2.1 X-ray Diffraction Analysis (XRD)

X-ray diffraction (XRD) is a well-known technique for studying crystalline materials' phase composition and structure [116]. The XRD results, in particular, show information about crystal orientation, phase, and structure parameters like crystallinity, crystal defects, strain, and average grain size [116]. The XRD principle is based on the X-rays scattered within the crystal's atoms due to the electron density. A path difference occurs when the X-ray beam comes into contact with the crystal planes [116]. As a result, the X-rays scattered from various crystal planes will interfere, either constructively or destructively. The XRD pattern will form when the constructive interference condition is satisfied, which occurs only when the incident X-rays are in phase. Bragg's law (Eq. 3.1) defines it as the angle at which the constructive interference condition is satisfied [116].

$$n\lambda = 2d \sin\theta \quad \text{Eq. (3.1)}$$

Where λ is the wavelength of the x-rays, d is the interplanar spacing, n is an integer and θ is the Bragg diffraction angle. Scheme (3.1) shows the Bragg's diffraction path.



Scheme 3.1. Bragg diffraction schematic

In this work, a CuK α x-ray source with a wavelength of 1.54 Å was used for all XRD experiments. A Rigaku Miniflex 600 X-Ray Diffraction (XRD) is shown in Fig. (3.2).

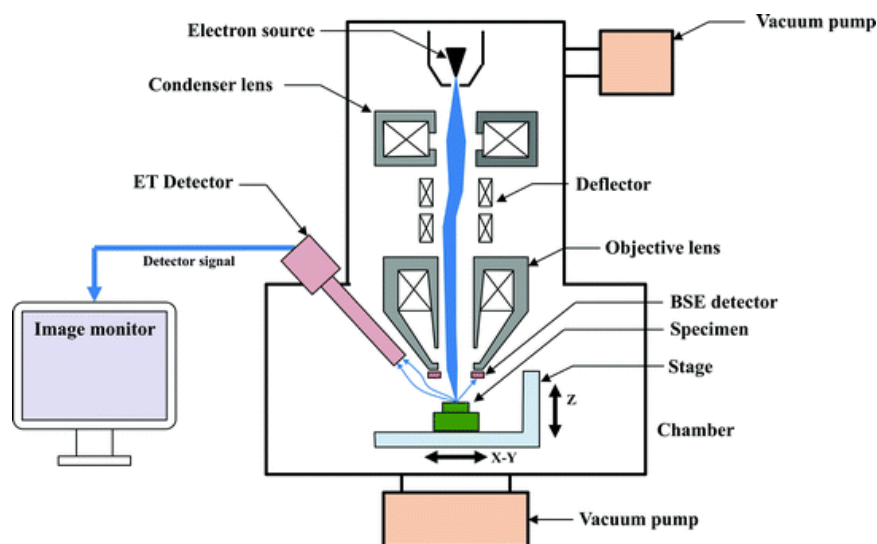


Figure 3.2. Photograph of the XRD unit (IRC-HES lab / KFUPM)

3.2.2 Field emission scanning electron microscopy and energy-dispersive X-ray spectroscopy (FE-SEM and EDS)

The FE-SEM imaging technique reveals information about the morphological properties of the tested samples [117]. A focused electron beam is used in this technique to scan the sample's surface using one of the two different signals: backscattered electron and secondary electron signals [117]. The morphology of the sample's surface is determined by the signal contrast of backscattered or secondary electrons. In general, the backscattered electron signal contrast is used to determine the compositional difference, whereas the secondary electron signal contrast is used to

investigate the morphology of the samples. Scheme (3.2) shows the schematic diagram for the FE-SEM basic component.



Scheme 3.2. Schematic diagram for the FE-SEM basic component [118]

Furthermore, energy-dispersive X-ray spectroscopy analysis is used for semi-quantitative and qualitative measurements by analyzing the X-ray signals released by the sample. An electrically conductive layer should be used to coat the non-conductive samples to prevent the accumulation of electrons on the specimen's surface.

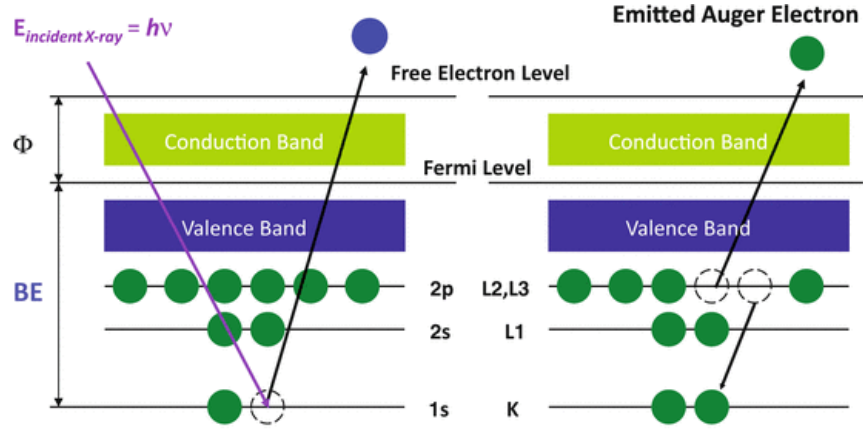
To identify the nanostructure and the morphology of our fabricated thin films photoanodes, the electron microscope micrographs were taken with a Field Emission Scanning Electron Microscopy (Tescan Lyra-3). Fig. (3.3) shows the actual photograph of the used FE-SEM instrument located at the IRC-HES imaging lab, KFUPM.



Figure 3.3. A photograph of the FE-SEM instrument, IRC-HES imaging lab, KFUPM.

3.2.3 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a technique for characterizing samples using the photoelectric effect to reveal information about their chemical composition. Specifically, the analyzed sample is excited with X-ray radiation generated by Al or W X-ray source [119]. If the X-ray energy exceeds the electron's binding energy in the sample's atoms, the electrons will be ejected out of the sample [120]. The energy spectrum of these ejected photoelectrons can give information about the composition and the chemical state from the sample's surface. In the XPS analysis, the core level electrons are the main target in this analysis since their binding energies are specific to the element from which they have emitted [120]. The energy level diagram of the photoemission process is shown in scheme (3.3).



Scheme.3.3. Energy level diagram of the photoemission process [121]

For a specific material, the energy required to extract the core-level electron to the vacuum level is equal to the electron's binding energy plus the work function of that specific material. Einstein's relation of the photoelectron effect (Eq. 3.2) describes the relation between the incident X-ray photon energy and the binding energy of the excited electron [122].

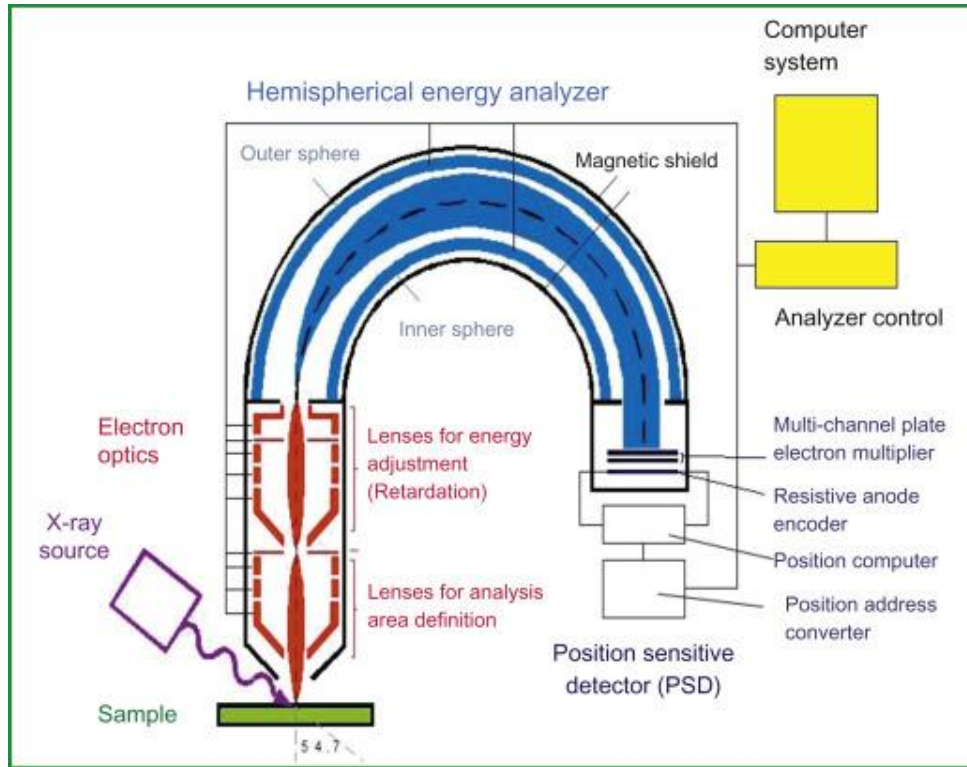
$$E_k = h\nu - E_b \quad \text{Eq. (3.2)}$$

Where E_k the kinetic energy of the ejected electron, $h\nu$ is the photon energy of the x-ray excitation source, and E_b is the binding energy of the excited electron. However, it is more convenient to use the Fermi-level (E_{bf}) as a measurement reference in an actual experiment environment [122]. To do so, Einstein's equation could be reformed as follows: (Eq. 3.3)

$$E_k = h\nu - (E_{bf} + \varphi) \quad \text{Eq. (3.3)}$$

Where φ is the work function of the spectrometer. Additionally, actual measurements can reveal that the binding energies of electrons in a particular shell are shifted relative to

their theoretical value. This shift occurs as a result of the valence electrons' screening effect on the core electrons at various material oxidation states [122]. The XPS instruments' primary component is illustrated in the schematic diagram below, scheme. (3.4).



Scheme (3.4) A schematic illustration of XPS primary component [123]

In this work, the chemical components of the fabricated photoanodes were studied by a typical XPS Model: ESCALAB250XI, XPS. The photograph of the used XPS, located at the Physics department, KFUPM, is shown in Figure (3.4).



Figure 3.4. XPS photograph (Physics department / KFUPM)

3.2.4 Ultraviolet-visible spectroscopy (UV-Vis)

Ultraviolet-visible spectroscopy (UV-Vis) is an optical characterization method that depends on the capability of the material to transmit, reflect, or absorb light [124]. The reflectance, absorption, and transmission are complementary to each other as they correspond to the aspect of light-matter interaction. This technique uses monochromatic white light with a wide range of wavelengths in nm to irradiate the tested sample. The photon energy of this light can be calculated using the following equation (Eq. 3.4) [125]:

$$E = \frac{h c}{\lambda} \quad \text{Eq. (3.4)}$$

where E is the energy in eV, h is the Planck's constant, c is the speed of light and λ is the wavelength of the light in nm.

In the case of a semiconducting specimen, if the incident photon energy is equal to or higher than the bandgap of the material, then a photoexcitation process will occur as a result of incident photons absorption by the valance band electrons, which will be excited to its conduction band. If the incident photons have lower energy than the bandgap of the semiconductor, then the photons will be transmitted. In general, the basic principle of the UV-Vis technique is a measurement of the number of photons transmitted with respect to its wavelength or energy. The detector determines the transmittance (T) as a function of the light's wavelength or photon energy. Equation (3.5) can be used to convert transmittance directly to absorbance [125].

$$Abs = \log \left(\frac{1}{T} \right) \quad \text{Eq. (3.5)}$$

The absorption coefficient (α , eVcm^{-1}) as a function of energy can be calculated by taking the thickness of the film into account, and the optical band gap can be determined from the Tauc plot [125].

$$\alpha h\nu = A(h\nu - E_g)^n \quad \text{Eq. (3.6)}$$

Where E_g is the band gap, and $n = \frac{1}{2}$ and 2 for direct and indirect optical transitions respectively.

In this work, optical transmittance and optical band gap measurements of the prepared thin-film sensors were carried out using a double beam UV/Vis spectrophotometer (Agilent, Cary 5000 UV-Vis-NIR) in the wavelength range of 200-

800 nm. Fig. (3.5) shows the photograph of the UV. Vis's instrument is located at IRC-HES lab, KFUPM.



Figure 3.5. A photograph of the UV-Vis instrument located at IRC-HES lab, KFUPM.

3.3 Photoelectrochemical measurements

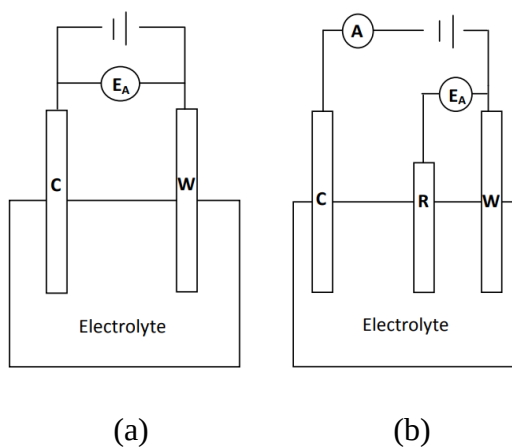
A photoelectrochemical cell is a common type of device that generates photocurrent by contacting a semiconductor with an electrolyte. It consists of a photoactive semiconductor working electrode and a counter electrode made of metal. Both electrodes are immersed in the electrolyte and are regulated via a potentiostat.

3.3.1 Potentiostat

A potentiostat is a system that controls the potential delivered to a working electrode with respect to a reference electrode and monitors the current flowing between the working electrode and a third electrode, referred to as the auxiliary electrode. These electrodes can be connected with the potentiostat in two configurations; two-electrodes and three-electrodes [126].

The two-electrode configurations consist of a working electrode on which the intended chemistry occurs and a counter electrode that serves as the cell's other half. The applied potential is measured between the working and counter electrodes, and the resulting current is measured in one of these electrodes [127]. In a two-electrode configuration, the counter electrode serves two purposes [127]. It completes the circuit, allowing charge to flow through the cell, and also ensures that the interfacial potential remains constant regardless of the current. Under most circumstances, it is impossible to meet both of these requirements. Maintaining a constant counter electrode potential while current flows is extremely difficult in a two-electrode system. This fact, combined with an inability to compensate for the voltage drop across the solution, results in insufficient control of the working electrode potential in a two-electrode system. Two distinct electrodes are preferable for carrying current and maintaining a reference voltage [127].

The three-electrode system eliminates a large number of the disadvantages associated with the two-electrode configuration. It consists of a working electrode, a counter electrode, and a reference electrode [127]. Without conducting any current, the reference electrode serves as a reference for measuring and controlling the working electrode potential. Therefore, it should maintain a constant electrochemical potential at low current densities [127]. Additionally, because the reference electrode conducts such a small amount of current, the iR drop between the reference and working electrodes is frequently quite small. Thus, the three-electrode system provides a much more stable reference potential and compensates for the iR drop across the solution [127]. This translates into superior control over the potential of the working electrode. The Saturated Calomel Electrode and the Ag/AgCl electrode are the two most frequently used laboratory reference electrodes [128]. The counter electrode's primary function in the three-electrode configuration is to conduct all the current required to balance the current observed at the working electrode.



Scheme (3.5) Simple schematic of (a) two-electrodes, (b) three-electrodes configurations.

3.3.2 Photoelectrochemical measurements for $W_{18}O_{49}$ and WO_3 photoanodes.

The photoelectrocatalytic performance measurements, chronoamperometry, linear sweep voltammetry, and electrochemical impedance spectroscopy of the $W_{18}O_{49}$ and WO_3 photoanodes were studied in a quartz cell attached to a potentiostat (Voltalab, model: PGZ 402, Colorado, USA) with a three-electrode measurement system. $W_{18}O_{49}$ and WO_3 films, saturated calomel electrode (SCE), and platinum coil were used as working electrodes, reference electrode, and counter electrode, respectively. A 0.1 M aqueous sodium sulfate (Na_2SO_4) solution was used as an electrolyte. A 300-watt xenon lamp (Model: Max-303, Tokyo, Japan) was used as an illumination source with a wavelength (λ) range of 300 to 600 nm and 100 mW cm^{-2} light intensity. The charge transfer resistance (R_{ct}) of the deposited films was evaluated under dark and light using electrochemical impedance spectroscopy (EIS).

3.3.3 Photoelectrochemical measurements for Co–Pi/BiVO₄ and Co–Pi/BiVO₄/WO₃ photoanodes.

The photoelectrochemical measurements were carried out in three-electrode configurations by using a NOVA potentiostat (PGSTAT 302N). The $BiVO_4$ and modified Co–Pi/ $BiVO_4$ photoanodes with the geometrical area of 0.25 cm^2 were used as the working electrodes with Ag/AgCl (3.0 KCl) as the reference and Pt as the counter electrode. An aqueous solution of 0.5 M phosphate solution (PBS) was used in the Teflon made cell with a quartz window from one side for photoelectrochemical measurements. The solar simulator from 1002 SunLiteTM (ABET technologies) to obtain simulated solar light and calibrated from

the silicon reference cell. The measured potential vs. Ag/AgCl ($E_{Ag/AgCl}$) reference electrode was converted to the reversible hydrogen electrode (RHE) by following Eq. (3.7)

$$E_{RHE} = E_{Ag/AgCl} + 0.0591 \cdot pH + E_{Ag/AgCl}^0 \quad \text{Eq. (3.7)}$$

where $E_{Ag/AgCl}^0$ is the standard electrode potential = 0.198, and the pH of PBS is 7.0.

The chronopotentiometry response for BiVO₄ and Co-Pi/BiVO₄ photoanodes were measured to calculate IPCE response at 1.23 VRHE. The collimated monochromatic LED light source (high-power LEDs–Thorlabs) with different wavelengths were used, and the intensity of light was calibrated by using photodiode (FDS100-CAL, Thorlabs). The IPCE % values were calculated by using Eqn. (3.8):

$$IPCE (\%) = \frac{1240 J_{ph}}{\lambda P_{light}} \times 100 \quad \text{Eq. (3.8)}$$

where J_{ph} , P_{light} , and λ are the photocurrent density (mA cm⁻²), a power density of the light (mW cm⁻²), and incident light wavelength, respectively.

The electrochemical impedance spectroscopy results were measured by using the same NOVA Potentiostat electrochemical setup. Nyquist plots were measured at various potentials with the frequency range from 0.1 Hz to 100 kHz at 10 mV amplitude-frequency under standard illumination conditions. Additionally, the Mott-Schottky plots were measured at 10 kHz in a potential window from 0.3 – 1.4 V_{RHE} in the dark.

3.4 Theoretical calculation

Density functional theory (DFT) is an efficient method for estimating the electronic structural properties of solids, molecules, and atoms [129]. It employs the fundamental laws of quantum physics to gain a quantitative knowledge of material qualities. Unlike the many-body wave function method, DFT theory uses one-body density as a fundamental variable [129]. The density of the many-body wave function is a function of $3N$ coordinates. However, density functional theory is the only function of three spatial coordinates; therefore, it is computationally feasible even for large systems [129].

DFT describe the ground state of systems of N -interacting electrons using the following Hamiltonian ($\hat{H}$) equation [129]:

$$\begin{aligned}\hat{H} &= \hat{T} + \hat{V} + \hat{V}_{ee} \\ &= -\sum_{i=1}^N \frac{\nabla_i^2}{2} + \sum_{i=1}^N V(\mathbf{r}_i) + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\end{aligned}\quad \text{Eq. (3.9)}$$

Where $\hat{T}$ is the kinetic energy operator, $\hat{V}$ is the potential energy operator, and $\hat{V}_{ee}$ is the interaction energy operator.

The fundamental roles of the density functional theory were described by the famous Hohenberg–Kohn theorem, which can be summarized as follows [129]:

- 1- For any system with interacting electrons, the external potential $V(\mathbf{r})$, Hamiltonian, and other physical properties can be uniquely determined from the ground state electron density $n(\mathbf{r})$ of that system.
- 2- For any system characterized by ground-state potential v_o , the ground-state density $n_0(\mathbf{r})$ and energy E_0 can be obtained using a variational principle that involves only

the density; in which, for a proper ground state density, the ground-state energy can be written as a function of the density $E_{v_0}[n]$, which in turn gives the ground-state energy E_0 . The densities function should hold the following inequality:

$$E_0 = E_{v_0}[n_0] < E_{v_0}[n] \quad \text{Eq. (3.10)}$$

3- The energy functional can be written in terms of a functional $F[n]$ as follows:

$$E_{v_0}[n] = F[n] + \int d^3r v_0(r)n(r) \quad \text{Eq. (3.11)}$$

Where $F[n]$ is a universal functional that describes the particle-particle coulomb interaction and is independent of the potential $v_0(r)$ of the particular system under consideration, that is, it has the same functional form for all systems.

Since the explicit density dependence of $F[n]$ remains unknown, several approximations have been suggested, such as Thomas–Fermi approximation and Kohn–Sham equations. Kohn–Sham equations are the heart of modern density functional theory. It has a form of single-particle Schrodinger equation in which the density is computed from the N single-particle orbits occupied in the ground state Slater determinant [129]

$$n(r) = \sum_i^{occ} |\varphi_i(r)|^2 \quad \text{Eq. (3.12)}$$

The main idea of the Kohn-Sham equations is to buildup a single particle potential $v_s(r)$ that the density of the auxiliary noninteracting system equals the density of the interacting system of interest. For that, the universal functional in the Hohenberg–Kohn theorem can be written in the following form [129]:

$$F[n] = T_s[n] + U[n] + E_{xc}[n] \quad \text{Eq. (3.13)}$$

Where $T_s[n]$ is the noninteracting kinetic energy, $U[n]$ is the classical electrostatic energy of the charge distribution, and $E_{xc}[n]$ is the exchange-correlation energy functional, which describes the exact kinetic and electron-electron interaction energies [129].

The exchange-correlation functions have several forms, such as the local density approximation (LDA) [130], the generalized gradient approximation (GGA) [131], and hybrid functionals (HSE, B3YLP,... etc.) [132]. The simplest approximation is the LDA, which assumes that the exchange-correlation energy at a point is equal to that of a uniform electron gas with the same density at that point. By including the electron density gradient, the GGA attempts to incorporate the effects of inhomogeneities; as such, it is a semi-local method. Additionally, the hybrid functional is nothing more than a linear combination of two or more exchange-correlation functionals [133].

3.4.1 Theoretical calculation of WO_x

DFT and pseudopotential methods were carried out to obtain the first principle band structure and density of state (DOS) calculations of WO₃ using Vienna ab initio simulation (VASP) package. Generalized gradient approximation (GGA) and Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional were used to find the standard band structure and DOS of WO_x. 630 eV was set as an energy cut-off for a basis set. The $6 \times 4 \times 5$ k-mesh of the Monkhorst–Pack scheme was used to simplify the Brillouin zone for bulk WO_x. 10^{-6} eV per atom was used as self-consistent field (SCF) tolerance. Hybrid functional DFT calculation using B3YLP correction functional was used to get an accurate band gap value.

3.4.2 Theoretical calculation of BiVO₄

Density functional theory (DFT) was used to study the electronic band structure properties with the help of the Vienna ab initio simulation package (VASP) [134] with the projector augmented-wave (PAW) method [135]. A generalized gradient approximation (GGA) and the Perdew–Burke–Ernzerhof (PBE) were utilized to define the exchange and correlation effects [136]. A conventional cell of pure BiVO₄ was relaxed using a plane-wave energy cut-off of 400 eV and a mesh size of 6×7×4 using the Monkhorst-Pack method. BiVO₄ unit cell was built from the monoclinic-BiVO₄ structure with a vacuum region of about 11 Å in thickness in the Z direction to calculate its ionization energy and electron affinity.

CHAPTER 4

TUNGSTEN OXIDE PHOTOANODES

This chapter has studied the influence of the tungsten oxide film deposition methods and configuration on its photocatalytic activity. Initially, both PLD and sputtering methods were explored for fabricating the tungsten oxide photoanode. As illustrated in Fig. (4.0a), the photocurrent density of the tungsten oxide film prepared by PLD was unusable due to the film's degradation inside the aqueous electrolyte solution (Na_2SO_4). On the other hand, the film made by sputtering disposition had better stability over three successive test cycles than the PLD deposited film, as indicated in Fig. (4.0b), and over two hours of continuous illumination, as illustrated in the coming sections.

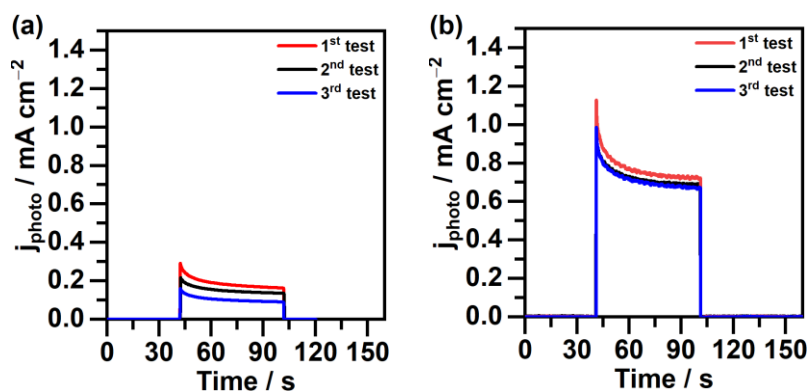


Figure 4.0. Chopped-light stability test for tungsten oxide films prepared by (a) PLD and (b) sputtering deposition methods.

Tungsten oxide phases; $\text{W}_{18}\text{O}_{49}$ and WO_3 , were prepared based on their sputtering deposition configuration, as described in Chapter 3. For each tungsten oxide phase, the effect of tungsten oxide layer thickness, annealing temperature, and annealing environment on PEC performance was investigated and presented in the following sections.

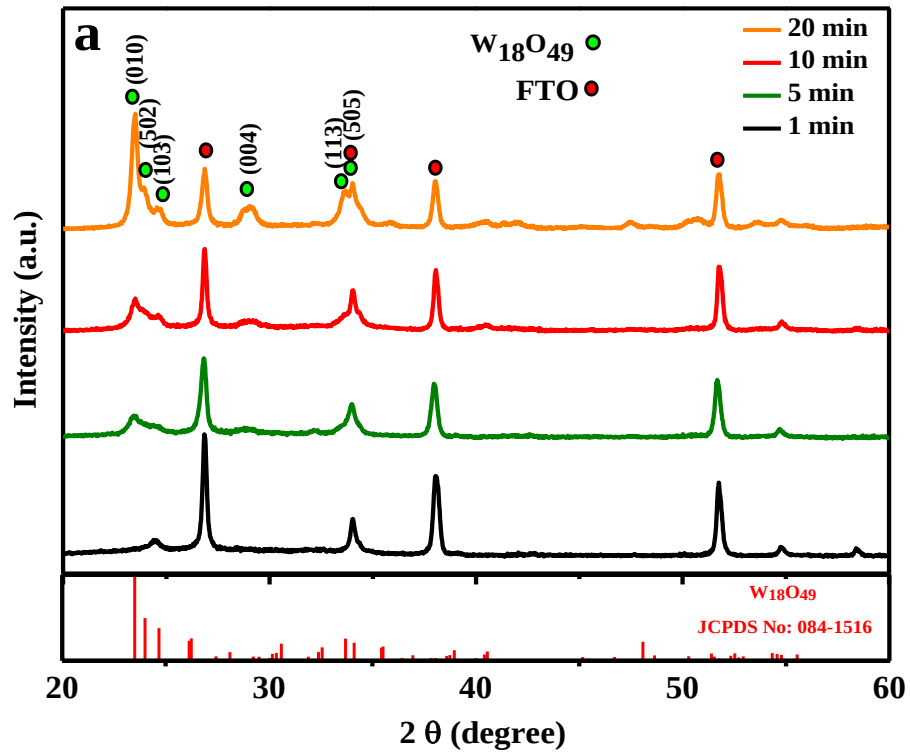
4.1 Structural, morphological, compositional, and optical analysis of $W_{18}O_{49}$ photoanode's films.

4.1.1 XRD results of $W_{18}O_{49}$ photoanode's films

Figure (4.1) shows the XRD patterns of the sputtered W film and $W_{18}O_{49}$ films prepared under different conditions. The diffraction patterns of the $W_{18}O_{49}$ films synthesized by post-annealing of sputtered W films are presented in Fig. (4.1a). As can be observed, the XRD of films prepared after different deposition times shows sharp reflections at 26.8° , 34.1° , 38.1° , 51.8° , and 54.8° , which are attributed to FTO glass substrate. Furthermore, the diffractions centered at 23.5° , 24.0° , 24.6° , 28.9° , 33.5° , and 34.0° are ascribed to (010), (502), (103), (004), (113), and (505) planes of monoclinic $W_{18}O_{49}$ with P2/m space group (JCPDS No: 84-1516) [137]. With increasing film thickness (deposition time), the intensity of characteristic diffractions of $W_{18}O_{49}$ is increasing. The increase of crystallinity with film thickness has also been reported in the literature and could be attributed to the energy of the impinging particles [138].

Figure (4.1b) shows the phase evolution from W to $W_{18}O_{49}$ as a function of annealing temperature. As can be seen, the diffractions of the as-fabricated w film and those annealed at 100°C and 200°C show the patterns of the FTO substrate only, indicating the amorphous nature of the deposited films at these annealing temperatures. As the temperature increased to 400°C , the change of the amorphous to the crystalline phase is demonstrated by the appearance of the diffractions at 35.8° , 40.3° , and 44.1° . These reflections are attributed to (002), (110), and (112) planes of the W_3O phase with Pm-3n space group (JCPDS No: 41-1230) [139]. Formation of $W_{18}O_{49}$ was observed at higher temperature; the XRD patterns of the W film annealed at 500°C and 600°C in air atmosphere

matches well with the monoclinic phase of $W_{18}O_{49}$, confirming the transformation of the W_3O film into $W_{18}O_{49}$ thin film. Thermal treatment of the W_3O films in the air provides further oxygen molecules that are needed for the formation of $W_{18}O_{49}$. Notably, no other diffraction is observed after thermal heating procedures.



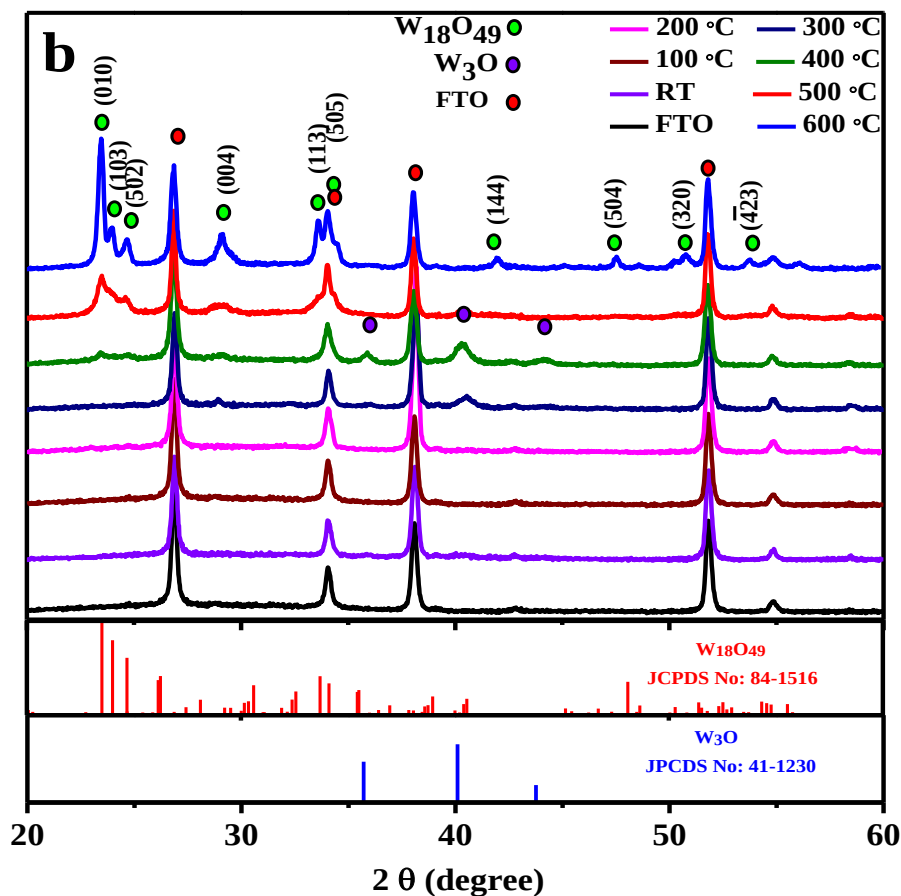


Figure 4.1. XRD patterns of the (a) $W_{18}O_{49}$ films with varies thickness fabricated by post annealing of sputtered W film at 500 °C in air (b) metallic W film to $W_{18}O_{49}$ phase transformation as a function of post annealing treatment.

4.1.2 FE-SEM results of $W_{18}O_{49}$ photoanode's films

The surface morphologies of the fabricated films were investigated in detail by FE-SEM. Figure (4.2) shows the FE-SEM images of the $W_{18}O_{49}$ films obtained after post-annealing of sputtered W films prepared as a function of deposition time. It can be observed that the thinnest film, deposited for 1 min, has a film thickness of 52 nm (Fig. 4.2a, e), is mainly consists of closely packed crystal grains, which are spherical in shape with an

average grain size ranging between 20 and 40 nm, numerous large particles with an average size of 70 nm, and small sheets. The length and diameter of these sheets are determined to be about 1.5 μm and 20 nm, respectively. Upon increasing the deposition time to 5 min, Fig. (4.2b, f), the flat and compact surface of the $\text{W}_{18}\text{O}_{49}$ film evolved into a film with a thickness of 146 nm that attached with various large sheets over several micrometers. This transformation may be due to the formation of planar defects induced by the structural strain caused by heat treatment followed by the aggregation process. The film deposited for 10 min has a thickness of 290 nm, as shown in Fig. (4.2c, g). It was a form of well-distributed and interconnected nanosized sheets without any significant voids. Meanwhile, $\text{W}_{18}\text{O}_{49}$ film deposited for 20 min shows uniform and stacked sheets to form a nanorods-like structure with a thickness of 550 nm, as shown in Fig. (4.2d, h).

Low and high-magnification FE-SEM images of the sputtered W films annealed at different temperatures are shown in Fig. (4.3). It can be clearly noticed from Fig. (4.3) that the microstructure of the films annealed at 100 °C and 200 °C revealed a compact, voids-free, and smooth microstructure with small grains. At 300 °C, the deposited film started to crack, forming a first oxide phase (W_3O) as a result of particles accumulation. With further heating, the particles built-up to form small sheets, as shown in the samples annealed at 400 °C. At 500 °C, all the nanoparticles accumulated in groups to form uniform $\text{W}_{18}\text{O}_{49}$ nanosheets. By increasing the annealing temperature to 600 °C, the $\text{W}_{18}\text{O}_{49}$ nano-sheets grew vertically to form a pillar-like structure, as shown in the high-resolution inset image of the 600 °C annealed sample.

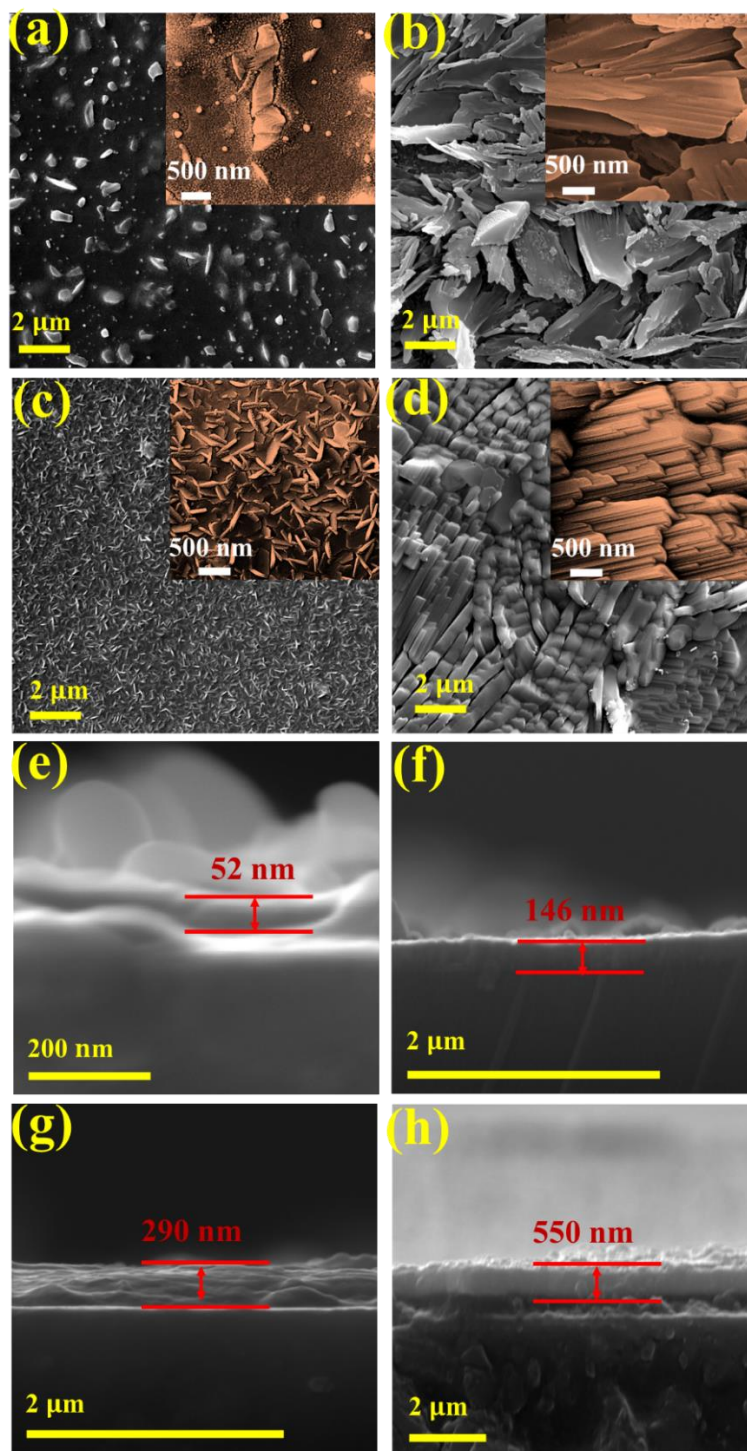


Figure 4.2. FE-SEM images of $W_{18}O_{49}$ films deposited for (a) 1, (b) 5, (c) 10, and (d) 20 min. and FE-SEM cross-section images of $W_{18}O_{49}$ films deposited for (e) 1, (f) 5, (g) 10, and (h) 20 min. All the films were annealed at 500 °C in air.

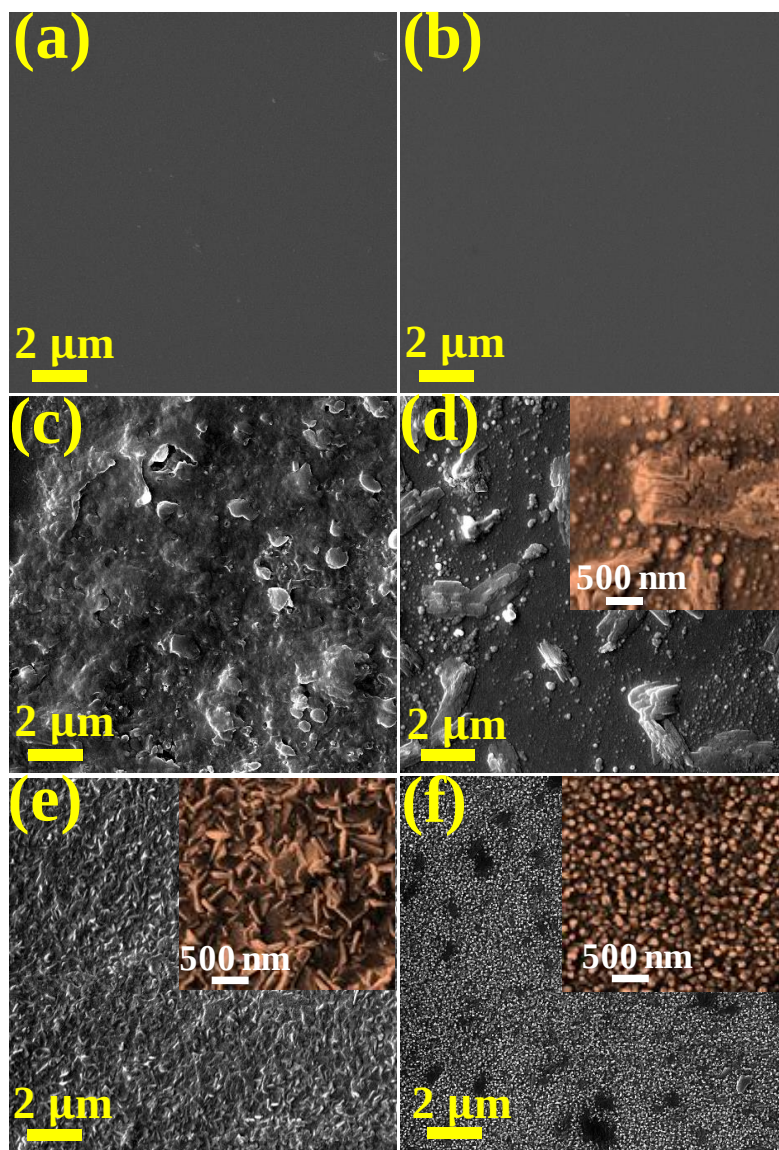


Figure 4.3. Low and high magnification FE-SEM images of the W films annealed at (a) 100, (b) 200, (c) 300, (d) 400, (e) 500, and (f) 600 oC in air.

4.1.3 UV-Vis results of $W_{18}O_{49}$ photoanode's films

The optical properties of the fabricated films are presented in Fig. (4.4). Figure (4.4a) shows the influence of $W_{18}O_{49}$ film's thickness on the ability to absorb light in the

visible and UV ranges. As can be seen, the light absorption increased with increasing the film's thickness in both visible and UV ranges. This behavior can be attributed to the increase in the average particle size caused by the increase of the W mass thickness. Furthermore, the absorption edge of $W_{18}O_{49}$ films shifted to a shorter wavelength (blue shift) with increasing the deposition time, which can presumably be ascribed to the quantum size effect. The band gap energy (E_g) of the fabricated thin films is estimated from the Tauc equation, Eq. (3.6), described in chapter 3 [140,141]. From Fig. (4.4b), it was observed that the bandgap decreases, from 3.65 eV (1 min) to 3.18 eV (20 min), as a result of increasing the thickness of the films. A similar shift in the band gap of thin films induced by the variation of the thickness has been reported elsewhere [142]. Furthermore, annealing temperature also affected the optical properties of the $W_{18}O_{49}$ films. Films annealed at temperatures 100 °C to 400 °C were opaque, indicating the metallic nature of the films, while $W_{18}O_{49}$ film annealed at 500 °C and 600 °C (Fig. (4.4c)) showed a certain level of light absorption in the UV and visible range. Moreover, $W_{18}O_{49}$ film annealed at 600 °C showed a lower absorption level compared to the film annealed at 500 °C. This can be attributed to variation in the morphology of the two films, as indicated by the FE-SEM images. The band gap measurement plot of the $W_{18}O_{49}$ films annealed at 500 °C and 600 °C is shown in Fig. (4.4d). The band gap of $W_{18}O_{49}$ films annealed at 500 and 600 °C are calculated to be 3.45 and 3.50 eV. The value of the band gap slightly increased with increasing annealing temperature. This can presumably be due to the improvement in the crystallinity that resulted in the decrease of localized states in the band gap [143].

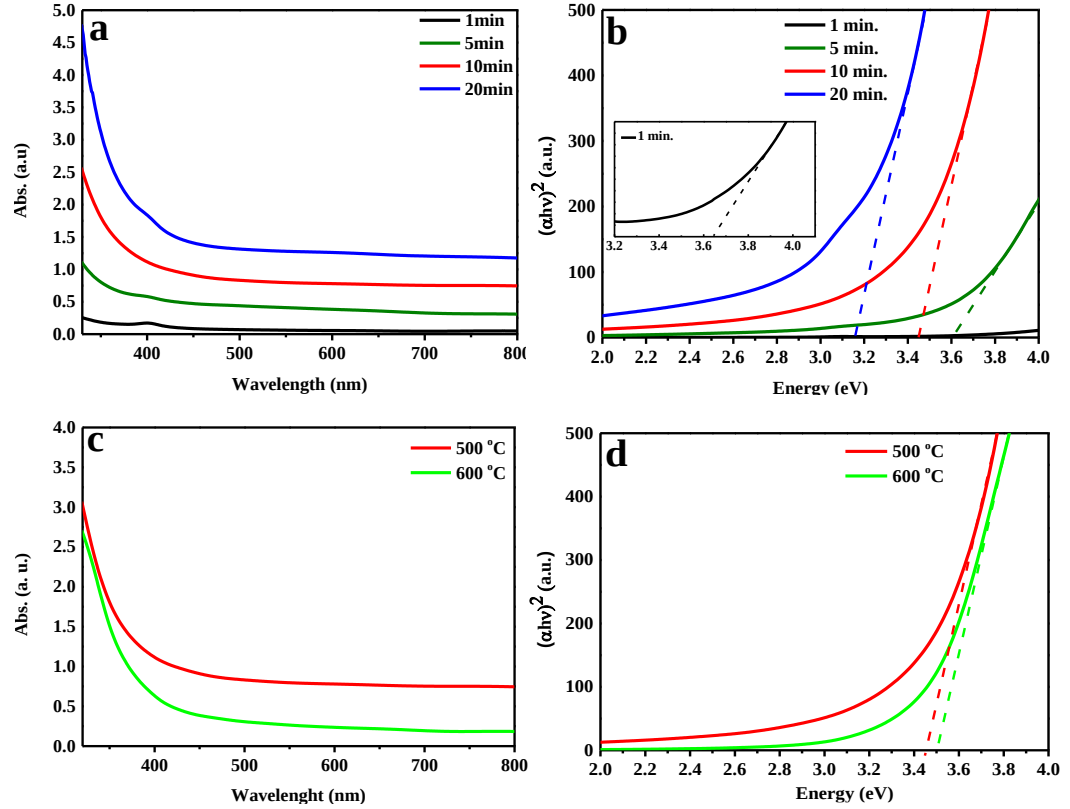


Figure 4.4. UV-Vis absorption spectra and band gap of $W_{18}O_{49}$ films as a function of deposition time (a and b), and UV-Vis absorption spectra and Tacu's plot of $W_{18}O_{49}$ films (c and d) fabricated by post-annealing of sputtered W films at 500 and 600 °C in air.

4.1.4 XPS results of $W_{18}O_{49}$ photoanode's films

X-ray photoelectron spectroscopy (XPS) was performed to study the chemical and bonding environment of the fabricated films. Fig. (4.5a, b) shows the XPS survey scans of the as-deposited W film and $W_{18}O_{49}$ film prepared at 500 °C. The results show the presence of W and O, confirming the high purity of the fabricated films. Moreover, the change in W 4f and O 1s peak intensities of these two films reveal the transformation of metallic W film to the oxide phase. The W 4f high-resolution spectra were de-convoluted to present the

chemical binding energies, i.e., W^0 ($W4f_{7/2}$ (31.1 eV), $W4f_{5/2}$ (32.9 eV)), W^{5+} ($W4f_{7/2}$ (35.0 eV) W^{6+} ($W4f_{7/2}$ (35.0 eV), $W4f_{5/2}$ (37.1 eV)) and W^{x+} ($W4f_{7/2}$ (eV), $W4f_{5/2}$ (eV), which is an intermediate oxidation state between W^0 and W^{4+} [144,145]. Fig. (4.5c) demonstrated the as-grown W core level XPS spectra of $W4f$, which shows the 7/2 and 5/2 spin-orbit doublet for the W valence state. The presence of the small peaks at 31.6 and 33.8 eV is assigned to W^{x+} such as W_3O . A typical XPS wide scan spectrum for the $W_{18}O_{49}$ thin film fabricated by post-annealing treatment of the as-deposited film at 500 °C in the air is displayed in Fig. (4.5d). Compared with the W 4f of the as-deposited film, the W 4f peaks of the $W_{18}O_{49}$ films are shifted toward higher binding energy, indicating the formation of a high oxidation state of W (i.e., 5+, and 6+) [146,147]. The high-resolution XPS spectra of O 1s peaks of the as-fabricated sputtered W, and $W_{18}O_{49}$ films are demonstrated in Fig. (4.5e, f). The decomposition of the O1s peaks showed two distinct peaks: (1) the lattice oxygen peak located at 530.5 eV (O_L) and oxygen vacancy peak at about 532.3 eV (O_V) [148].

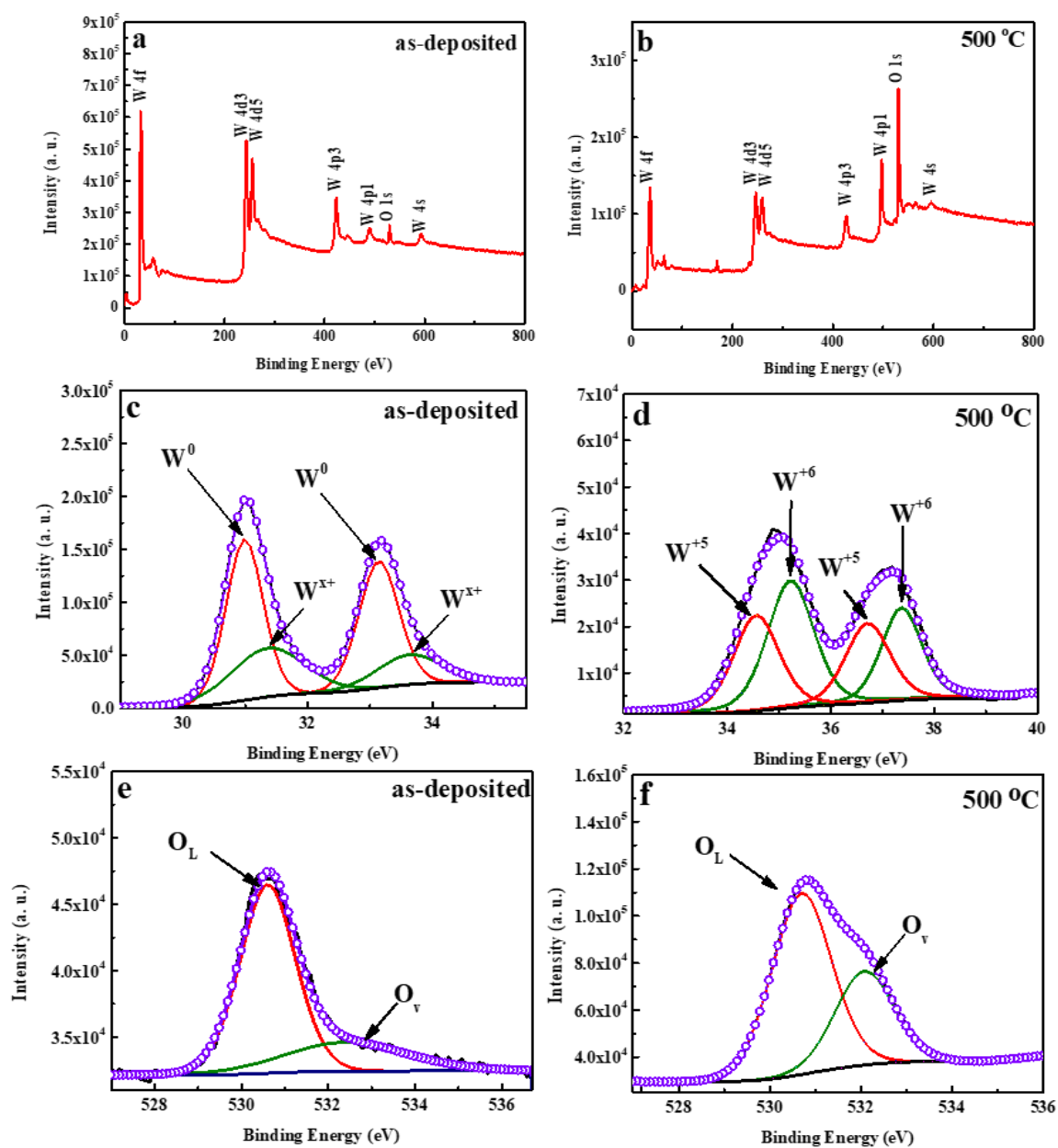


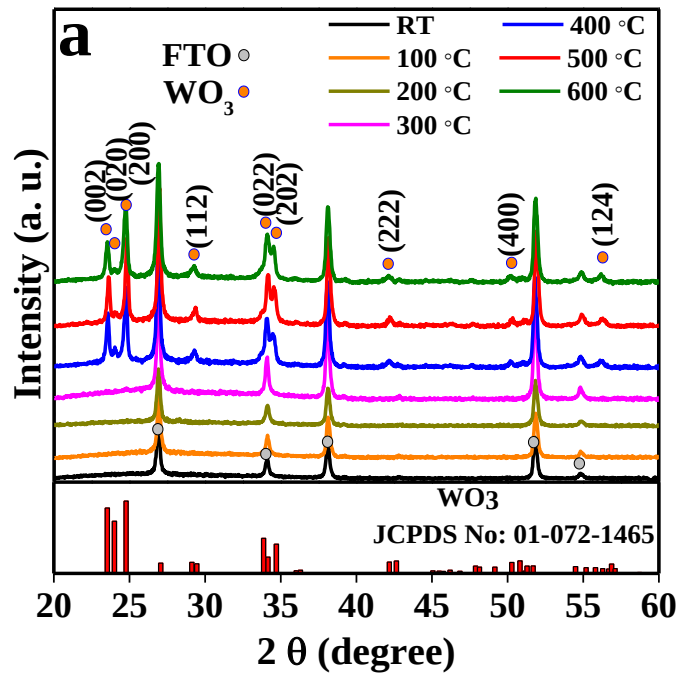
Figure 4.5. XPS spectra of: (a, b) the survey spectra, (c,d) W4f, and (e,f) O1s of the as-deposited and $W_{18}O_{49}$ film fabricated by post annealing of sputtered W film at 500 °C in air.

4.2 Structural, morphological, compositional, and optical analysis of WO₃ photoanode's films.

4.2.1 XRD results of WO₃ photoanode's films

The structural evolution of WO₃ as a function of annealing temperature, deposition time, and annealing environment was followed by X-ray diffraction (XRD). All the tested films were deposited on FTO substrate. Figure (4.6a) shows the XRD patterns of the WO₃ films annealed at different temperatures, starting from room temperature to 600 °C. It is clear that the as-deposited WO₃ film, as well as those annealed at 100, 200 and 300 °C, have an amorphous structure, as they were no presence of any diffraction peak. The diffractions appeared at 26.8°, 34.1°, 38.1°, 51.8°, and 54.8° correspond to FTO [149]. When the annealing temperature is increased to 400 °C, the amorphous phase is discerned to transform into a crystalline form. The diffractions recorded at 23.5°, 24.0°, 24.7°, 29.2°, 34.1°, 34.7°, 42.1°, 50.1°, and 56.2° are attributed to the crystalline phase of WO₃. These diffractions correspond to (002), (020), (200), (112), (022), (202), (222), (400), and (124) reflections, respectively. The recorded diffractions are in good agreement with those reported for the WO₃ monoclinic structure with P21/n space group (JCPDS No: 01-072-1465) [150,151]. A further increase in the calcination temperature from 400 °C to 600 °C did not show a noticeable impact on the XRD of the films. The change in XRD patterns as a function of deposition time (or film thickness) is shown in Figure (4.6b). All the films grew in the same WO₃ phase and preferred orientation along (200) plane. The improvement in the diffraction intensity of the films deposited for 10 min and above, compared with 5 min deposited film, can be attributed to the enhancement in the crystallinity with the increase in film thickness. The crystallinity improvement in the thicker films can be related

to the availability of a favorable medium for the atoms' thermal motion, which can lead to better alignment of crystallites [152]. Similar behavior was observed and reported for other metal oxides [153-156]. To investigate the impact of the annealing environment, the films were also annealed in vacuum and air. Figure (4.6c) compares the XRD patterns of the films obtained in vacuum and air by annealing at 500 °C. In case of the film annealed in vacuum showed a single, small, and broad diffraction at 23.9° suggesting the formation of the WO_x phase. The weak crystallinity of WO_x film might be attributed to the insufficient supply of oxygen atoms that can help in the growth of kinetically preferred orientation [157].



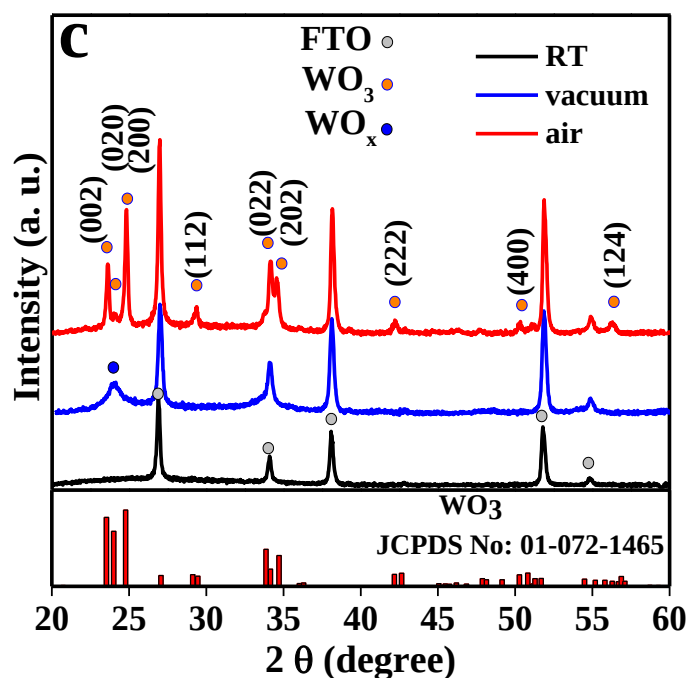
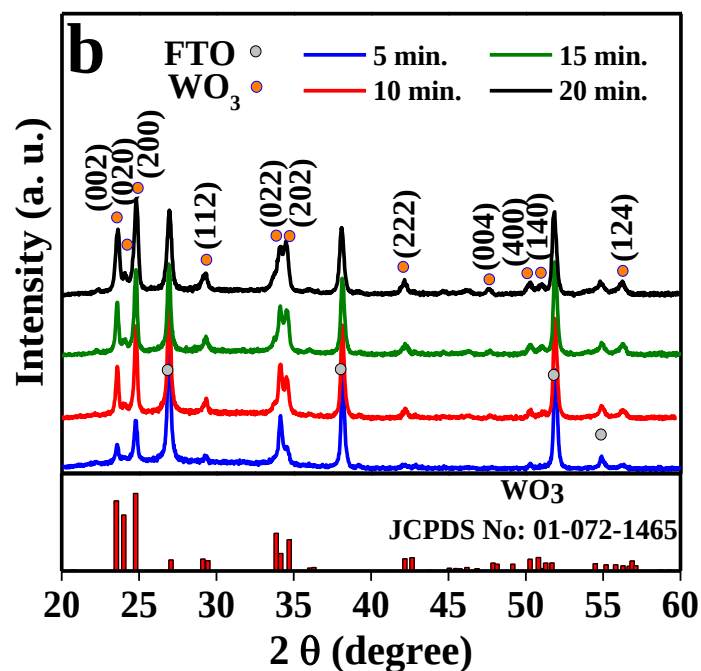


Figure 4.6. XRD patterns of WO_3 films: (a) annealed at different temperatures in air, the deposition time was 10 min, (b) prepared with different deposition times, annealed at 500 °C in air, and (c) annealed in vacuum and air, deposition time = 10 min and annealing temperature = 500 °C.

4.2.2 FE-SEM results of WO₃ photoanode's films

The information about the surface morphologies and the thickness of the WO₃ thin films were obtained by field-emission scanning electron microscopy (FES-EM). The qualities of the WO₃ films collected after post-annealing at different temperatures in the air are shown in Figure (4.7a, g). For comparison, the image of the WO₃ films annealed at 500 °C in vacuum is shown in Fig. (4.7h). The surfaces of the as-deposited and the films annealed at 100 °C, 200 °C, and 300 °C were dense, smooth, and crack-free, as shown in Fig. (4.7a, b, c, and d), respectively. The morphology change started with slight cracking for the film annealed at 400 °C (Fig. 4.7e). These cracks might be due to the phase transition from the amorphous to the crystalline phase, as observed by the XRD. The cracks became more prominent for the film annealed at 500 °C as the tungsten oxide particles began to agglomerate (Fig. 4.7f). With a further increase in the heating temperature to 600 °C, the cracks increased significantly. The tungsten oxide particle aggregation increased to form a continuous sheet, as shown in Fig. (4.7g). The surface of the WO₃ film post-annealed at 500 °C in vacuum is smooth with fewer cracks as compared to its counterpart film annealed in air at the same temperature (Fig 4.7h).

The surface and the thickness of the WO₃ films obtained after different disposition times, annealed at 500 °C in air, are obtained by top-view and cross-section of FESEM images, as shown in Fig. (4.8). The WO₃ film deposited for 5 min shows a dense, rough texture and void-free morphology with a thickness of around 87 nm (Fig. 4.8a, e). When the deposition time increased to 10 min, a few cracks appeared on the film's surface as a result of thermal aggregation [149], and the film thickness was calculated to be around 156 nm (Fig. 4.8b, f). More cracks and voids appeared with increasing the deposition time to

15 and 20 min (Fig. 4.8c, d). The WO_3 film thickness increased to around 294 and 370 nm (Fig. 4.8g, h), respectively. The obtained results suggest that the evolution of the surface morphology of the WO_3 films was dependent on its deposition time or thickness. A similar conclusion was mentioned in previous studies [158-160]. It is worth noting that the evolution of the film's thickness was almost linear with the deposition time.

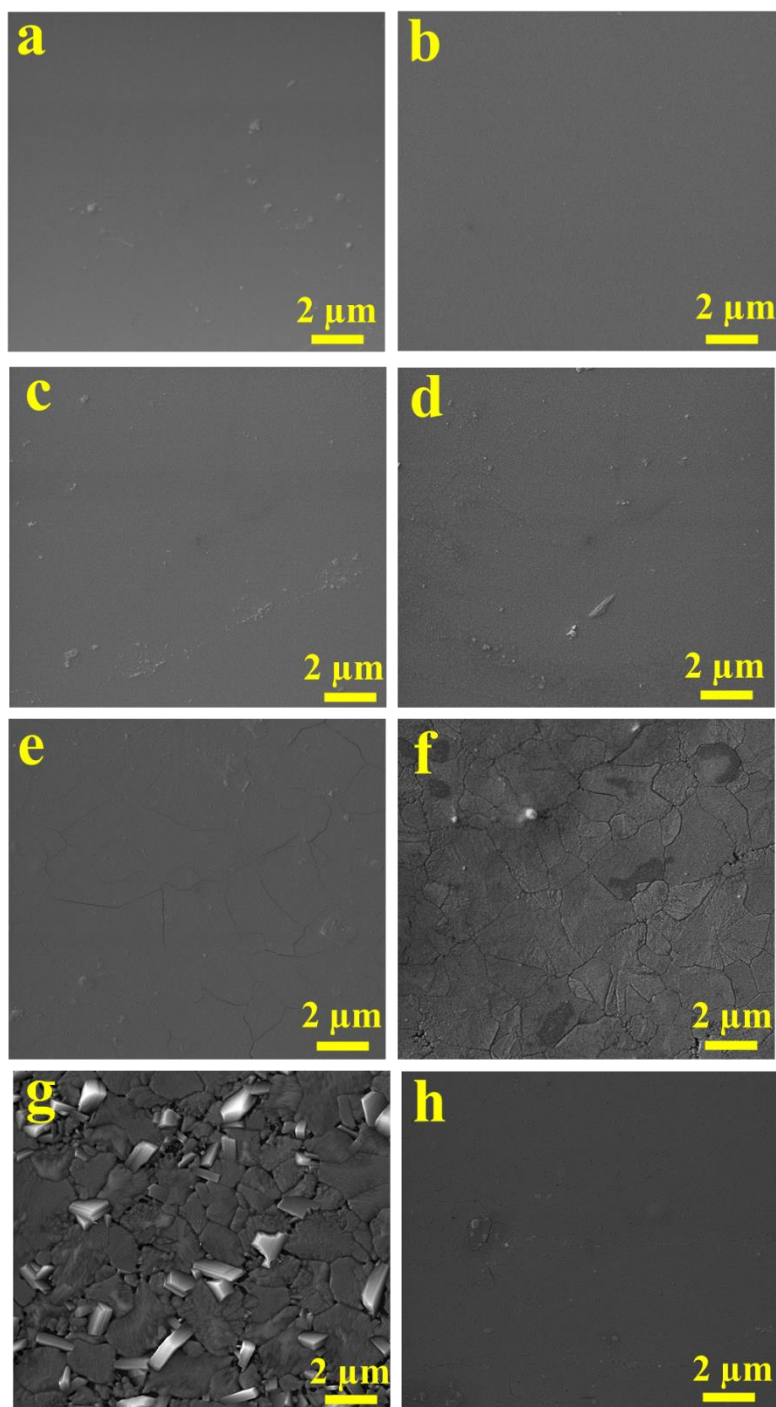


Figure 4.7. FESEM images of WO_3 films: (a) as-deposited, and annealed at (b) 100, (c) 200, (d) 300, (e) 400, (f) 500, and (g) 600 °C in air, and (h) the film annealed at 500 °C in vacuum. All samples are deposited for 10 min.

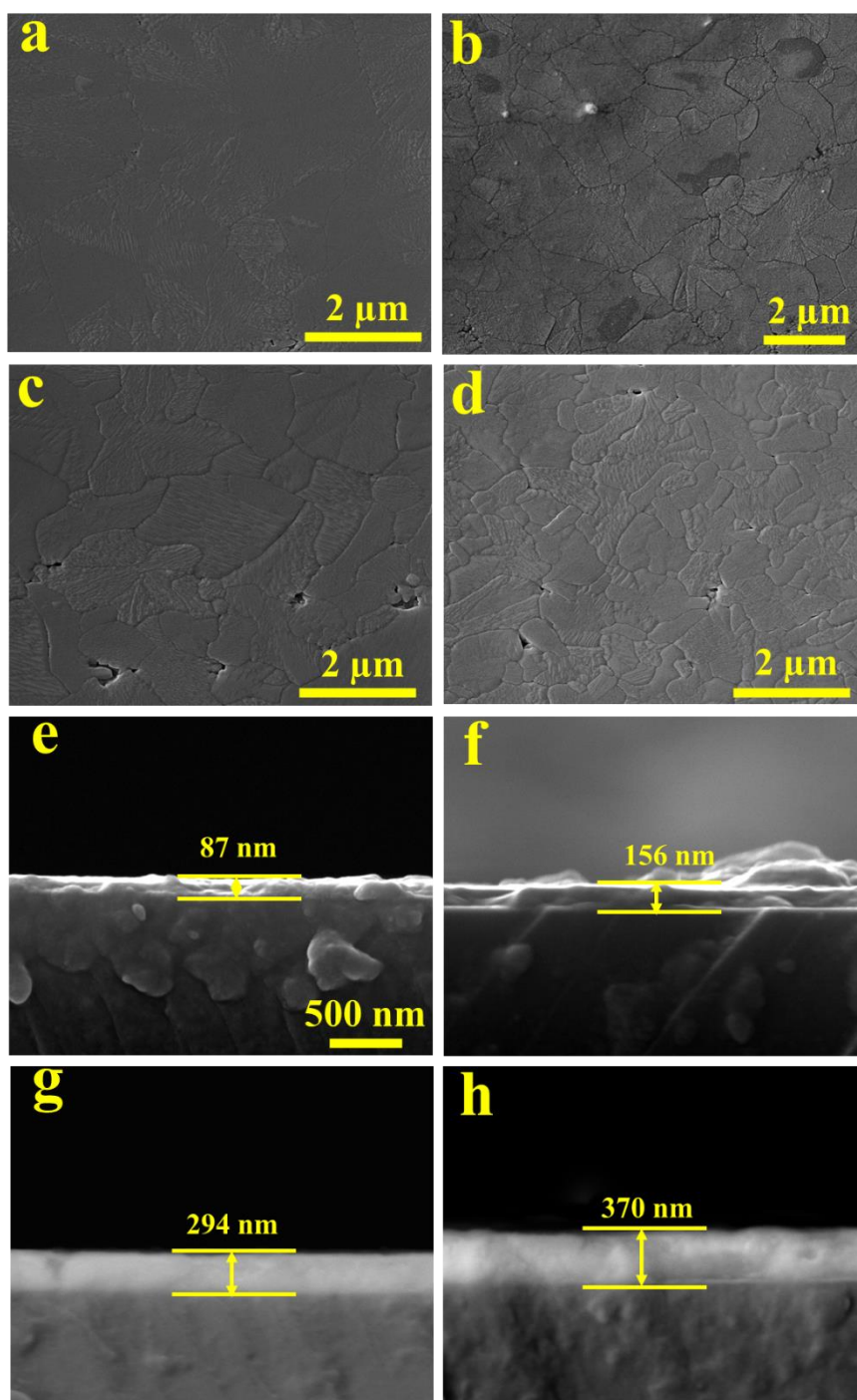


Figure 4.8. FESEM images of WO_3 films deposited for (a) 5, (b) 10, (c) 15, (d) 20 min, and their corresponding cross-section images (e) 5, (f) 10, (g) 15, (h) 20 min. All the films were annealed at 500 °C in air.

4.2.3 UV-Vis results of WO₃ photoanode's films

The optical properties of the WO₃ thin films were investigated by UV-Vis absorption spectroscopy in the wavelength range from 800 to 200 nm. The recorded spectra are shown in Fig. (4.9). Fig. (4.9a) shows the UV-Vis absorption spectra of WO₃ films annealed at different temperatures between 100 and 600 °C in air. The absorption spectra can be seen shifting to the shorter wavelength region as the post-annealing temperature increased to 600 °C. The increase in the absorption spectra in the visible region for the films that annealed at elevated temperature (400 – 600 °C) might be due to the increase in the scattered light caused by the increase in the grain size and surface roughness, as confirmed by the FE-SEM findings [161,162]. The shift in the fundamental absorption edge toward a longer wavelength can be explained by investigating the features of the optical bandgap of the fabricated films using Tauc's relation, Eq. (3.6), for indirect band gap [140,163]. Figure (4.9b) shows the functional dependence of $(\alpha h\nu)^{1/2}$ versus the absorbed photon energy. The optical bandgap of WO₃ films can be estimated by extrapolating the liner part of $(\alpha h\nu)^{1/2}$ curves to zero [163]. The optical bandgap of WO₃ films decreased, from 3.2 eV for the as-deposited film to 2.7 eV for 600 °C annealed film, with the increase in the post-annealing temperature. This behavior can be attributed to the presence of thermal-induced defects [164]. Annealing at a high temperature can affect the nanostructure of WO₃ by introducing oxygen vacancies. These vacancies create sublevels between the conduction and valance band of the WO₃ band structure and hence decreasing its bandgap [165]. The influence of WO₃ film's thickness on UV-Vis light absorption was also investigated, as shown in Fig. (4.9c). The absorption spectra, below 600 nm, had significantly increased by the increase of the deposition time, presumably due to grain size

growth caused by the rise in the WO_3 mass thickness. The bandgap of the WO_3 films was found to decrease with increasing the deposition time. The WO_3 film deposited for 5 min showed the highest bandgap (2.9 eV) due to the quantum size confinement [160]. The bandgap decreased gradually to reach the lowest value (2.7 eV) for the film deposited for 20 min due to the size change from one dimension to the bulk material (Fig. 4.9d). The annealing atmosphere was also found to have an impact on the UV-Vis absorbance spectra and optical bandgap of the films, Fig. (4.9e, f), respectively. The film annealed in air exhibited a smaller light absorption at a higher wavelength (visible range) due to the formation of fully stoichiometric WO_3 film (Fig. 4.9e) [160,166]. The 500 °C vacuum-annealed film showed a higher bandgap (3.05 eV) compared to 500 °C air-annealed film (2.8 eV) (Fig. 4.9f); this might be due to the formation of non-stoichiometric tungsten oxide phase (WO_{3-x}). The formation of WO_{3-x} is discussed in the XPS results.

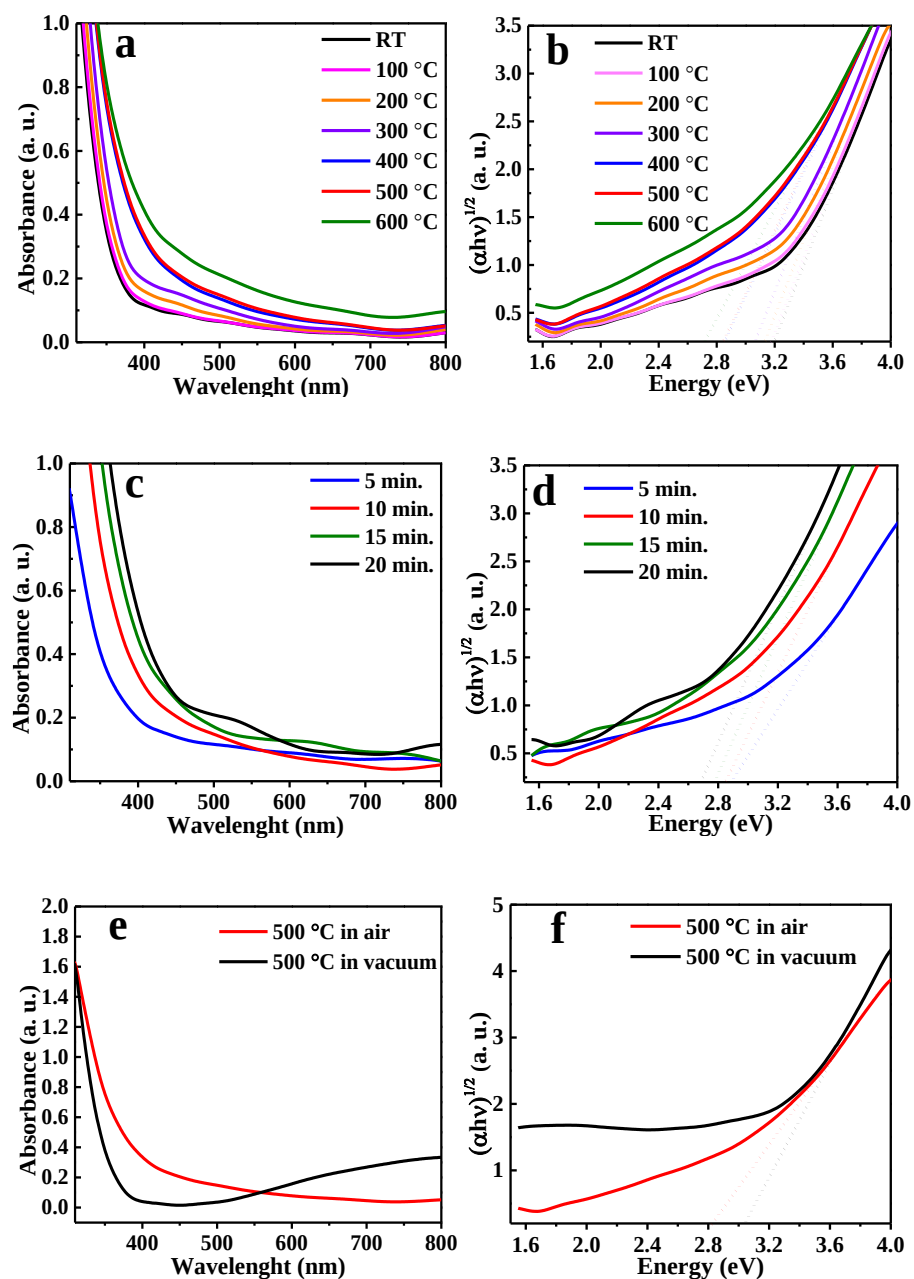


Figure 4.9. UV-Vis absorption spectra of WO_3 films as a function of (a) air annealing temperature, (c) deposition time, and (e) annealing atmosphere. Tauc's plot of WO_3 films as (b) air annealing temperature, (d) deposition time, and (f) annealing atmosphere.

4.2.4 XPS results of WO₃ photoanode's films

The compositional analysis of WO₃ films was performed using X-ray photoelectron spectroscopy (XPS), and the data is presented in Fig. (4.10). Figures (4.10a, b, c) show the XPS survey spectra of as-deposited, air-annealed, and vacuum-annealed (at 500 °C) WO₃ films. All the survey scan spectra confirm the presence of W and O without any impurities. Figures (4.10 d, e, f) demonstrate the deconvoluted peaks of W 4f spectra for the as-deposited WO₃ and WO₃ films annealed at 500 °C in air and vacuum, respectively. The deconvolution of high resolution XPS spectra of W 4f in as-deposited film shows two chemical binding energies of two different oxidation states; W⁺⁵ (at 33.9 eV (W 4f_{7/2}) and 36.2 eV (W 4f_{5/2})), and W⁺⁶ (at 35.7 eV (W 4f_{7/2}) and 37.9 eV (W 4f_{5/2})) [167,168] (Fig.4.10 d). The presence of W⁺⁵ oxidation state reflects the existence of crystal defects in the form of oxygen vacancies [169]. On the other hand, the high-resolution XPS spectrum of air-annealed WO₃ film shows only one binding energy spectrum, at 35.6 eV (W 4f_{7/2}) and 37.8 eV (W 4f_{5/2}), which is related to W⁺⁶ oxidation state (Fig. 4.10e). This confirms the formation of fully oxidized WO₃ film as a result of post-annealing treatment in the air. For the vacuum-annealed film (Fig. 4.10f), both binding energy spectra (oxidation states) of W⁺⁵ and W⁺⁶ were found at 33.8 eV (W 4f_{7/2}), 36.2 eV (W 4f_{5/2}), 35.8 eV (W 4f_{7/2}) and 37.9 eV (W 4f_{5/2}), respectively. This was caused by the absence of oxygen in the ambient annealing atmosphere. Figures (4.10g, h, i) show the deconvoluted peaks of O 1s spectra for the as-deposited WO₃ and WO₃ films annealed at 500 °C in air and vacuum, respectively. The high-resolution XPS spectrum of the O 1s for the as-deposited film was deconvoluted into two binding energies; one at 530.4 eV, which corresponds to lattice oxygen (O_L), and the other at 532.1 eV, which is due to the oxygen vacancy (O_v) (Fig.

4.10g) [170,171]. After the air-annealing treatment (Fig. 4.10h), it was observed that the number of oxygen vacancies reduced compared to the as-deposited film as a result of filling the vacancies by the absorbed oxygen from the ambient atmosphere [169]. The amount of oxygen vacancy in the vacuum-annealed film had not significantly changed due to the lack of oxygen molecules in this annealing atmosphere (Fig. 4.10i).

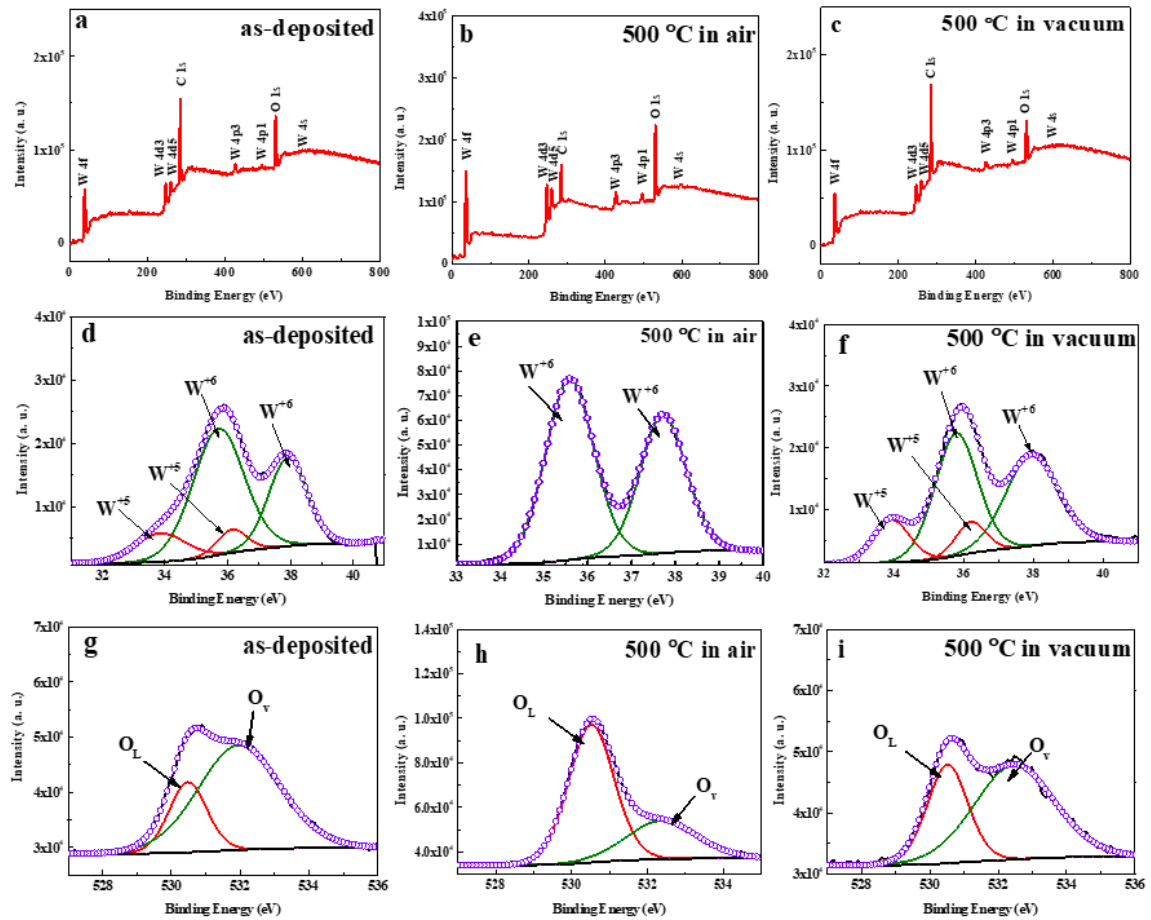


Figure 4.10. XPS spectra of (a, b, and c) survey scan, (d, e, and f) W 4f, and (g, h, and i) O 1s of the as-deposited, air-annealed (500 °C), and vacuum-annealed (500 °C) of WO₃ films, respectively.

4.3 Band structure calculations of $W_{18}O_{49}$

The theoretical bandgap and density of state (DOS) of the $W_{18}O_{49}$ phase were calculated using DFT calculations, as shown in Fig (4.11). The relaxed structure of the monoclinic $W_{18}O_{49}$ phase is depicted in Figure (4.11a). $W_{18}O_{49}$'s electronic band structure and projected density of state (pDOS) were determined using the GGA-PBE exchange-correlation function and are presented in Fig (4.11b). $W_{18}O_{49}$ has a bandgap of around 1.51 eV, which is relatively small compared to the optical bandgap value. This is a frequent issue with the GGA functional, as it severely underestimates bandgap computations [172]. The DOS reveals that the conduction band (CB) of $W_{18}O_{49}$ is dominated by W_5d orbitals, whereas the valance band is dominated by O_2p orbitals (VB). As illustrated in Fig. (4.11c), the bandgap calculation outcome was enhanced using a hybrid DFT calculation utilizing the B3YLP functional. As a result, the $W_{18}O_{49}$ phase was found to have a direct bandgap with an energy value of 2.2 eV.

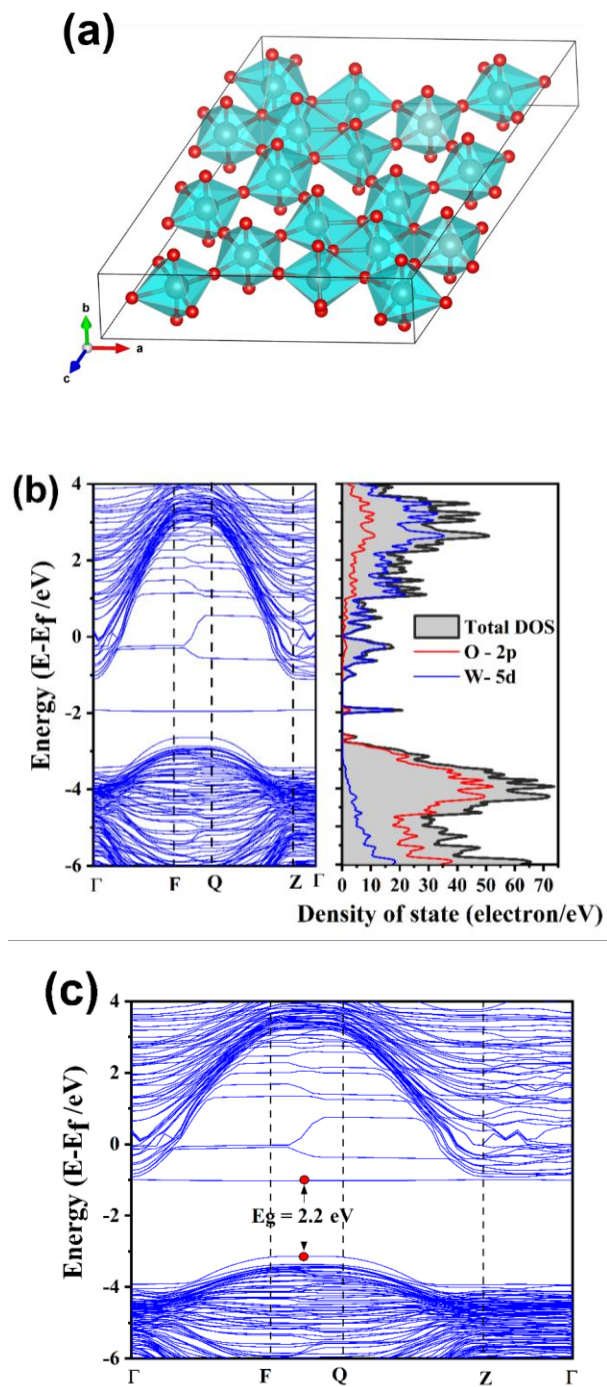


Figure 4.11. (a) $\text{W}_{18}\text{O}_{49}$ optimized structure, (b) $\text{W}_{18}\text{O}_{49}$ band structure and DOS calculations using GGA-PBE functional, and (c) $\text{W}_{18}\text{O}_{49}$ band structure calculation corrected by hybrid functional DFT.

4.4 Band structure calculations of WO₃

DFT calculations were performed to evaluate the theoretical bandgap and DOS of the WO₃ photoanode using a similar phase structure. Figure (4.12a) shows the optimized geometry of the monoclinic WO₃ structure. The electronic band structure and its projected density of state of WO₃, calculated by using the GGA-PBE exchange-correlation function, are shown in Fig. (4.12b). The bandgap of WO₃ was calculated to be around 1.14 eV, which is very small compared to the experimental value. This is a common problem with the GGA functional, which strictly underestimates the bandgap calculations [172]. The DOS shows that the conduction band (CB) of WO₃ is mainly associated with W_5d orbitals, while O_2p orbitals dominate the valance band (VB). The bandgap calculation was improved by introducing the hybrid DFT calculation using B3YLP functional, as presented in Fig. (4.12c). It was found that the calculated bandgap was improved to 2.61 eV (indirect bandgap), which is closed to the experimental value estimated in this article.

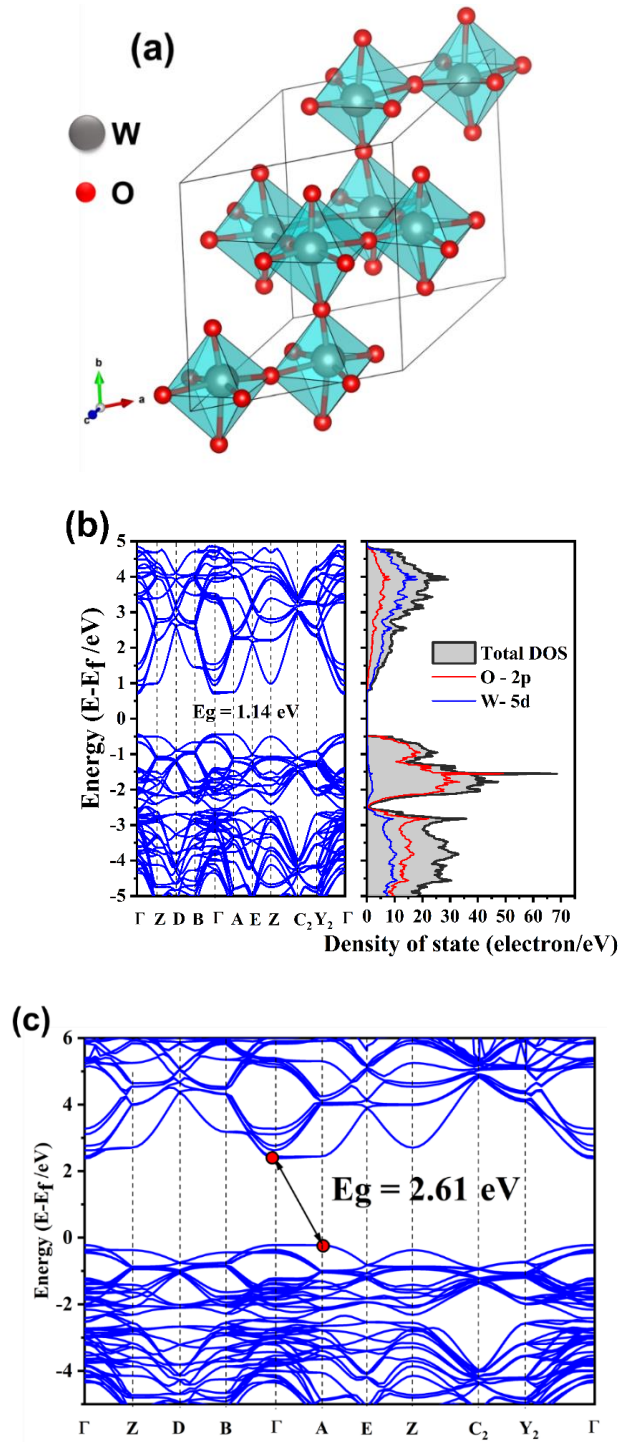


Figure 4.12. (a) WO_3 optimized structure, (b) WO_3 band structure and DOS calculations using GGA-PBE functional, and (c) WO_3 band structure calculation corrected by hybrid functional DFT.

4.5 Photoelectrochemical measurements of $W_{18}O_{49}$ photoanode's films.

The PEC performance of the fabricated $W_{18}O_{49}$ photoanode films was evaluated in 0.1 M of Na_2SO_4 electrolyte under the illumination of a 300 W Xenon lamp. Figure (4.13a) shows the photocurrent density generated by $W_{18}O_{49}$ films prepared at different deposition times at a bias of 0.6 V. Under dark, these samples did not produce any noticeable current. In the presence of light, photocurrent was measured to be 0.10, 0.25, 0.60, and 0.62 mA/cm^2 for $W_{18}O_{49}$ films deposited for 1, 5, 10, and 20 min, respectively. The weak photocurrent recorded in the presence of $W_{18}O_{49}$ thin films deposited 1 and 2 min could be ascribed to the discontinuity of the film's layer as indicated by FE-SEM images (Fig. 4.3). The interconnected sheets of $W_{18}O_{49}$ film deposited for 10 min showed significantly higher current density compared to the films prepared after a shorter deposition time. This can be correlated to the lower bandgap (3.45 eV) and hence its ability to generate a larger number of electron/hole pairs. $W_{18}O_{49}$ deposited for 20 min generated comparable or a slightly higher photocurrent than that of the film prepared after 10 min. A probable explanation can be as follows. All the photoelectrodes were illuminated from the front or coated side. The generated holes oxidize the water, while the electrons are transported to the counter electrode [88]. The photogenerated electrons have to diffuse through the entire film's thickness to reach the FTO/ $W_{18}O_{49}$ interface. In other words, an increase in the film thickness after the optimal point enlarges the diffusion path for electrons and thus increases the probability of electron/hole pair recombination [173]. Potential-current curves obtained under intermittent illumination are shown in Fig. (4.13b). The $W_{18}O_{49}$ films deposited for 10 and 20 min produced a higher photocurrent as compared to the films prepared after 1

and 5 min. It is noteworthy that no current was recorded under dark even at high potential (0.8 V vs. SCE). The effect of annealing temperature on the PEC performance of $W_{18}O_{49}$ films is shown in Fig. (4.13c). The potentiostatic measurements were carried out at 0.6 V vs. SCE. Since the as-prepared samples and those heated up to 300 °C (dashed line) were almost metallic in nature, the production of low currents was discerned under dark conditions. At 400 °C, the formation of the W_3O phase was observed, as confirmed by XRD and XPS. The film consisting of W_3O layers was found to be photoactive and produced a photocurrent of 0.4 mA/cm². Yet, generation of relatively high dark current was observed. The film obtained at 500 °C generated 0.6 mA/cm². This film was formed in the shape of an interconnected nanosheets structure, which has high light absorption and high oxygen vacancies as confirmed by UV-Vis and XPS results, respectively. These nanosheets were transformed into a nano pillar-like structure in the case of $W_{18}O_{49}$ prepared at 600 °C, resulting in reducing the absorbed light by the film, and hence, reducing its photocurrent density to 0.3 mA/cm². A similar trend was observed in the dark or light when LSV measurements were conducted at voltage range from 0.25 to 0.80 V vs. SCE, Fig (4.13d). At low biased voltages, 0.0 to 0.20 V, 400 °C sample generated higher dark current, compared with 500 °C and 600 °C, due to its metallic nature (W_3O phase).

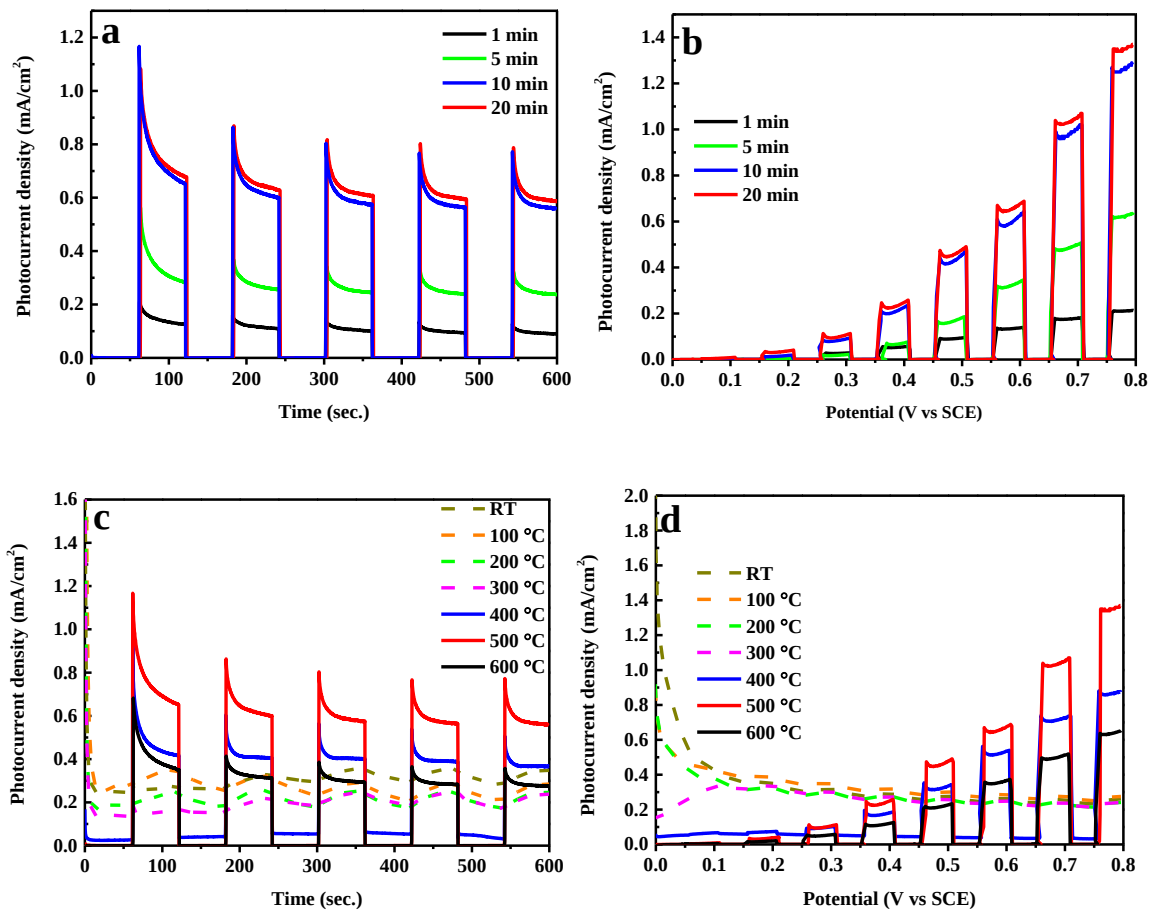


Figure 4.13. PEC performance measurements: Potentiostatic (a and d) and potentiodynamic (b and d) response of the films obtained at different deposition time and annealing temperatures. Measurements were carried out under intermittent light illumination.

The charge transfer process and electrical conductivity are very important factors in semiconductor photoanode materials. Figure (4.14) shows EIS results obtained at 0.6 V vs. SCE at a frequency ranging from 10^5 to 10^{-2} Hz in 0.1 M Na_2SO_4 electrolyte. Figure (4.14a) shows the Nyquist plots (imaginary vs. real impedance) of $\text{W}_{18}\text{O}_{49}$ films deposited at different sputtering deposition times and annealed at 500 °C. All the experiments and measurements were carried out under illumination. One time constant circuit was used as an equivalent circuit, in which solution resistance (R_s) is connected in series with a sub-circuit formed of a capacitor connected in parallel with charge transfer resistance (R_{ct}) [174]. It can be seen that the arc radius of the $\text{W}_{18}\text{O}_{49}$ films deposited for 20 min ($R_{ct}=135\ \Omega$) and 10 min ($R_{ct}=172\ \Omega$) was enormously short compared with 1 min ($R_{ct}=760\ \text{K}\Omega$) and 5 min ($165\ \text{K}\Omega$) $\text{W}_{18}\text{O}_{49}$ films, suggesting significantly faster charge transfer kinetics in the first-mentioned $\text{W}_{18}\text{O}_{49}$ films [175]. This result was in good agreement with the PEC results. Nyquist plots of W films annealed at 300, 400, 500, and 600 °C were recorded under illumination and shown in Fig (4.14b). $\text{W}_{18}\text{O}_{49}$ film fabricated at 500 °C (deposited for 10 min) showed a faster charge transfer kinetics ($R_{ct}=172\ \Omega$), compared to 600 °C ($R_{ct}=260\ \Omega$), due to its interconnected structure. Furthermore, film heated at 500 °C was also faster than the films prepared at 300 °C ($R_{ct}=430\ \Omega$) and 400 °C ($R_{ct}=240\ \Omega$) under light due to its oxide layer that has higher photocatalytic activity. Charge transfer resistance of $\text{W}_{18}\text{O}_{49}$ film fabricated at 500 °C was also recorded with and without the light, and the results are shown in Fig (4.14c). It can be seen that in the absence of light, the R_{ct} of the $\text{W}_{18}\text{O}_{49}$ film was significantly high (large semi-circle), which is in good agreement with the dark current shown in Fig. (4.14c, d), and reflects the high photocatalytic activity of $\text{W}_{18}\text{O}_{49}$ film. Figure (4.14d) shows the stability of the photocurrent density of $\text{W}_{18}\text{O}_{49}$ film deposited of 10 min

and annealed at 500 °C at a biased voltage of 0.6 V vs. SCE under illumination. A slow drop was observed at the beginning (first 2000 sec) due to the double layer charge capacitance at the $W_{18}O_{49}$ film/ Na_2SO_4 interface [176]. After that, the photocurrent density stabilizes at 0.56 mA/cm², and it maintained 100% of this value for 5200 sec, which indicates the excellent stability of the photo-anode film.

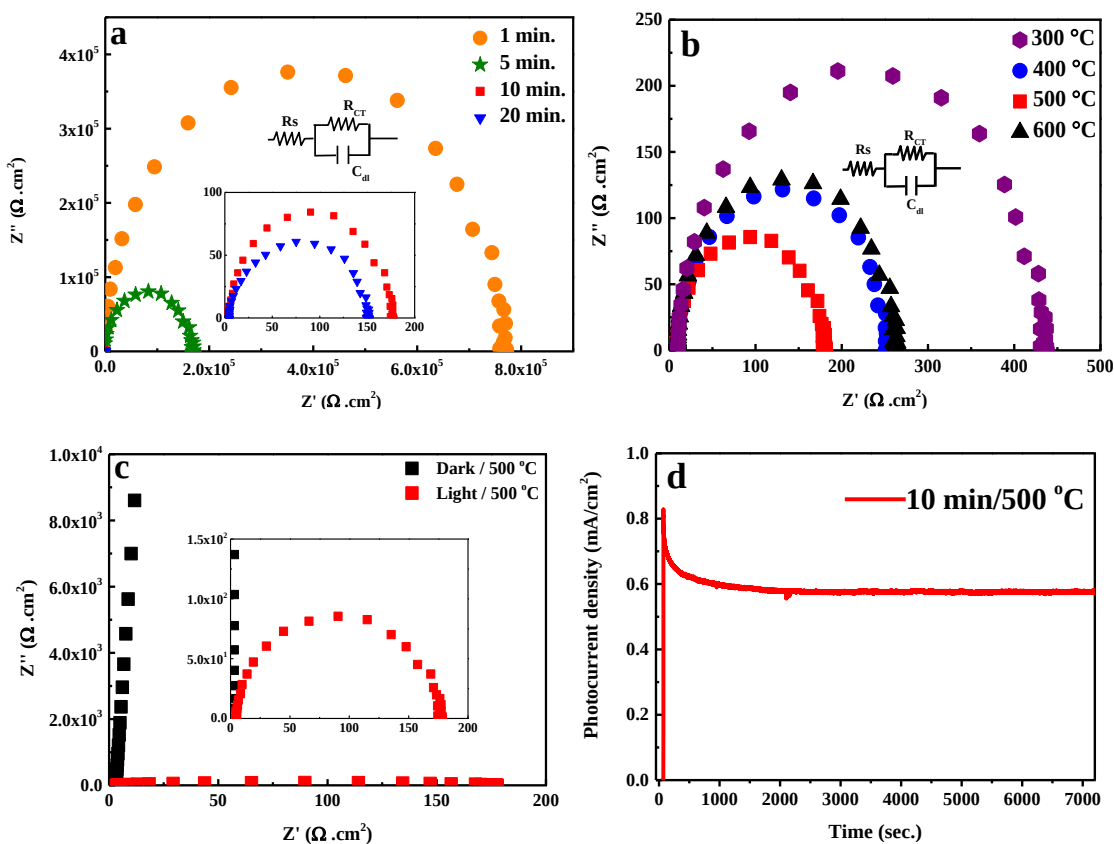


Figure 4.14. (a) Nyquist plots of W films annealed at 300, 400, 500, and 600 °C under light. (b) Nyquist plots of $W_{18}O_{49}$ films deposited for 1, 5, 10, and 20 min. under light. (c) Nyquist plots of $W_{18}O_{49}$ films deposited for 10 min and annealed at 500 °C under dark and light. (d) Stability test of $W_{18}O_{49}$ films deposited for 10 min and annealed at 500 °C under light for 7200 sec.

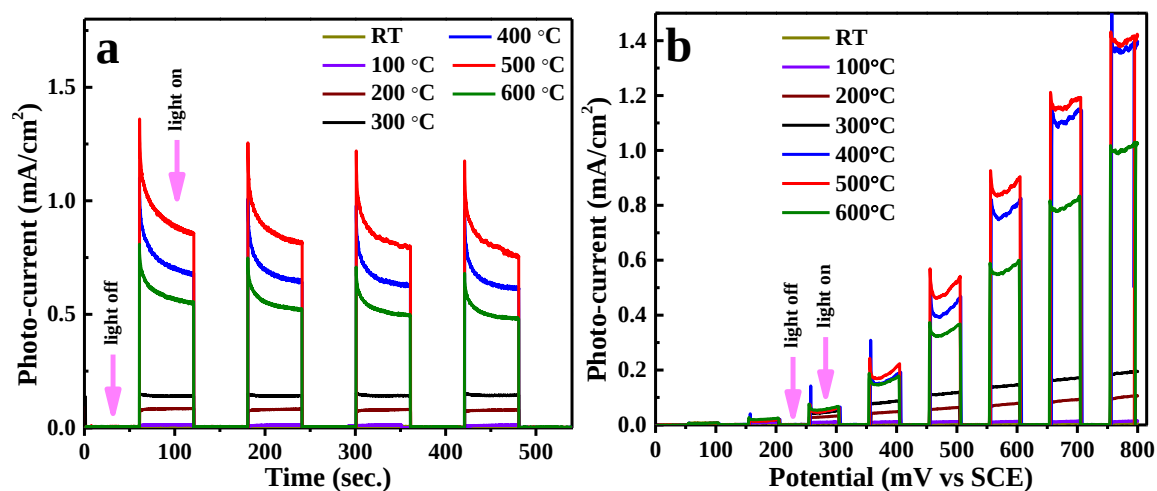
4.6 Photoelectrochemical measurements of WO₃ photoanode's films.

The PEC performance of the WO₃ films obtained under different conditions was evaluated under illumination using chronoamperometry and linear sweep voltammetry tests. All the PEC measurements were carried out in 0.1 M Na₂SO₄ aqueous electrolyte. The generation of photocurrent density as a function of time was investigated using light on/off chronoamperometry test. The results for the WO₃ films obtained after annealing at different temperatures are shown in Fig. (4.15a). The measurement was performed at 600 mV vs. SCE. The electrodes did not show any noticeable photocurrent when the light source was switched-off (~zero dark current). Meanwhile, an instantaneous current density was generated under illumination, indicating the photocatalytic behavior of the electrodes. It can be seen that the generated photocurrent density produced by these electrodes was dependent on their post-annealing temperature. For example, as-deposited film and films annealed at 100 – 300 °C showed a weak photocurrent (less than 0.2 mA/cm²). However, a dramatic improvement in the photocurrent was observed for the films annealed at 400 – 600 °C. The films obtained after heat treatment at 400, 500, and 600 °C produced 0.6, 0.9, and 0.7 mA/cm², respectively. This improvement can be rationalized in terms of electrical conductivity, which is likely to increase with the phase transition of WO₃ from amorphous to crystalline, as confirmed by the XRD [177]. In addition, it can be correlated to the films' bandgap; a smaller bandgap can absorb more light, and hence more electron/hole pairs can be generated. Although WO₃ film annealed at 600 °C has a smaller bandgap than the film obtained at 500 °C, the large number of cracks present in the former film can affect its surface continuity, which in turn can decrease its conductivity. Linear sweep voltammetry (I – V) curves of WO₃ films, annealed at a different temperature, were obtained in the range

of 0 – 800 mV vs. SCE (Fig. 4.15b). The I – V curves showed that the photocurrent of these electrodes increases with the increase in forward potentials under illumination, which agrees with the n-type semiconductor [178,179]. Besides, all the electrode films did not generate any dark current at higher potential (800 mV), indicating a complete photo-responsive behavior. The effect of deposition time on the PEC performance was also investigated, and the results are shown in Fig. (4.15c). The maximum photocurrent (0.9 mA/cm²) was recorded with the film deposited for 10 min, followed by the films deposited for 5 min (0.7 mA/cm²) 15 min (0.6 mA/cm²), and 20 min (0.4 mA/cm²). As determined by the FESEM, the respective thickness of the films deposited for 5, 10, 15 and 20 min are 87 nm, 156 nm, 294 nm, and 2370 nm. The film's thickness can have a significant impact on electrical conductivity and charge transfer resistance [152]. Therefore, a thinner film might have many grain boundaries that can increase the scattered charge carriers [152]. On the other hand, the thicker film's resistance can also be increased due to the increase in the charges diffusion path [173]. Similar photocatalytic behavior was observed in the current-potential (I–V) curves for all thicknesses (Fig. 4.15d). The annealing atmosphere was found to have a substantial effect on the PEC activity of the WO₃ films (Fig. 4.15e). A smaller photocurrent (0.1 mA/cm²) was generated from the vacuum-annealed film; this might be due to its high resistivity (low crystallinity) or due to the formation of non-photo-active phase (WO_{3-x}). The PEC activity of the vacuum-annealed film remains low even at high potential; 0.2 mA/cm² at 800 mV vs SCE (Fig. 4.15f).

The stability of the photoanodes is an important metric. The WO₃ film prepared after 10 min deposition time followed by annealing at 500°C in the air was selected to evaluate the photoelectrochemical stability. The current-time curve recorded at a potential

of 600 mV for 120 min is shown in Figure (4.15f). The photoelectrode showed an instantaneous generation of photocurrent when the light was turned on, followed by a slight decrease during the first 20 min, presumably as a result of electrical double layer capacitance i.e., accumulation of charge carriers at the electrolyte/film interface. After 20 min, the photoelectrode exhibited highly stable photocurrent generation, and the photocurrent remained stable at $\sim 0.75 \text{ mA/cm}^2$ for 100 min. After 100 min, the photocurrent decreased sharply when the light was turned off. This suggests that the recorded photocurrent was the result of photoexcitation of the WO_3 and water oxidation reaction in the presence of light.



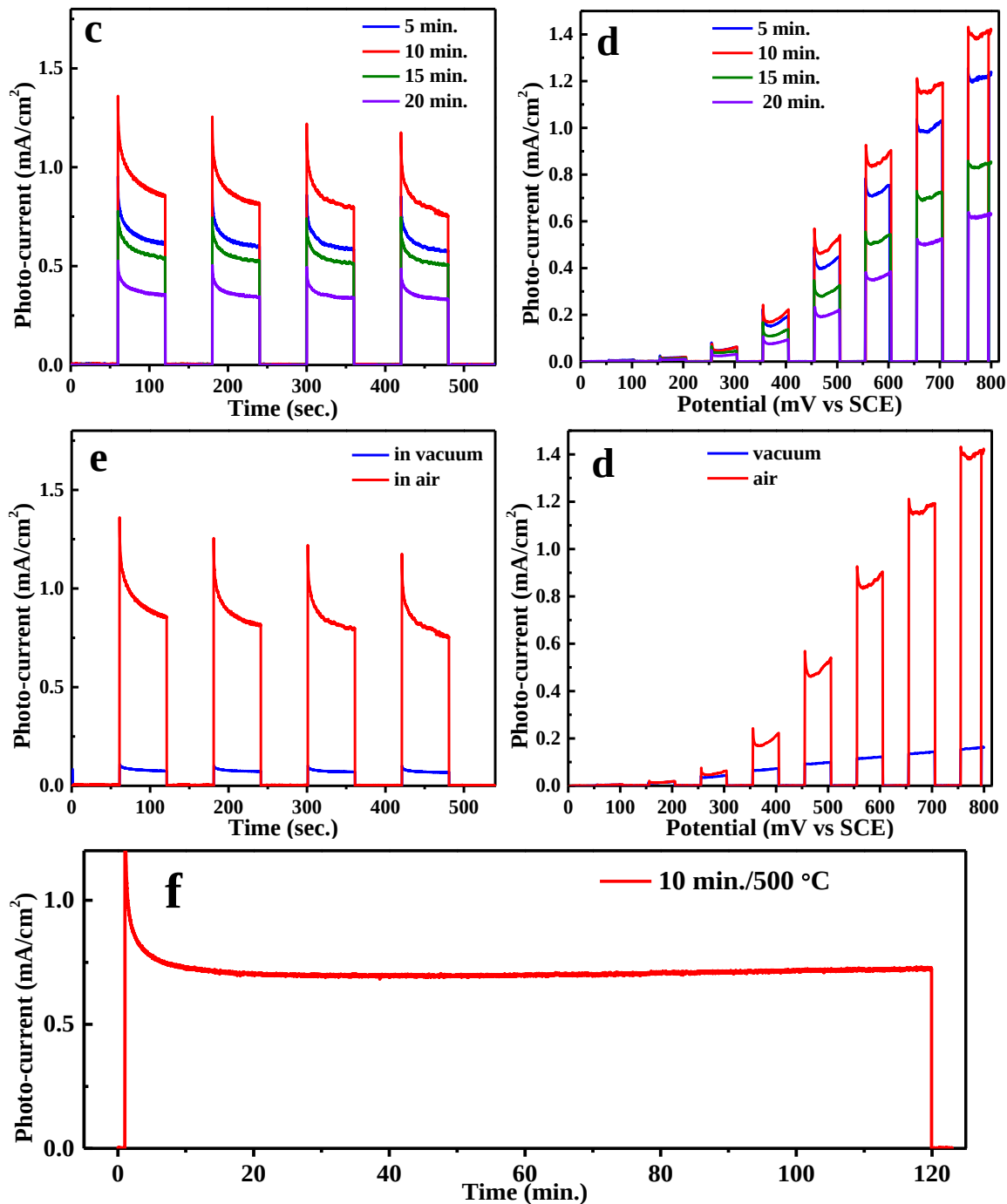


Figure 4.15. PEC performance measurements; light on/off chronoamperometry and LSV measurements for WO₃ films (a, b) annealed at different temperatures in air, (c, d) different deposition time, and (e, f) in air and vacuum, annealed at 500 °C. (f) Stability test of WO₃ films deposited for 10 min and annealed at 500 °C under light for 120 minutes.

Electrochemical impedance spectroscopy (EIS) measurements were performed to study the resistivity and charge transfer process of the WO₃ films. The measurements were performed in the frequency range of 10⁵ to 10⁻² Hz. The Nyquist plots (imaginary vs. real impedance) of as-deposited and annealed (100 – 600 °C) WO₃ films are shown in Fig. (4.16a). The results were obtained in the presence of light. All the impedance data was fitted with a Randle circuit, which consists of a charge transfer resistance (R_{ct}) that is connected with a capacitor in parallel and solution resistance (R_s) in series [180]. It can be observed that the charge transfer resistance of the films annealed at 400 °C and above are significantly smaller (R_{ct} = 147, 166, and 289 Ω for 500, 400, and 600 °C, respectively) as compared to the films annealed at 300 °C and below (R_{ct} = 4.7, 7.1, 28.6, and 77.5 K Ω for 300, 200, 100 °C, and room temperature). These findings are in good agreement with XRD and PEC results; the crystalline WO₃ films showed lower resistance and higher photocatalytic activity than amorphous films. The Nyquist plots of the WO₃ films, annealed at 500 °C in air, obtained with different deposition times (or film thickness) are shown in Fig. (4.16b). The R_{ct} of the films deposited for 5, 10, 15, and 20 min are calculated to ~250, ~147, ~348, and ~433 Ω , respectively. An optimal film's thickness is required to avoid high charge follow resistance in thinner films and electron/hole pair recombination in the thicker films. To highlight the effect of light on conductivity, the Nyquist plots of the WO₃ film (deposition time = 10 min, annealing temperature = 500 °C) were recorded under light and dark conditions. The results are compared in Fig. (4.16c). As evident, a huge charge transfer resistance (R_{ct} = 250 k Ω) is registered in the absence of light, explaining the negligible dark current noticed during on/off chronoamperometry measurements.

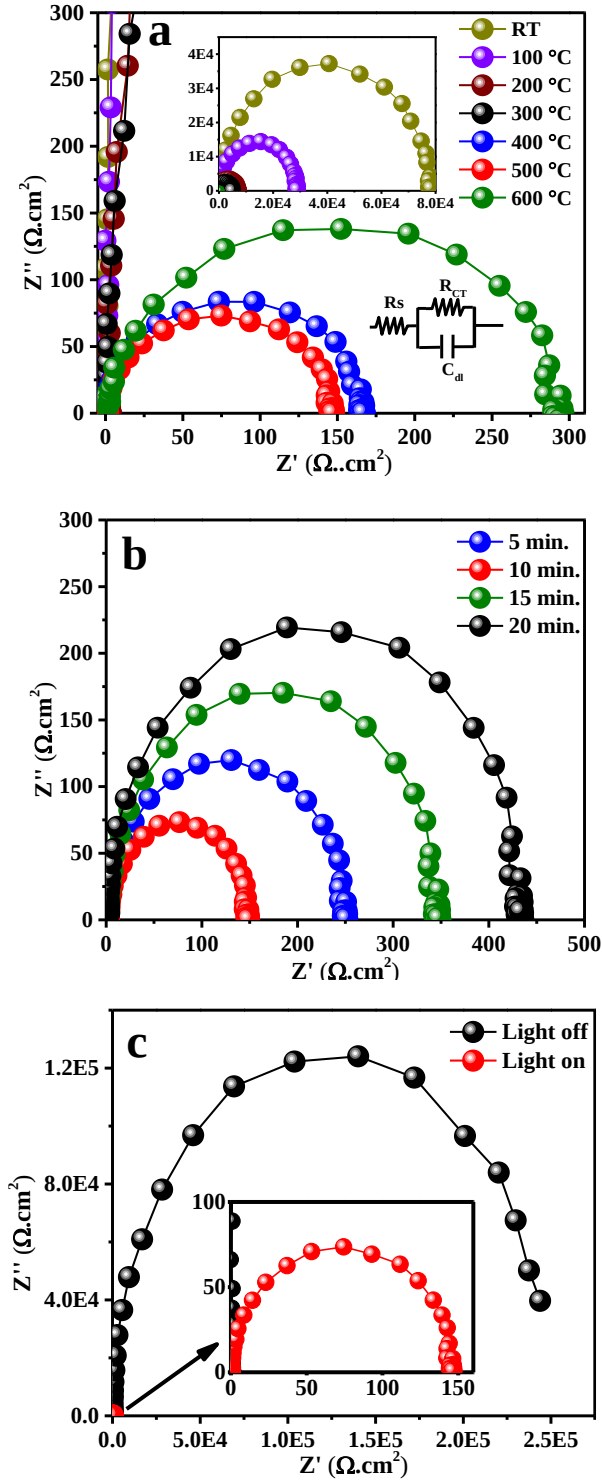


Figure 4.16. Nyquist plots of the WO₃ films: (a) annealed in air at different temperature, (b) deposited for different time, (c) comparison under dark and light conditions. Nyquist plots of WO₃ films deposited for 10 min and annealed in air at 500 °C under dark and light.

CHAPTER 5

Co–Pi/BiVO₄ PHOTOANODES

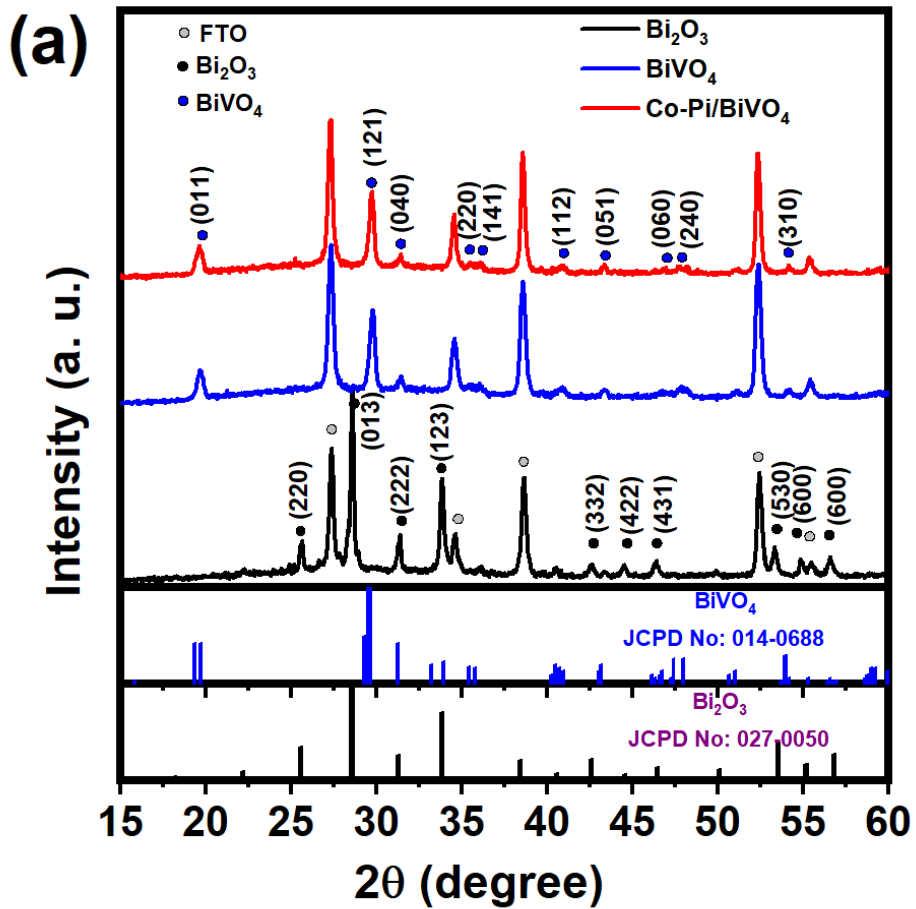
In this chapter, we developed a BiVO₄ photoanode using a combination of sputtering and drop-casting techniques. These fabrication methods aimed to produce a highly active and stable film by avoiding the degradation of the film and the texture less morphology of the BiVO₄ photoanode. Furthermore, we attempted to reduce electron-hole surface recombination by adding Co–Pi nanoparticles on the surface of the BiVO₄ photoanode.

5.1 Structural, morphological, compositional, and optical analysis of Co–Pi/BiVO₄ photoanode's films.

5.1.1 XRD results of Co–Pi/BiVO₄ photoanode's films

The X-ray diffraction (XRD) of Bi₂O₃, BiVO₄, and Co–Pi /BiVO₄ films prepared with a deposition time of 5 min are shown in Fig. (5.1a). For Bi₂O₃, the diffraction patterns at $2\theta = 25.5, 28.5, 31.2, 33.8, 42.6, 44.4, 46.6, 53.3, 54.8,$ and 56.6° correspond to a tetragonal phase of Bi₂O₃ (JCPD no: 027-0050) [181,182]. After adding the vanadium oxide precursor and heat treatment, the Bi₂O₃ films transformed completely into the monoclinic BiVO₄ phase (JCPD no. 14-0688). The formation of monoclinic BiVO₄ was confirmed by the diffractions at $2\theta = 19.6, 29.7, 31.4, 35.4, 36.0, 40.8, 43.4, 46.8, 47.7,$ and 54.3° . Transformation of Bi₂O₃ into BiVO₄ is found to be dependent on the film thickness, which in turn depends on deposition time. The Bi₂O₃ films prepared with different deposition times, such as 1, 5, 10, 20, and 30 min, and modified with vanadium precursor were heated at 450 °C. The evolution in XRD patterns is shown in Fig. (5.1b). It can be seen that Bi₂O₃

films prepared at 1 and 5 minutes were completely transformed into BiVO_4 films, whereas the films prepared at 10, 20, and 30 min partially retained the Bi_2O_3 phase. Such behavior can be correlated to the incomplete diffusion of the vanadium precursor solution into the thick Bi_2O_3 films. There were no discernible diffraction patterns for Co-Pi in the Co-Pi/ BiVO_4 sample. This could be either due to the non-crystalline nature of Co-Pi or the small amount of Co-Pi loaded onto the BiVO_4 surface.



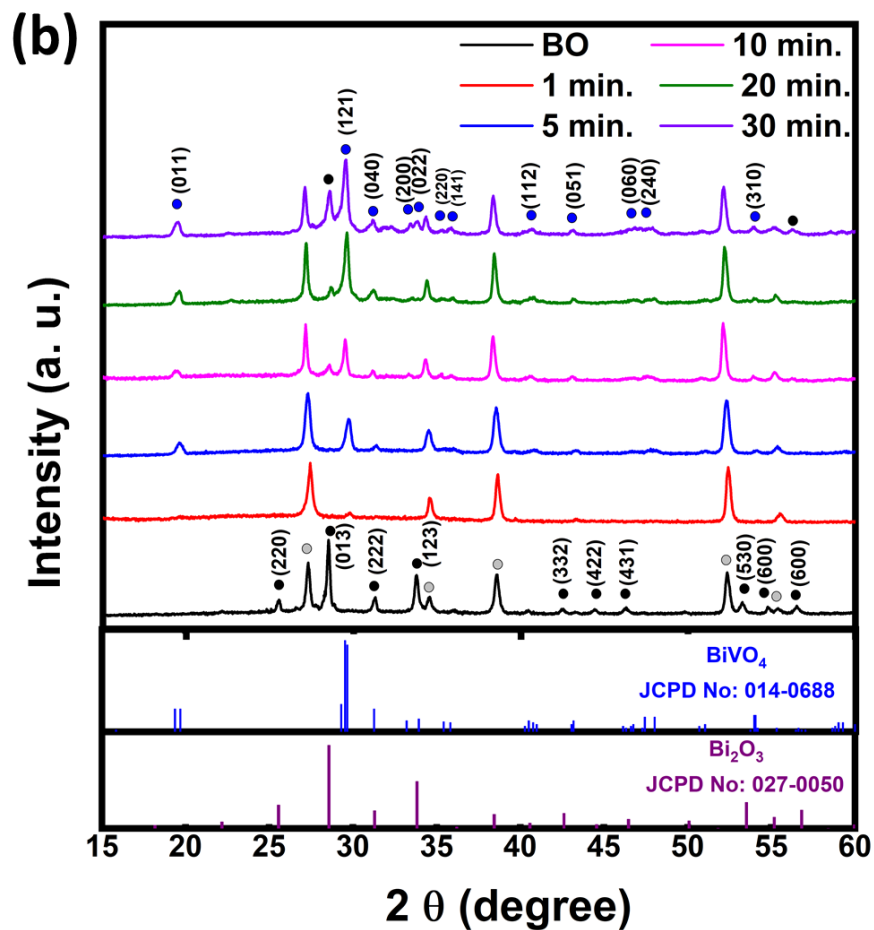


Figure 5.1. X-ray diffractions of (a) Bi₂O₃, BiVO₄, and Co–Pi/BiVO₄ films. Deposition time = 5 min, annealing temperature = 450 °C. (b) Bi₂O₃ and BiVO₄ films fabricated at 1-, 5-, 10-, 15-, and 20-min. deposition time, and annealed at 450 °C with the addition of 30 μ l of vanadium precursors.

5.1.2 FE-SEM results of Co–Pi/BiVO₄ photoanode's films

FESEM was used to investigate the morphology and thickness of the fabricated films. The surface of the Bi₂O₃ film is shown in Fig. (5.2a). As can be seen, the Bi₂O₃ film has a very rough and compact thin film layer. The thickness of the Bi₂O₃ film, obtained by cross-section FESEM image (Fig. 5.2b), was approximately 276 nm. The transformation from Bi₂O₃ to BiVO₄ resulted in the growth of a uniform and pinhole-free BiVO₄ film with interparticle porosity, as illustrated in Fig (5.2c). A low magnification FE-SEM images of BiVO₄ film were shown in Fig. (5.2.1). The thickness of BiVO₄ increased to 330 nm (Fig 5.2d) compared to the Bi₂O₃ film. The surface of the Co–Pi/BiVO₄ film is shown in Figure (5.2e). The tiny particles on the surface, ranging in size from 100 to 150 nm, are the Co–Pi co-catalyst [183]. The EDS spectrum of the Co–Pi/BiVO₄ film, depicted in Fig. (5.2f), confirms the presence of the Co, Bi, V, and O elements. The EDS spectrum also contains peaks corresponding to the gold coating and the FTO glass substrate.

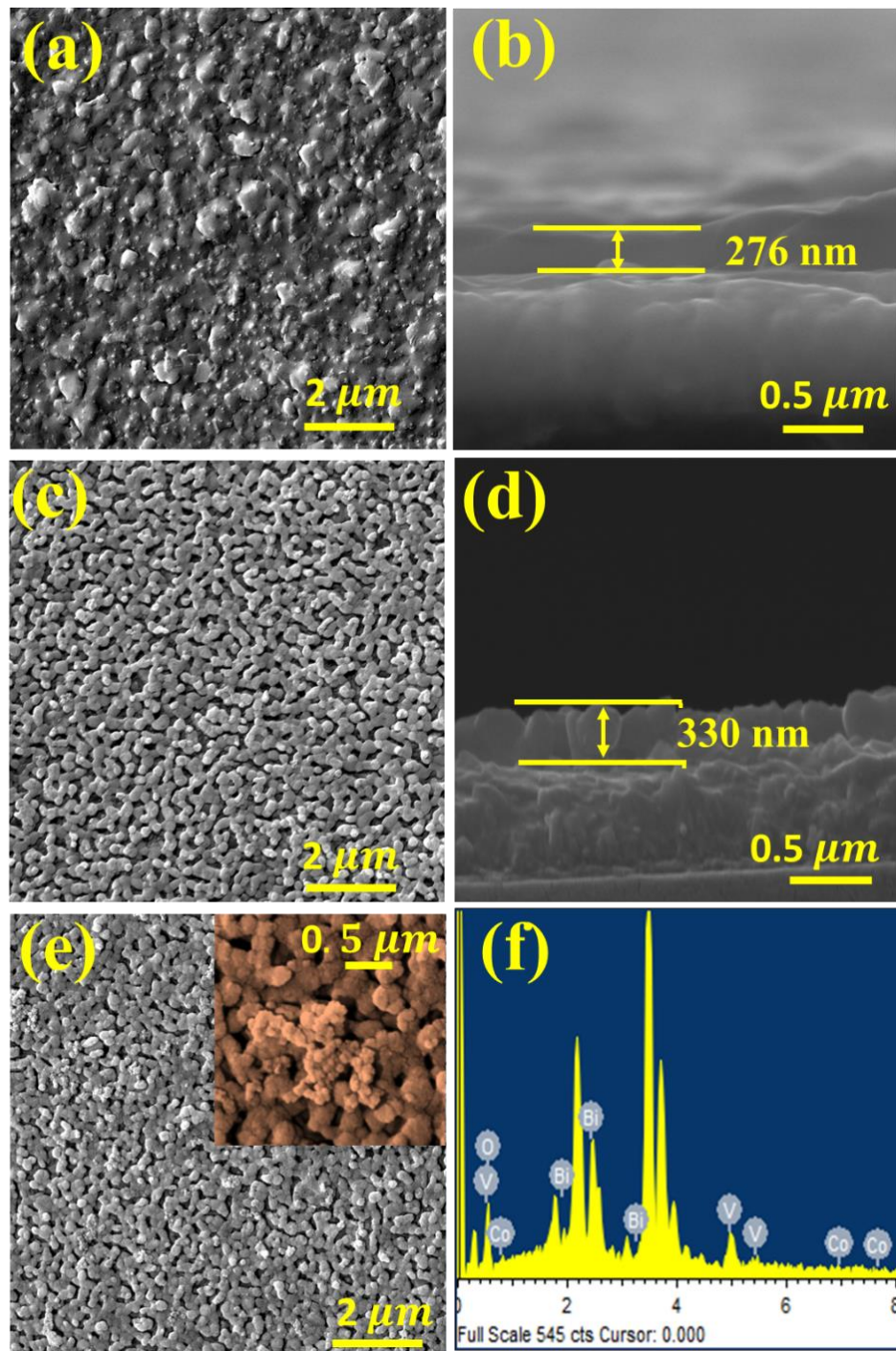


Figure 5.2. FESEM images of (a) Bi_2O_3 , (c) BiVO_4 , (e) Co-Pi/BiVO_4 films. FESEM cross-section images of (b) Bi_2O_3 , (d) BiVO_4 films. EDS spectrum (f) of Co-Pi/BiVO_4 films.

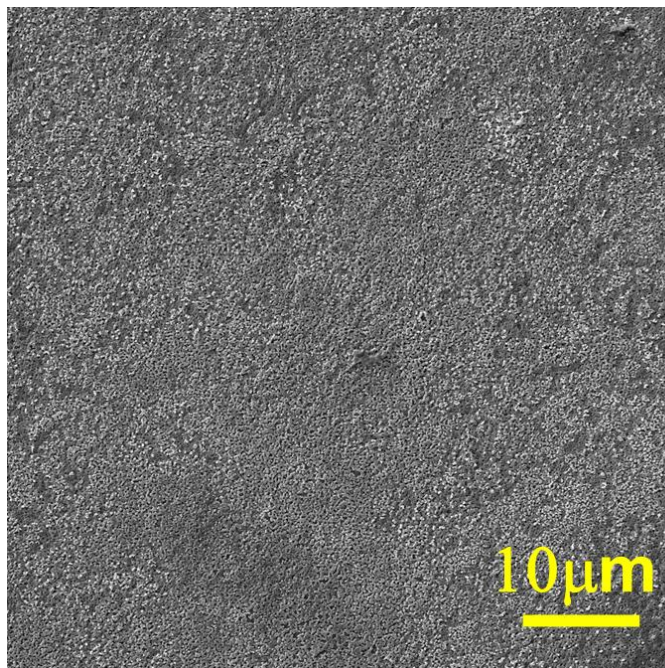


Figure 5.2.1. Low magnification FE-SEM images of BiVO₄ film

5.1.3 UV-Vis results of Co–Pi/BiVO₄ photoanode’s films

UV–vis spectra were measured to characterize the optical properties of the fabricated films, as illustrated in Fig. (5.3). As seen in Fig. (5.3a), the synthesized BiVO₄ film exhibits a substantial increase in absorption when compared to the Bi₂O₃ film. Additionally, it was observed that the addition of Co–Pi slightly increased the absorption wavelength edge in the Co–Pi/BiVO₄ sample. The optical bandgap (E_g) was estimated using Tauc’s equation, Eq. (3.6), as described in Tauc's plot [140], Fig. (5.3b). The bandgap of Bi₂O₃ film was ~ 2.7 eV. The BiVO₄ optical bandgap decreased to 2.36 eV. The addition of Co–Pi had a slight effect on the BiVO₄ film's optical bandgap.

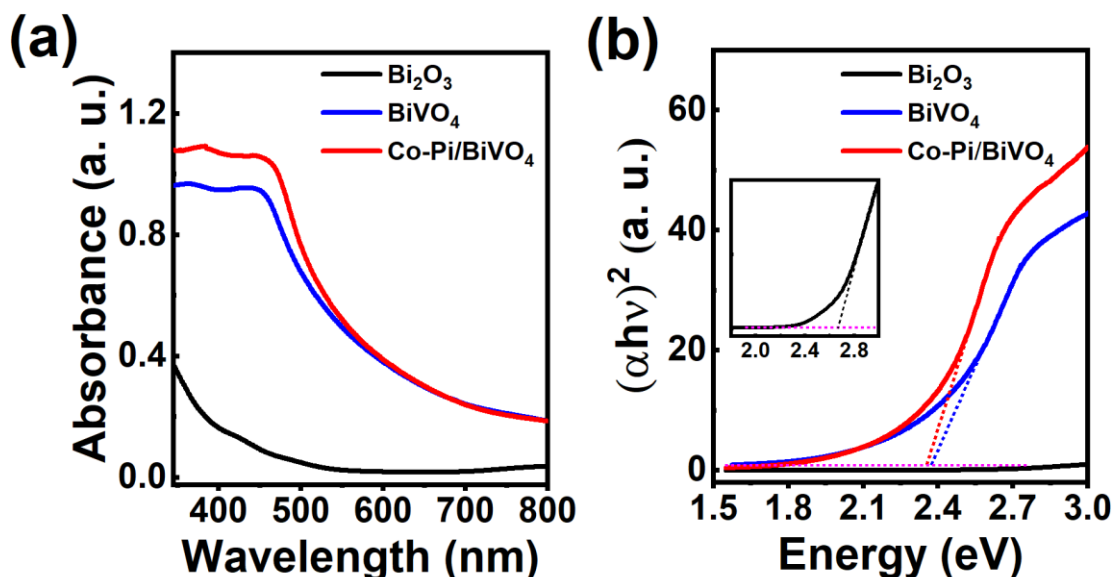


Figure 5.3. (a) UV-Vis absorption spectra of Bi_2O_3 , BiVO_4 , and Co-Pi/ BiVO_4 films and (b) Tauc's plots of Bi_2O_3 , BiVO_4 and Co-Pi/ BiVO_4 films.

5.1.4 XPS results of Co-Pi/ BiVO_4 photoanode's films

The composition of BiVO_4 and Co-Pi/ BiVO_4 photoanode films was investigated using X-ray photoelectron spectroscopy (XPS). The results are shown in Fig (5.4). The presence of all elements is indicated by the XPS survey spectrum in Fig. (5.4a), confirming the purity of the fabricated BiVO_4 sample. Figure (5.4b-f) shows the high-resolution spectra of each element. For instance, Fig. (5.4b) shows the existence of a Bi^{3+} valance state with binding energies of 159.7 eV ($\text{Bi } 4f_{7/2}$) and 164.9 eV ($\text{Bi } 4f_{5/2}$) [113]. The presence of the doublet peaks is attributed to spin-orbit coupling. The XPS spectra of V 2p, shown in Fig. (5.4c), reveals the presence of V^{5+} with doublet peaks at 516.7 eV ($\text{V } 2p_{3/2}$) and 524.2 eV ($\text{V } 2p_{1/2}$) [113]. Figure (5.4d) illustrates the deconvoluted peaks of O 1s. The peak with the highest binding energy, 531.3 eV, was assigned to the surface absorbed oxygen

species (O_{abs}), while the peak with the lowest binding energy, 530.4 eV, was assigned to the lattice oxygen species (O_L) [184]. In the Co–Pi / $BiVO_4$ sample (Fig. 5.4e), Co $2p_{3/2}$ and Co $2p_{1/2}$ were detected at 781.1 eV and 793.2 eV [185]. Moreover, the peak detected at 133.4 eV is attributed to the phosphate P 2p [185]. The presence of Co 2p and P 2p peaks support the existence of Co–Pi in the $BiVO_4$ film.

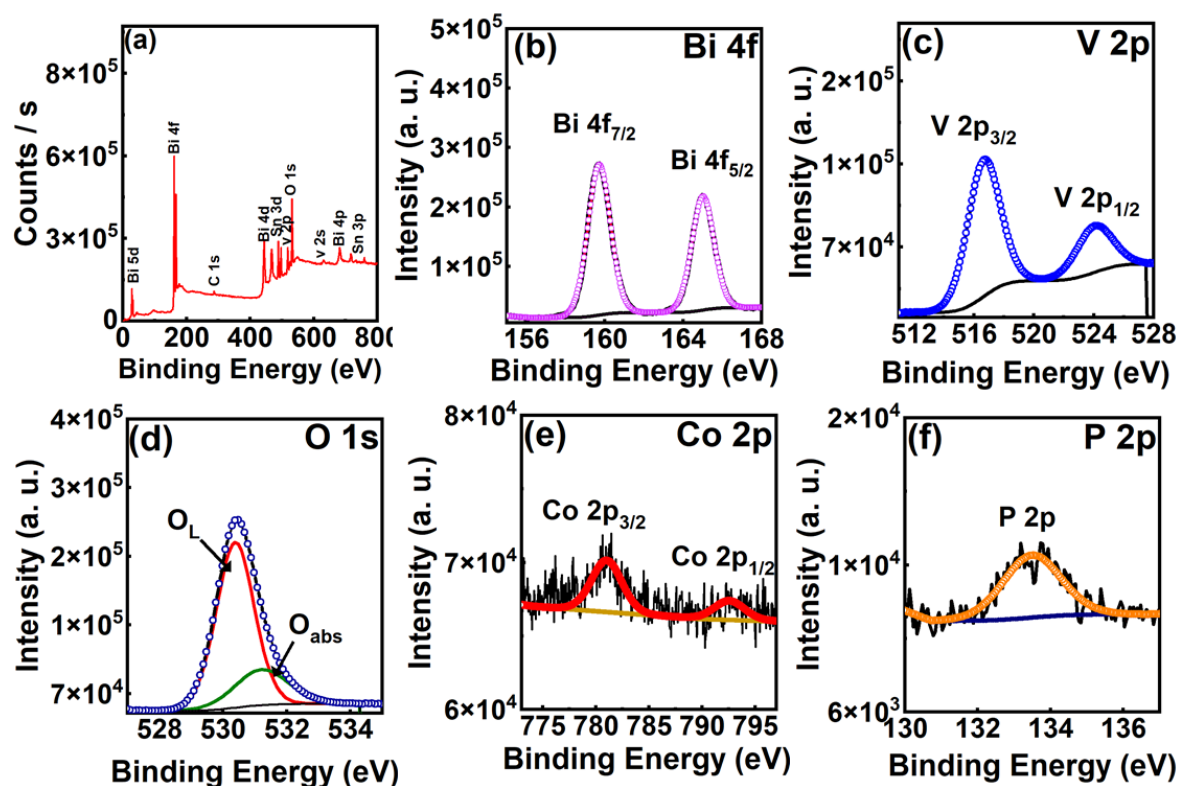


Figure 5.4. XPS spectra of of Co–Pi / $BiVO_4$: (a) survey scan, (b) Bi 4f, (c), V 2p, (d) O 1s, (e) Co 2p, and (f) P 2p.

5.2 Band structure calculations of $BiVO_4$

To investigate the band structure characteristics of the monoclinic $BiVO_4$ structure, the relaxed geometries of its unit cell were obtained and analyzed. Figure (5.5) presents the band structure and projected density of states (pDOS) of $BiVO_4$. According to the band

structure plot, the indirect bandgap was calculated to be 2.01 eV, around 0.4 eV lower than the experimental value (2.4 eV) [186], which is due to the limitations of using GGA functionals [187]. The valance band maximum (VBM) is located between G and A points but closer to A high symmetry points, whereas the conduction band is located at A point. The projected density of states demonstrates that the orbitals of O atoms dominate the valance band of the BiVO₄ unit cell. The conduction band, on the other hand, is dominated by V atom orbitals.

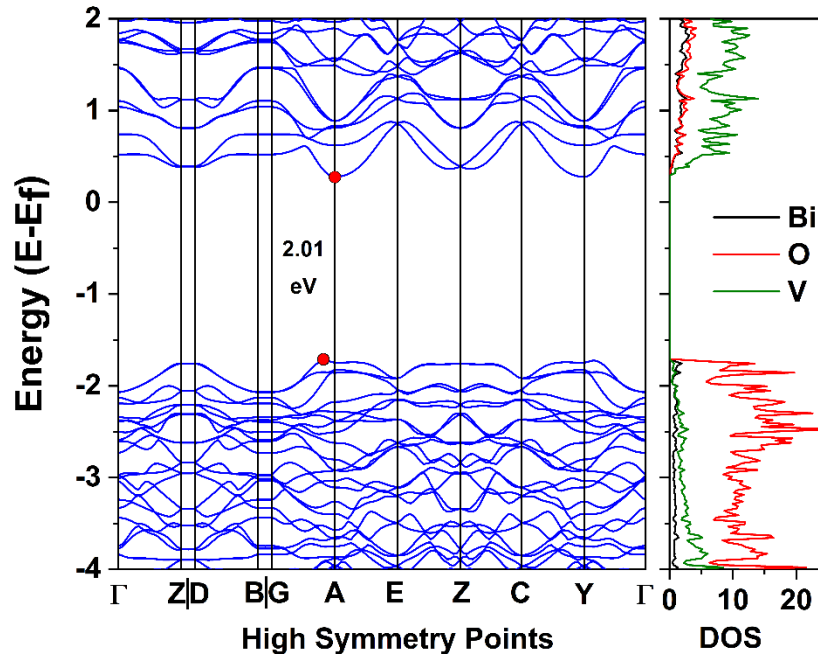


Figure 5.5. Band structure and pDOS of BiVO₄ structure

5.3 Photoelectrochemical measurements of Co–Pi/BiVO₄ photoanode

The results of the photoelectrochemical studies are shown in Fig. (5.6). As can be seen in Fig. (5.6a), the thickness of the base film had a significant impact on the photocurrent density. For example, the photocurrent density of BiVO₄ film made from a 1

min-based film is low (0.15 mA cm^{-2} at $1.23 \text{ V}_{\text{RHE}}$). This is most likely due to the presence of an excessive number of grain boundaries, which can be exacerbated by scattered charge carriers [188]. The photocurrent densities generated by BiVO_4 samples prepared with 5, 10, and 15-min base films were nearly identical and equal to 0.9 mA cm^{-2} at $1.23 \text{ V}_{\text{RHE}}$. Furthermore, the photocurrent density of the BiVO_4 film synthesized from the 20-minute base film decreased to 0.3 mA cm^{-2} at $1.23 \text{ V}_{\text{RHE}}$. This could be due to the presence of both BiVO_4 and Bi_2O_3 phases or due to an increase in film resistance caused by an increase in the charge's diffusion path [173,189]. A comparison of the PEC performance of the optimized BiVO_4 and the initial Bi_2O_3 electrode is shown in Fig. (5.6.1a). To improve the performance of the BiVO_4 photoanode, a hole scavenger test was performed by measuring LSV in the presence of $0.5 \text{ M Na}_2\text{SO}_3$, as shown in Fig (5.6b). In this test, all photogenerated holes are likely to be consumed in sulfite oxidation with a fast charge transfer rate [190]. The BiVO_4 film, made from a 5 min base film, had the highest photocurrent density. For instance, at $1.23 \text{ V}_{\text{RHE}}$, the photocurrent density increased from 0.9 mA cm^{-2} to $\sim 3.1 \text{ mA cm}^{-2}$. The significant increase in photocurrent generated in the presence of Na_2SO_3 indicates that all photogenerated holes on the BiVO_4 surface undergo SO_3^{2-} oxidation. [191]. This observation clearly suggests that the low photocurrent of BiVO_4 had been primarily due to fast charge carrier recombination on BiVO_4 surface and/or a low water oxidation kinetic process. The photocurrent density was lower in samples with BiVO_4 and Bi_2O_3 phases (fabricated at 10, 15, and 20 minutes). This could be due to the presence of Bi_2O_3 , which forms an improper alignment of the bands of bilayer $\text{BiVO}_4/\text{Bi}_2\text{O}_3$ film. Because the band edges of Bi_2O_3 are higher than those of the BiVO_4

layer, holes transfer from the valence band of BiVO₄ to Bi₂O₃, reducing the number of holes on the BiVO₄ layer's surface and thus lowering the photoanode's activity [192].

Interestingly, the photocurrent increased to 2.87 mA cm⁻² at 1.23 V_{RHE} with a 0.25 V_{RHE} onset potential after loading Co–Pi on a thickness-optimized BiVO₄ photoanode, which is close to the photocurrent achieved in the presence of the hole scavenger (Fig. 5.6c). The photocurrent onset potential exhibits a 570 mV negative shift, indicating that surface charge recombination is minimized following Co–Pi loading. As shown in Fig. (5.6.1b), the loading of Co–Pi onto the surface of the BiVO₄ was optimized using photoelectrodeposition at different time intervals (1–5 min). The increase in photocurrent caused by Co–Pi OER on a BiVO₄ photoanode was confirmed further by measuring incident photon-to-current efficiency (IPCE). The IPCE of Co–Pi/BiVO₄ and BiVO₄ obtained at 1.23 V_{RHE}, and 420 nm is shown in Figure (5.6d). The Co–Pi/BiVO₄ has about 25% IPCE while that of pure BiVO₄ is 9%. This finding is consistent with the LSV results. The increase in the IPCE value is due to the surface modification of the BiVO₄, not because of the difference in light absorption ability, as demonstrated by the UV-Vis absorption results. For practical application, the stability of photocurrent in the PEC process is crucial. The chopped light chronoamperometry of Co–Pi/BiVO₄ and bare BiVO₄ photoanodes at 1.23 V_{RHE} under standard illumination conditions are shown in Fig. (5.6e). The photocurrents profile of the BiVO₄ and Co–Pi modified BiVO₄ film confirm their stability. In addition, the samples were again tested by continuous illumination for 2 h at 1.23 V_{RHE}, as shown in Fig. (5.6f). The BiVO₄ photoanode demonstrates excellent stability. The Co–Pi/BiVO₄, on the other hand, had shown a rapid decrease in the initial period, followed by a slight continuous decline to reach 2.5 mA cm⁻².

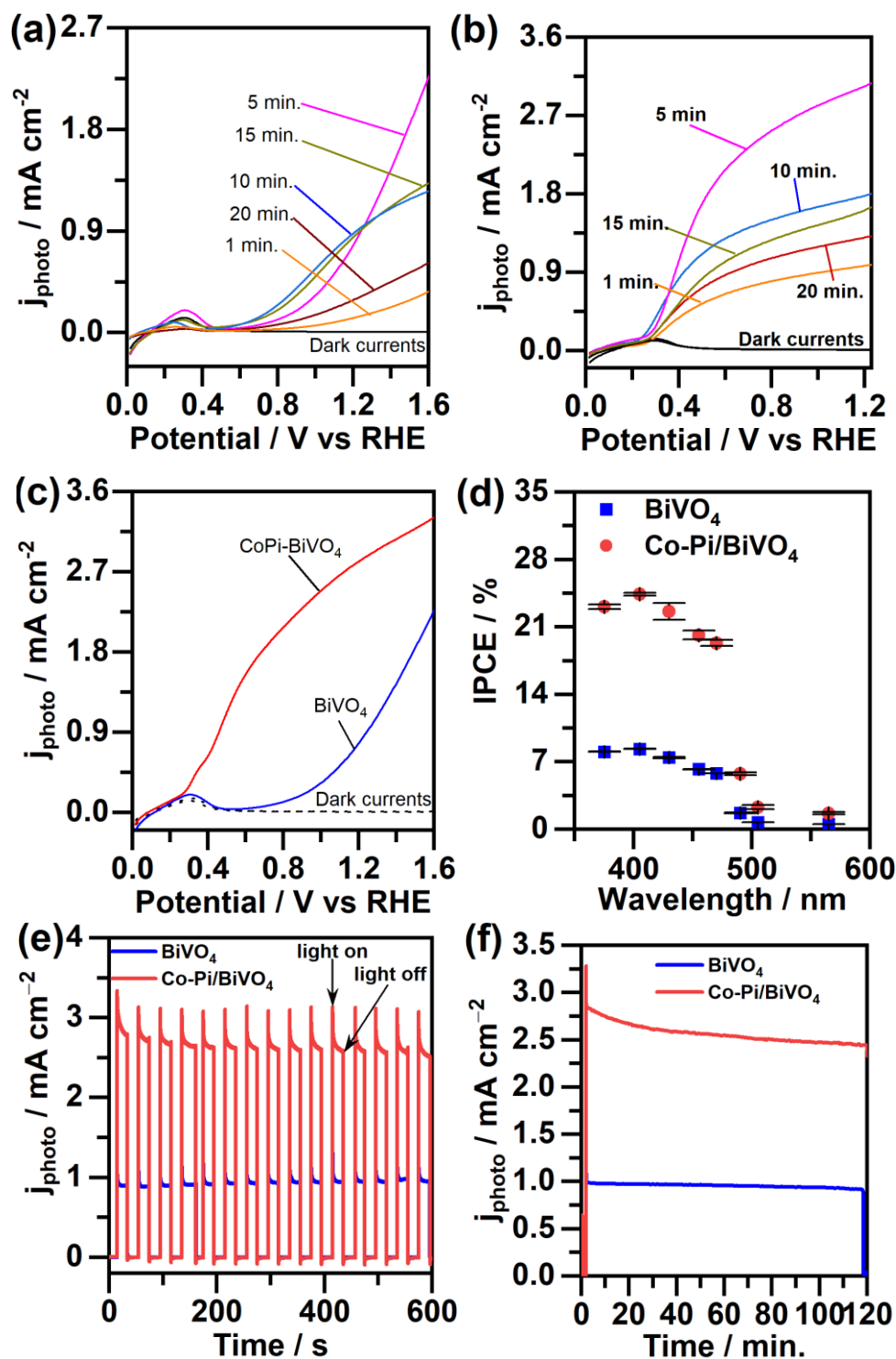


Figure 5.6. (a) LSVs of BiVO₄ samples with different thicknesses, (b) LSVs recorded in the presence of hole scavenger (Na₂SO₃), (c) comparative LSVs of BiVO₄ and Co-Pi/BiVO₄, (d) IPCE of BiVO₄ and Co-Pi/BiVO₄, (e) photocurrent under intermittent illumination for 600 s, (f) stability test for 2 h.

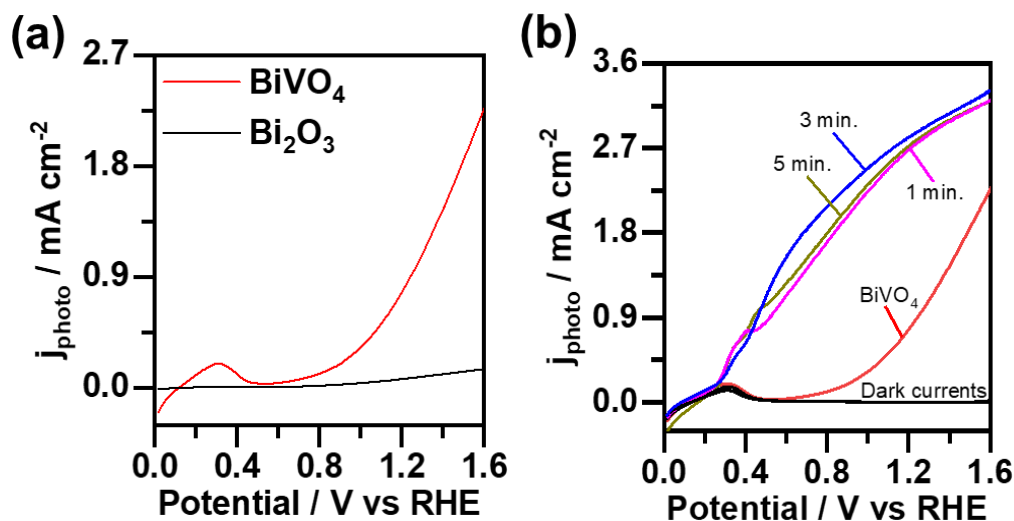


Figure 5.6.1. (a) I–V curves for photoelectrochemical water oxidation of BiVO_4 and Bi_2O_3 photoanodes measured in 0.5 M PBS under simulated solar light (1 sun, AM 1.5G). (b) I–V curves for photoelectrochemical water oxidation of Co–Pi deposited on BiVO_4 photoanodes at different deposition times.

The anodic spike observed immediately after illumination of Co–Pi/ BiVO_4 is higher than that of the BiVO_4 . This indicates that hole accumulation on the Co–Pi/ BiVO_4 surface is greater than for bare BiVO_4 . The transient photocurrent (TPC) was measured at 1.23 V_{RHE} under standard illumination conditions to verify this assumption. Both BiVO_4 and Co–Pi/ BiVO_4 photoanodes exhibit anodic photocurrent spikes, as shown in Fig. (5.7a). The anodic spike (I_m) was observed following a sudden illumination, which was caused by the accumulation of holes on the electrode space charge layer. When the light is turned off, the anodic spike decays to reach the stable photocurrent (I_s). During steady-state photocurrent, the rate of hole transfer to the surface is stabilized with the rate of hole recombination and the rate of hole transfer at the semiconductor electrolyte interface (SEI) for OER. The negative transient photocurrent (cathodic spike) is observed after the light is

turned off due to the recombination of bulk electrons with holes accumulated in the space charge layer during illumination. The transient decay time (τ) of the Co–Pi/BiVO₄ and BiVO₄ photoanodes were further evaluated by including the normalized parameter D in the TPC measurements to gain more insight into the charge carrier at surface states. The time at which $\ln(D) = -1$ define τ value, and the D parameter can be calculated by using Eqn. 5.1 [193] :

$$D = (I_t - I_s) / (I_m - I_s) \quad \text{Eq. (5.1)}$$

where I_t , I_m , and I_s are time-dependent current, anodic photocurrent spike, and steady-state current, respectively.

As shown in Fig. (5.7b), τ is calculated by plotting $\ln(D)$ vs. time. The τ for BiVO₄ and Co–Pi/BiVO₄ photoanodes were estimated to be 0.10 and 0.89 s, respectively. It has been demonstrated earlier that the higher the value of τ , the slower the recombination on the surface [194]. In the case of the BiVO₄, the holes recombine with electrons from the CB, reducing the availability of holes on the surface, resulting in less photocurrent. In the case of the Co–Pi/ BiVO₄ photoelectrode, the holes are picked up by Co–Pi and then released to oxidize the water, and hence the holes remain available for a longer period of time (9 times). The higher photocurrent was achieved for the Co–Pi/BiVO₄ photoanode due to the longer availability of these holes, indicating that suppressed surface recombination and enhanced charge transfer properties are observed for the water oxidation process.

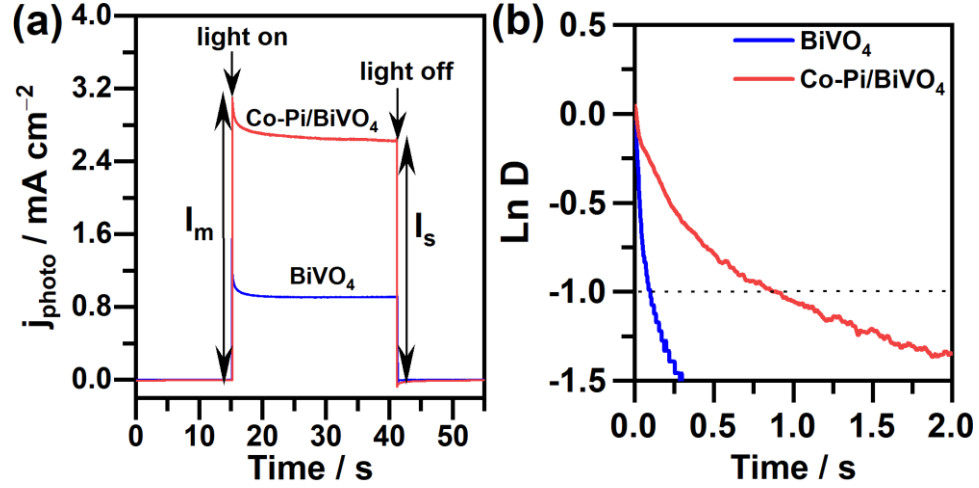


Figure 5.7. (a) Transient photocurrent (TPC) response, and (b) transient decay time for BiVO_4 and Co-Pi/BiVO_4 electrodes at 1.23 V_{RHE} under standard illumination conditions in 0.5 M PBS.

The Mott-Schottky (M-S) plots can be used to determine the carrier density (N_d) and the flat-band potential (E_{fb}) for semiconductor materials [195]. The n-type characteristic property was observed from the positive slope of M-S for both BiVO_4 and Co-Pi/BiVO_4 photoanodes, as illustrated in Fig. (5.8a). The N_d and E_{fb} are extracted from the M-S equation, Eq. 5.2: [195]

$$\frac{1}{C_{\text{SC}}^2} = \frac{2}{q\epsilon\epsilon_0 A^2 N_d} \left(E - E_{\text{fb}} - \frac{kT}{q} \right) \quad \text{Eq. (5.2)}$$

where C_{sc} is the space charge layer capacitance (F cm^{-2}), q is the elementary charge (1.60×10^{-19} C), ϵ is the relative dielectric constant of BiVO_4 (68) [32], ϵ_0 is the vacuum permittivity ($8.85 \times 10^{-12} \text{ N}^{-1}\text{C}^2 \text{ m}^{-2}$), A is the geometrical area in (cm^2), N_d is the carrier density (cm^{-3}), E is the applied potential (V), E_{fb} is the flat band potential (V), k is the Boltzmann constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$), and T is the absolute temperature (298 K).

The lower slope of Co–Pi/BiVO₄ indicates that the Co–Pi electrode has a higher charge carrier density than the BiVO₄ electrode. N_d values calculated for BiVO₄ and Co–Pi/BiVO₄ are $5.36 \times 10^{20} \text{ cm}^{-3}$ and $1.43 \times 10^{21} \text{ cm}^{-3}$, respectively. After Co–Pi passivation on the BiVO₄ electrode, the cathodic shift in E_{fb} was observed. The E_{fb} was shifted by 210 mV from 0.66 V_{RHE} to 0.45 V_{RHE}. The cathodic shift in E_{fb} makes electrons more likely to suppress the onset potential for the water oxidation process [196].

The photoelectrochemical impedance spectroscopy method was used to investigate the effect of the Co–Pi layer on the BiVO₄ electrode, as shown in Fig (5.8b). The Nyquist plots of BiVO₄ and Co–Pi/BiVO₄ obtained at 0.6 V_{RHE} were fitted to the equivalent circuit to compare the charge transfer resistance at the surface. After modifying the BiVO₄ photoanode with Co–Pi, the charge transfer resistance is significantly reduced. The charge transfer resistance (R_{ct}) of BiVO₄ and Co–Pi/BiVO₄ photoanodes were approximately 6.6 and 0.74 k Ω , respectively. Because of the extended lifetime of photogenerated holes and passivation effect observed in TPC and V_{ph} results, the decrease in charge transfer resistance makes more holes available at the surface of Co–Pi/BiVO₄ and participate in the water oxidation reaction. As a result, a higher photocurrent was observed for Co–Pi/BiVO₄ photoanode as compared to the BiVO₄.

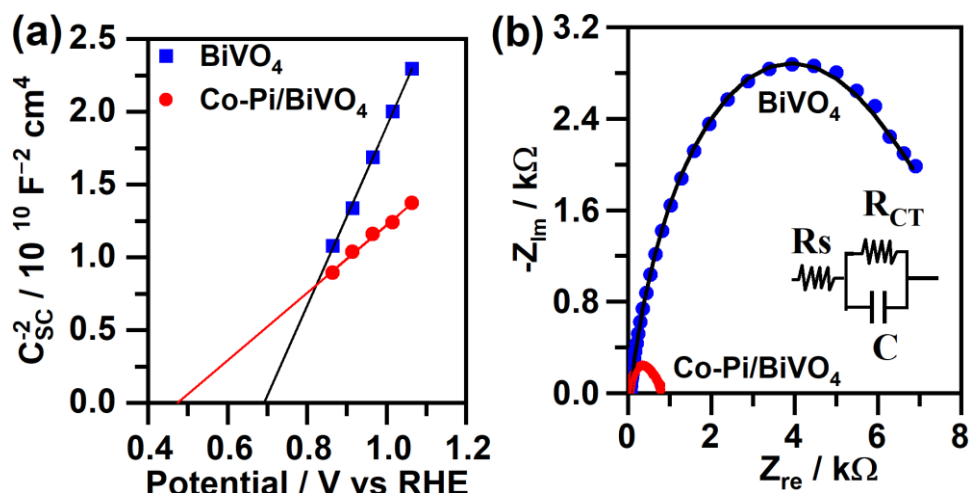
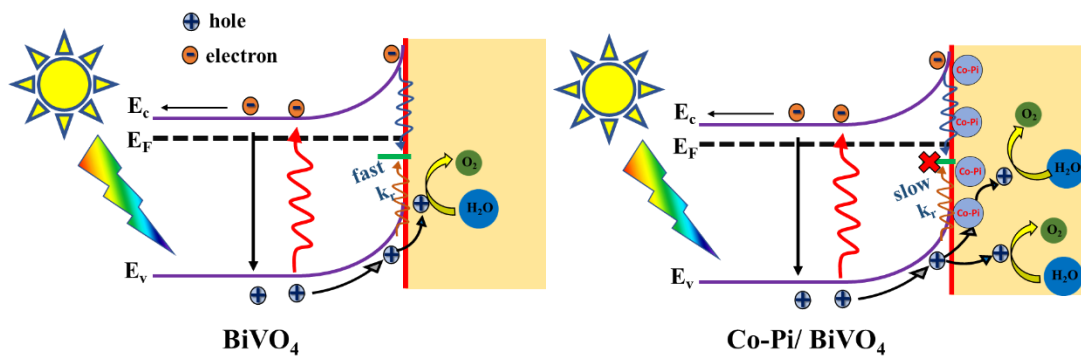


Figure 5.8. (a) Mott-Schottky plots (b) Nyquist plot of BiVO_4 and Co-Pi/BiVO_4 photoanodes under standard illumination conditions (AM 1.5 G), measured in 0.5 M PBS.

5.4 Charge transfer mechanism of photo-induced charge carriers in Co-Pi/BiVO_4 photoanodes

On the basis of the photoelectrochemical and EIS results, the role of Co-Pi on the surface of BiVO_4 has been summarized in Scheme (5.1). For the BiVO_4 photoanode, the photogenerated holes at the semiconductor/electrolyte interface can either (1) recombine with the electrons in the conduction band or (2) separate and transfer to oxidize water. The former process occurs at a much faster rate than the latter process. The recombination rate of holes on BiVO_4 is minimized by functionalizing with Co-Pi to passivate the surface recombination state of BiVO_4 . By the loading of Co-Pi on BiVO_4 , the lifetime of photogenerated holes is extended, and these holes are utilized in water oxidation rather than recombining at the surface states. Thus, passivation prevents the holes from recombining at the surface states, allowing for the water oxidation process to take place.



Scheme 5.1. A plausible elementary process occurs in BiVO₄ photoanode (1) without the Co-Pi (b) with the Co-Pi.

CHAPTER 6

Co–Pi/BiVO₄/WO₃ PHOTOANODES

In this chapter, we attempted to reduce both bulk and surface electron-hole pair recombination of the photoanode by forming BiVO₄/WO₃ heterostructure film and surface modification with Co–Pi nanoparticles. The PEC performance of our final product Co–Pi/BiVO₄/WO₃ photoanode was compared with the individual BiVO₄ and WO₃ films, as well as with the bare BiVO₄/WO₃ photoanode.

6.1 Structural, morphological, compositional, and optical analysis of Co–Pi/BiVO₄/WO₃ photoanode's films.

6.1.1 XRD results of Co–Pi/BiVO₄/WO₃ photoanode's films

The cryptographic properties of synthesized WO₃, BiVO₄, and BiVO₄/WO₃ photoanodes were investigated using X-ray diffraction (XRD), as shown in Fig. (6.1). The red circles indicate the diffraction patterns associated with the FTO substrate. The WO₃ films exhibit diffraction peaks at 23.5°, 24.0°, 24.7°, 29.2°, 34.1°, 34.7°, 42.1°, 50.1°, and 56.2°, respectively, which correspond to the planes (002), (020), (200), (112), (022), (202), (222), (400), and (124). These peaks are consistent with WO₃'s monoclinic structure phase (JCPDS No: 01-072-1465) [197,198]. For the BiVO₄ film, the diffraction peaks at 19.6°, 29.7°, 31.4°, 35.4°, 36.0°, 40.8°, 43.4°, 46.8°, 47.7°, and 54.3° are attributed to the (011), (121), (040), (220), (141), (112), (051), (240), and (310) planes. This diffraction pattern is matched with the monoclinic BiVO₄ structure (JCPD no. 14-0688) [199], which is the preferable structural phase in photocatalytic application [200]. In the case of the

BiVO₄/WO₃ bilayer film, the diffraction pattern reveals the presence of both BiVO₄ and WO₃ monoclinic structures. There were no additional peaks associated with the interaction of the two layers. Additionally, no evidence for the existence of Co–Pi was observed in the case of the Co–Pi/BiVO₄/WO₃ film.

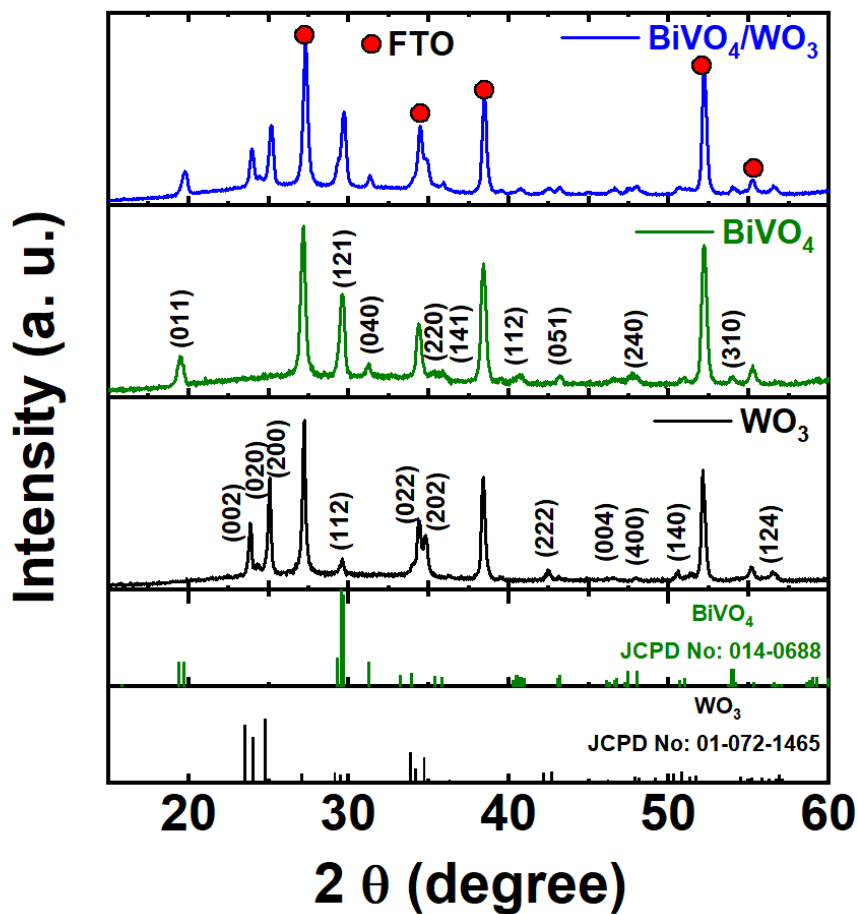


Figure 6.1. X-ray diffractions of WO₃, BiVO₄, and BiVO₄/WO₃ films photoanode.

6.1.2 FE-SEM results of Co–Pi/BiVO₄/WO₃ photoanode's films

Scanning electron microscopy (SEM) was used to examine the morphology of the synthesized WO₃, BiVO₄, BiVO₄/WO₃, and Co–Pi/BiVO₄/WO₃ photoanodes, which are

shown in Fig. (6.2). The WO_3 film has a uniform texture less surface with few cracks, as shown in Fig (6.2a). The thickness of the WO_3 film was determined to be 156 nm, as previously reported [189]. The morphology of the BiVO_4 film is depicted in Fig. (6.2b). The image shows the formation of the BiVO_4 film as an interparticle porosity structure. This structure has a large surface area, which is beneficial to the oxygen evolution process. The BiVO_4 layer's tackiness was measured to be around 330 nm. The top view SEM image of the $\text{BiVO}_4/\text{WO}_3$ film, Fig. (6.2c), shows a similar structure to the pure BiVO_4 film, indicating that the BiVO_4 film is uniformly deposited on the surface of the WO_3 film. The Co–Pi was deposited on $\text{BiVO}_4/\text{WO}_3$ film's surface in the form of a nanoparticle with an approximate diameter of 100 nm, as shown in Fig. (6.2d). The EDS spectrum of the Co–Pi/ $\text{BiVO}_4/\text{WO}_3$ film, depicted in Fig. (6.2e), confirms the presence of the Co, P, Bi, V, W, and O elements. The EDS spectrum also contains peaks corresponding to the gold coating and the FTO glass substrate.

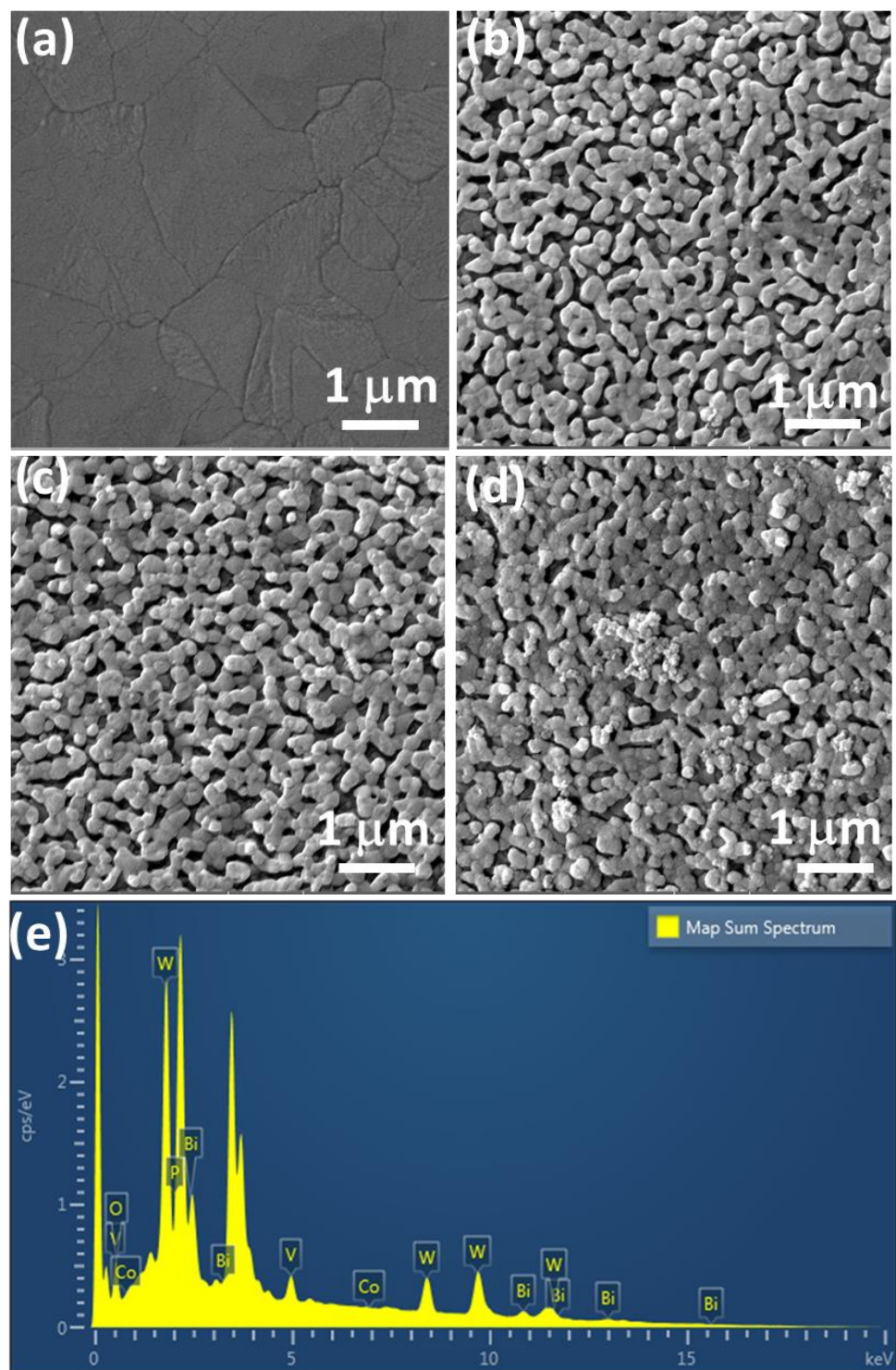


Figure 6.2. FESEM images of (a) WO₃, (b) BiVO₄, (c) BiVO₄/WO₃, and (d) Co-P/BiVO₄/WO₃ films. (e) EDS spectrum of Co-Pi/BiVO₄ films.

6.1.3 UV-Vis results of Co–Pi/BiVO₄/WO₃ photoanode's films

UV-Vis absorbance spectroscopy was used to determine the light-harvesting ability and optical band gap of the synthesized photoanode films WO₃, BiVO₄, BiVO₄/WO₃, and Co–Pi/BiVO₄/WO₃, Fig. (6.3). The UV-vis absorption results in Fig. (6.3a) indicate that the WO₃ film has an absorption edge at approximately 455 nm (blue region). In contrast, the BiVO₄ film begins to absorb light at approximately 580 nm (yellow region). Deposition of the BiVO₄ layer on the surface of the WO₃ film shifted its absorption edge to 636 nm (red region). Additionally, it was observed that adding Co–Pi has no discernible effect on the BiVO₄/WO₃ absorption capacity. The UV-Vis absorption behavior of these photoanodes was further investigated by estimating their optical band gap using Tauc's plot [140], Fig. (6.3b). The optical band gap plot was created using Tauc's equation, Eq. (3.6). The optical band gap of WO₃ film was estimated by extrapolating the liner part of $(\alpha h\nu)^{1/2}$ versus the energy of the absorbed photon (indirect bandgap). The optical band gap of WO₃ was found to be 2.72 eV. On the other hand, the optical band gap of BiVO₄, BiVO₄/WO₃, and Co–Pi/BiVO₄/WO₃ were obtained by extrapolating the linear part of $(\alpha h\nu)^2$ versus the energy of the absorbed photon (direct bandgap). The optical band gap of BiVO₄ film was estimated to be 2.37 eV. A narrower optical band gap was observed in the case of BiVO₄/WO₃ bilayer film, which indicates that the heterostructure of BiVO₄/WO₃ photoanode has a better light-harvesting ability compared to individual BiVO₄ and WO₃ photoanodes. Moreover, the addition of Co–Pi didn't affect the bandgap of BiVO₄/WO₃ film, which agrees with its absorption behavior.

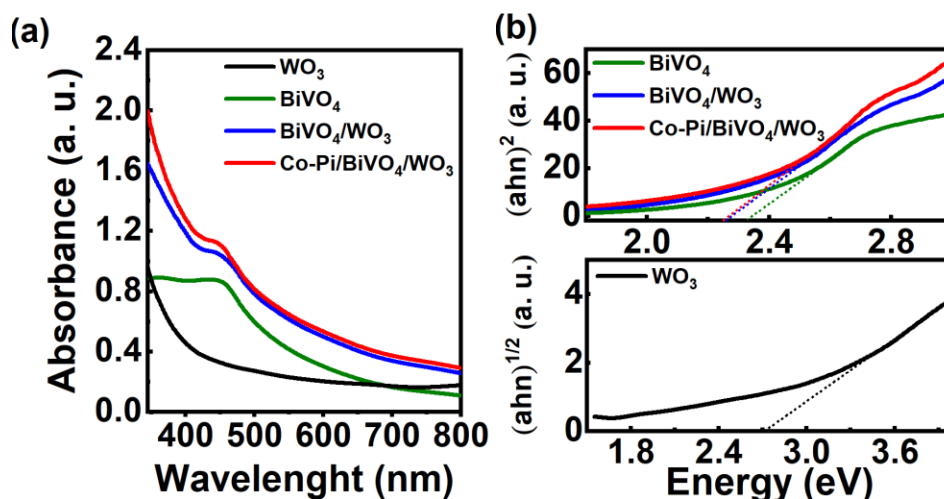


Figure 6.3. (a) UV-Vis absorption spectra and (b) Tauc's plots of WO_3 , BiVO_4 , $\text{BiVO}_4/\text{WO}_3$, and $\text{Co-Pi/BiVO}_4/\text{WO}_3$ films.

6.1.4 XPS results of $\text{Co-Pi/BiVO}_4/\text{WO}_3$ photoanode's films

The compositional analysis of the fabricated $\text{Co-Pi/BiVO}_4/\text{WO}_3$ film was studied using X-ray photoelectron spectroscopy (XPS), Fig. (6.4). To verify the purity of the fabricated film, a survey scan was performed at binding energies ranging from 0 to 800 eV, which included only the spectra of W 4f, P 2p, Bi 4f, W 4d, C 1s, Bi 4d, O 1s, Bi 4p, and Co 2p, Fig. (6.4a). Figure (6.4b) illustrates the high resolution of the Bi 4f XPS spectra peaks. The presence of the Bi 4f doublet peaks at 159.7 eV ($\text{Bi } 4f_{7/2}$), and 164.9 eV ($\text{Bi } 4f_{5/2}$) binding energies was due to spin-orbit coupling [113]. Additionally, the energies of these peaks indicate the existence of the bismuth valance state Bi^{3+} [113]. The XPS spectrum of V 2p is shown in Fig. (6.4c). V 2p doublet peaks at binding energies of 516.7 eV ($\text{V } 2p_{3/2}$) and 524.2 eV ($\text{V } 2p_{1/2}$) are associated with the vanadium valance state V^{5+} [113]. Figure (6.4d) shows the deconvoluted peaks of high-resolution O 1s peaks. The O 1s peaks at 530.4 eV are associated with oxygen species bound within the lattice (O_L), whereas the other O 1s peak at 530.4 eV is associated with oxygen species absorbed on the film's surface (O_{abs})

[184]. The XPS spectra of W 4f is displayed in Fig. (6.4e). The binding energies of W 4f doublet peaks are 35.6 eV (W 4f_{7/2}) and 37.8 eV (W 4f_{5/2}), which is corresponded to tungsten oxidation state W⁺⁶ [148]. The presence of Co–Pi on the surface of the BiVO₄/WO₃ film is confirmed by the high-resolution XPS spectra of P 2p and Co 2p shown in Fig. (6.4f, g). P 2p's XPS peak was observed at a binding energy of 133.4 eV, whereas Co 2p's doublet XPS peak was observed at pending energies of 781.1 eV (Co 2p_{3/2}) and 793.2 eV (Co 2p_{1/2}) [185].

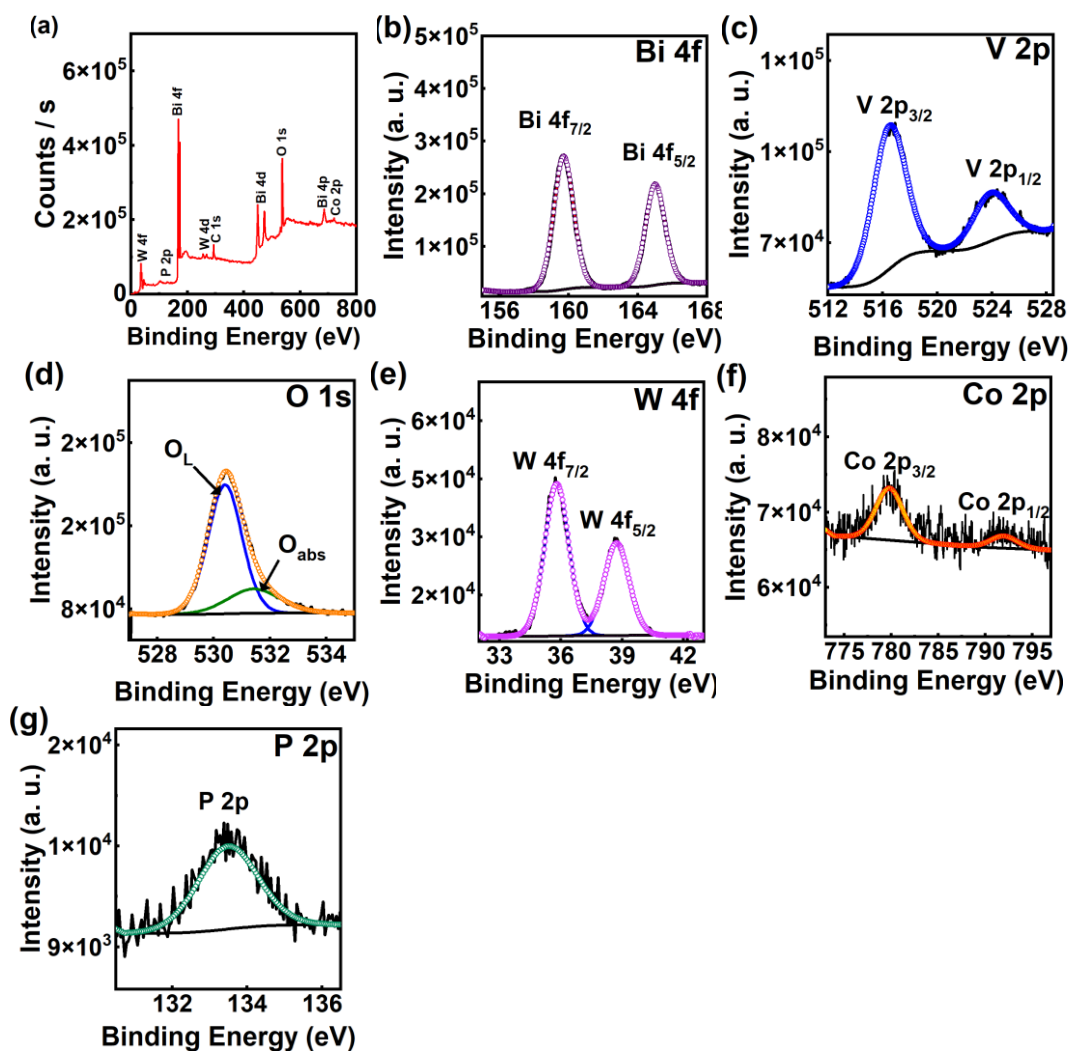


Figure 6.4. XPS spectra of Co–Pi /BiVO₄/WO₃: (a) survey scan, (b) Bi 4f, (c), V 2p, (d) O 1s, (e) W 4f, (g) P 2p, and (f) Co 2p.

6.2 Photoelectrochemical measurements of Co–Pi/BiVO₄/WO₃

photoanode

The photoelectrochemical performance of the fabricated Co–Pi/BiVO₄/WO₃ photoanodes was tested, as shown in Fig (6.5). Figure (6.5a) depicts the photocurrent density of heterostructured BiVO₄/WO₃ photoanodes with varying WO₃ thicknesses (deposition times; 1,5,10, and 15 min.). The generated photocurrent density increased with increasing the thickness of the WO₃ film from 1 to 10 minutes to reach around 2.45 mA/cm² at 1.23 V_{RHE} and then decreased with a thicker WO₃ layer (15 min. deposition time). This is due to the charge transport properties of the WO₃ layers with different thicknesses, as demonstrated in our previous reported article (chapter 4) [189]. In brief, thinner films have a higher electrical resistance, which could be attributed to a large number of grain boundaries that scattered the charge carriers. In the case of thicker films, however, increasing the charge's diffusion length also increases the film's resistance. The hole scavenger test was used to further evaluate the photocatalytic capability of the synthesized BiVO₄/WO₃ photoanodes, as shown in Fig (6.5b). In this test, the LSV of a BiVO₄/WO₃ photoanode was measured in the presence of 0.5 M Na₂SO₃, in which all photogenerated holes at the surface are likely to be consumed in sulfite oxidation with a high charge transfer rate. Compared to the primary water oxidation test, the presence of Na₂SO₃ resulted in a significant increase in the photocurrent density of the BiVO₄/WO₃ photoanode (4.7 mA/cm² at 1.23 V_{RHE}). This improvement indicates that the BiVO₄/WO₃ photoanode generated a large number of holes that undergo SO₃²⁻ oxidation. Furthermore, the lower photocurrent density observed in the primary test was due to the slow water oxidation

kinetic process and/or electron-hole recombination at the surface of the BiVO₄/WO₃ photoanode.

Co–Pi co-catalyst was deposited on the surface of the BiVO₄/WO₃ heterostructured film using the photoassisted-electrochemical deposition method to minimize its surface electron-hole recombination effect. The optimized Co–Pi disposition was found to significantly impact the photocurrent density of the BiVO₄/WO₃ films, as shown in Fig. (6.5c). Explicitly, the photocurrent density generated by the Co–Pi/BiVO₄/WO₃ photoanode was equal to 3.7 mA/cm² at 1.23 V_{RHE}, which is approximately 66% higher than the photocurrent generated by the bare BiVO₄/WO₃ photoanode and around 275% higher than the individual BiVO₄ and WO₃ photoanodes. The Co–Pi disposition optimization onto the surface of BiVO₄/WO₃ photoanode films was carried out at various potentials (0.1-0.4 V) and time intervals (30 60, 90, and 120 sec) as shown in Fig. (6.5.1a, b). Figure (6.5d) depicts the chopped light chronoamperometry of Co–Pi/BiVO₄/WO₃, BiVO₄/WO₃, BiVO₄, and WO₃ photoanodes at 1.23 V_{RHE} under standard illumination conditions. All of the fabricated films were found to have good stability over five cycles measured at 60 second time intervals. Furthermore, when the light is turned off, all samples exhibit almost zero dark currents, indicating that the current density generated by these samples is purely due to photocatalytic activity and not electrocatalytic behavior. The stability of the fabricated photoanodes was further examined under a 2 hours illumination at 1.23 V_{RHE}, as shown in Fig. (6.5e). The photocurrent of the Co–Pi/BiVO₄/WO₃ photoanode decreased gradually over 2 hours of illumination, which can be attributed to the degradation of the Co–Pi particles. BiVO₄/WO₃, BiVO₄, and WO₃, on the other hand, demonstrated good stability throughout the illumination period. Figure (6.5f) shows the

incident photon-to-current efficiency (IPCE) of the Co–Pi/BiVO₄/WO₃, BiVO₄/WO₃, BiVO₄, and WO₃ photoanodes at 1.23 V_{RHE} under standard illumination conditions. At the light wavelength, 430 nm, the Co–Pi/BiVO₄/WO₃ photoanode has an efficiency of about 25%, while the BiVO₄/WO₃, BiVO₄, and WO₃ photoanode has 16%, 7%, and 6%, respectively. The increase in the IPCE value of the Co–Pi/BiVO₄/WO₃ compared to the bare BiVO₄/WO₃ was due to the loading of the Co–Pi on the BiVO₄/WO₃ film's surface and not due to the narrower bandgap as shown in the UV-Vis results. Furthermore, the enhancement of BiVO₄/WO₃ compared to the individual BiVO₄ and WO₃ was due to electron-hole separation at the heterostructure junction.

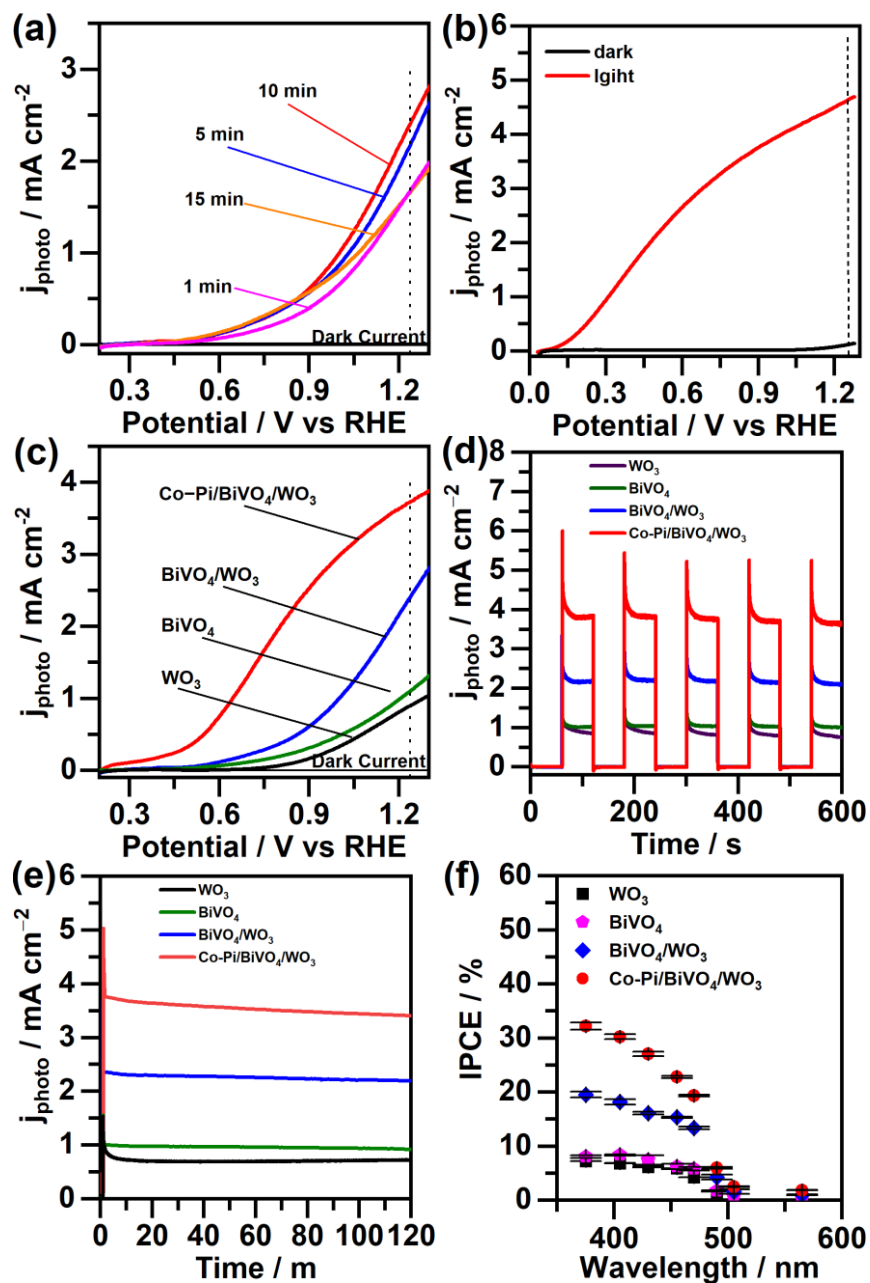


Figure 6.5. (a) LSVs of BiVO₄/WO₃ samples with different WO₃ thicknesses, (b) LSV of BiVO₄/WO₃ recorded in the presence of hole scavenger (Na₂SO₃), (c) comparative LSVs of Co-Pi/BiVO₄/WO₃, BiVO₄/WO₃, BiVO₄, and WO₃, (d) photocurrent under intermittent illumination for 600 s, (e) stability test for 2 h, (f) IPCE of Co-Pi/BiVO₄/WO₃, BiVO₄/WO₃, BiVO₄, and WO₃.

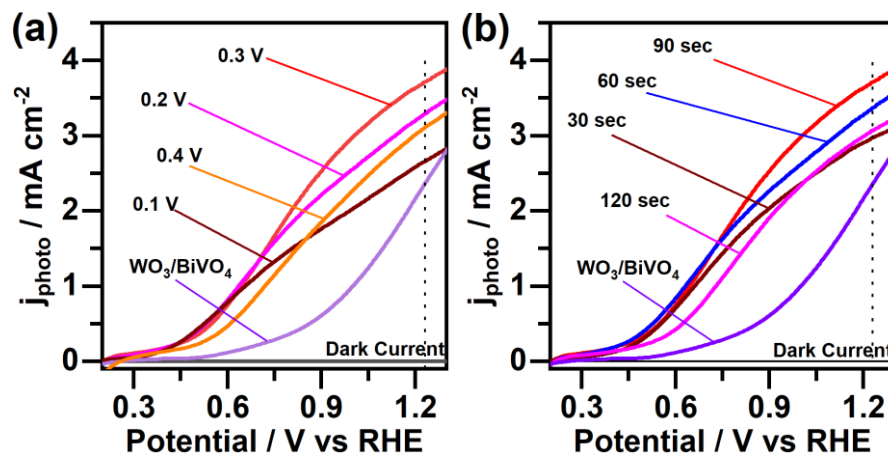


Figure 6.5.1. Co–Pi disposition optimization onto the surface of BiVO₄/WO₃ photoanode films at (a) various potentials and (b) time intervals.

The transient photocurrent (TPC) decay time measurement was performed at 0.9 V_{RHE}, as shown in Fig (6.6a), to obtain a qualitative assessment of charge transfer and electron-hole recombination in the fabricated photoanodes. To gain a better understanding of the lifetime of trapped holes at surface states, the transient decay times (τ) of the Co–Pi/BiVO₄/WO₃, BiVO₄/WO₃, BiVO₄, and WO₃ photoanodes were evaluated. The following formula, Eg. (5.1), was used to determine the normalized photocurrent (D) from the TPC response.

$$D = (I_t - I_s) / (I_m - I_s) \quad \text{Eg. (5.1)}$$

where I_t , I_m , and I_s are time-dependent current, anodic photocurrent spike, and steady-state current, respectively.

The time (τ) at which $\ln D = -1$ is referred to as the transient decay time, as illustrated in Fig (6.6b). WO₃, BiVO₄, BiVO₄/WO₃, and Co-Pi/BiVO₄/WO₃ photoanodes had transient decay times of 0.3 s, 0.5 s, 0.9 s, and 6.5 s, respectively. The decay time of

bare BiVO₄/WO₃ is slower than that of individual BiVO₄ and WO₃ photoanodes. This is due to the charge separation mechanism induced at the BiVO₄/WO₃ interface by the heterostructure junction. Additionally, deposition of Co-Pi on the surface of the BiVO₄/WO₃ films significantly reduced electron-hole surface recombination and increased their lifetime by rapidly picking up photogenerated holes from the film's surface and releasing them to oxidize the water. Thus, the photogenerated holes in the Co-Pi/BiVO₄/WO₃ photoanode have a roughly sevenfold longer lifetime than the bare BiVO₄/WO₃, providing enough time for the slow kinetics of water oxidation to occur.

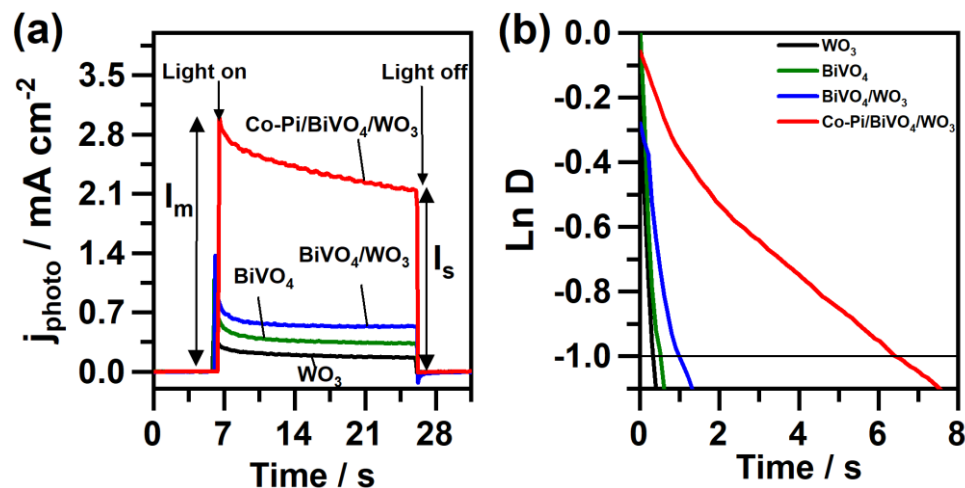


Figure 6.6. (a) Transient photocurrent (TPC) response, and (b) transient decay time for WO₃, BiVO₄, BiVO₄/WO₃, and Co-Pi/BiVO₄/WO₃ photoanodes at 0.9 V_{RHE} under standard illumination conditions.

The Mott-Schottky (M-S) plots can be used to determine the flat-band potential (E_{fb}) and carrier density (N_d) for the fabricated photoanodes [195]. The n-type characteristic property was observed from M-S's positive slope for all WO₃, BiVO₄, BiVO₄/WO₃, and

Co-Pi/BiVO₄/WO₃ photoanodes as illustrated in Fig. (6.7a). The E_{fb} and N_d extracted from the M-S equation, Eq. (5.2). The flat band potentials (E_{fb}) of the fabricated samples were determined by extrapolating the linear part of the M-S curves to the potential axis. The E_{fb} of WO₃, BiVO₄, BiVO₄/WO₃, and Co-Pi/BiVO₄/WO₃ photoanodes were found to be 0.70, 0.68, 0.52, and 0.35 V_{RHE}, respectively. The cathodic shift in the E_{fb} value indicates an upward shift in the Fermi level, which will improve the charge carrier separation of the photoanode [201]. Furthermore, the lower E_{fb} potential of BiVO₄/WO₃ and Co-Pi/BiVO₄/WO₃ photoanodes when compared to individual BiVO₄ and WO₃ photoanodes indicates a lower bias voltage required to drive the oxygen evolution reaction [201]. Furthermore, the shallow slope in the M-S linear part indicates a higher concentration of charge carriers available at the space-charge region [201]. The highest charge carrier concentration of Co-Pi/BiVO₄/WO₃ is due to the long lifetime of the photogenerated holes achieved by the Co-Pi co-catalyst. Figure (6.7b) shows the photoelectrochemical impedance spectroscopy (EIS) measurements of the fabricated photoanodes at 0.9 V_{RHE}. The Nyquist plot of the WO₃, BiVO₄, BiVO₄/WO₃, and Co-Pi/BiVO₄/WO₃ photoanodes were obtained and fitted to the equivalent circuit to examine their charge transfer resistance (R_{ct}). The R_{ct} values of the fabricated photoanodes were found to be 0.11, 0.45, 1.0, and 1.3 kΩ for the Co-Pi/BiVO₄/WO₃, BiVO₄/WO₃, BiVO₄, and WO₃ photoanodes, respectively. The lower R_{ct} value in the case of the BiVO₄/WO₃ reveals a more efficient electron-hole separation and faster interfacial charge transport at the BiVO₄/WO₃ heterojunction [201]. Furthermore, the longer lifetime of the holes available for the water oxidation at the surface of the Co-Pi/BiVO₄/WO₃ film reflects a lower charge recombination rate, and hence, higher charge transport rate.

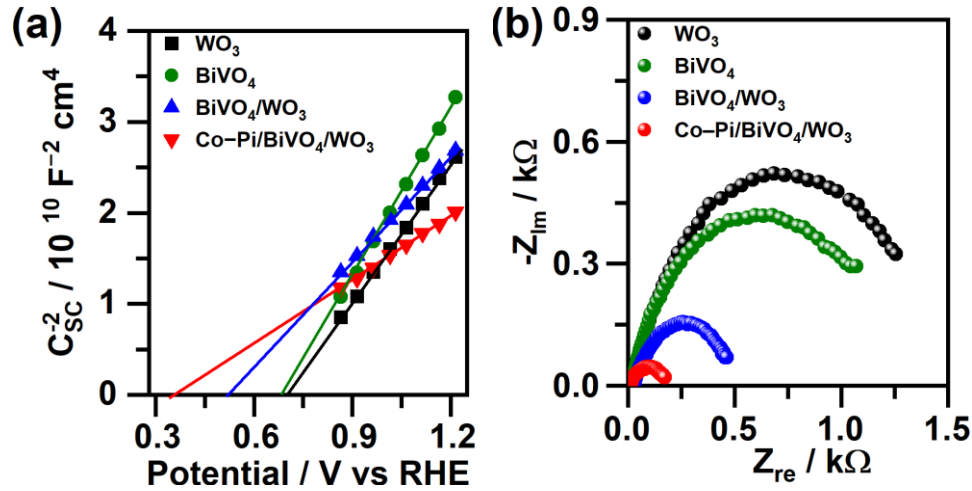


Figure 6.7. (a) Mott-Schottky plots, and (b) Nyquist plots of the $\text{Co-Pi/BiVO}_4/\text{WO}_3$, $\text{BiVO}_4/\text{WO}_3$, BiVO_4 , and WO_3 photoanodes under standard illumination conditions.

6.3 Charge transfer mechanism of photo-induced charge carriers in $\text{Co-Pi/BiVO}_4/\text{WO}_3$ photoanode.

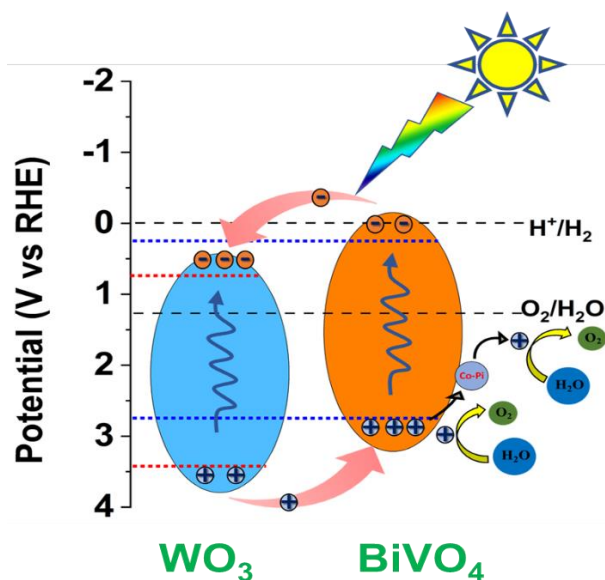
The optical bandgap of the synthesized BiVO_4 and WO_3 photoanodes were estimated to be 2.37 and 2.72 eV, as shown in Fig. (6.3a, b). The valance band (VB) and the conduction band (CB) edges of both photoanodes could be evaluated, with respect to hydrogen scale, using the following equations, Eq. (6.1a, b) [202].

$$E_{VB} = x - E^e + 0.5 E_g \quad \text{Eq. (6.1a)}$$

$$E_{CB} = E_{VB} - E_g \quad \text{Eq. (6.1b)}$$

Where E_{VB} and E_{CB} are the valance band and the conduction band energies, x is the electronegativity of the semiconductor photoanodes (6.59 eV for WO_3 , and 6.04 eV for BiVO_4) [108], E^e is the hydrogen-free electron energy (4.5 eV), and E_g is the bandgap of the semiconductor photoanode.

BiVO₄ and WO₃ photoanodes have valance band (VB) edges at 2.71 eV and 3.45 eV, respectively, and conduction band edges (CB) at 0.36 eV and 0.73 eV. As a result, the layers of BiVO₄ and WO₃ will form a type-II heterojunction. Because the VB edge of the WO₃ layer is more positive than the VB edge of the BiVO₄ layer in the potential hydrogen scale and the BiVO₄ layer's CB edge is smaller than the WO₃ layer's CB, the electron from the BiVO₄ CB will be transferred to the WO₃ CB. On the other hand, the holes in the WO₃'s VB will be transferred to the BiVO₄'s VB. Increasing the number of holes available at the BiVO₄ VB will ramp up the oxygen evolution reaction at the photoanode's surface. Further, more electrons from the WO₃ CB will be collected and transferred to the counter electrode for hydrogen reduction. Surface modification of a BiVO₄/WO₃ photoanode with Co–Pi increases the lifetime of the accumulated holes at the photoanode/electrolyte interface. The longer the lifetime of the photogenerated holes, the more available they are for oxidizing the water rather than going into surface electron-hole recombination, as in the case of the bare BiVO₄/WO₃ photoanode. The schematic diagram, scheme (6.1), below depicts the possible charge transfer mechanism of the Co–Pi/BiVO₄/WO₃ photoanode.



Scheme 6.1. below depicts the possible charge transfer mechanism of the Co–Pi/BiVO₄/WO₃ photoanode.

6.4 Theoretical calculation on charge transfer mechanism of photo-induced charge carriers in Co–Pi/BiVO₄/WO₃ photoanode.

The conduction and valance band edges of WO₃ and BiVO₄ were obtained by calculating their electron affinity and ionization energy [203] using DFT calculations, as shown in Fig (6.8a, b). The unit cell of both the WO₃ and BiVO₄ slabs was enlarged with vacuum space along the z-direction. The CB and VB potentials for WO₃ were determined to be 1.07 eV and 3.52 eV, respectively, and 0.62 eV and 2.63 eV for BiVO₄, respectively. In addition, the work function of each photoanode layer was calculated to investigate the equilibrium charge transfer of the BiVO₄/WO₃ heterostructure, as shown in Fig (6.8c, d). When the BiVO₄ layer is attached to the WO₃ layer, electrons flow from the lower work function of

the WO_3 (7.2 eV) to the higher work function of the BiVO_4 (7.8 eV) until their fermi-levels are equilibrated. Furthermore, the band edges calculation results show that the CB and VB edges of the BiVO_4 are higher than those of the WO_3 , indicating that the $\text{BiVO}_4/\text{WO}_3$ is forming a Type-II heterostructure, resulting in efficient photoexcited charge carrier separation and thus improved photocatalytic activity [204,205].

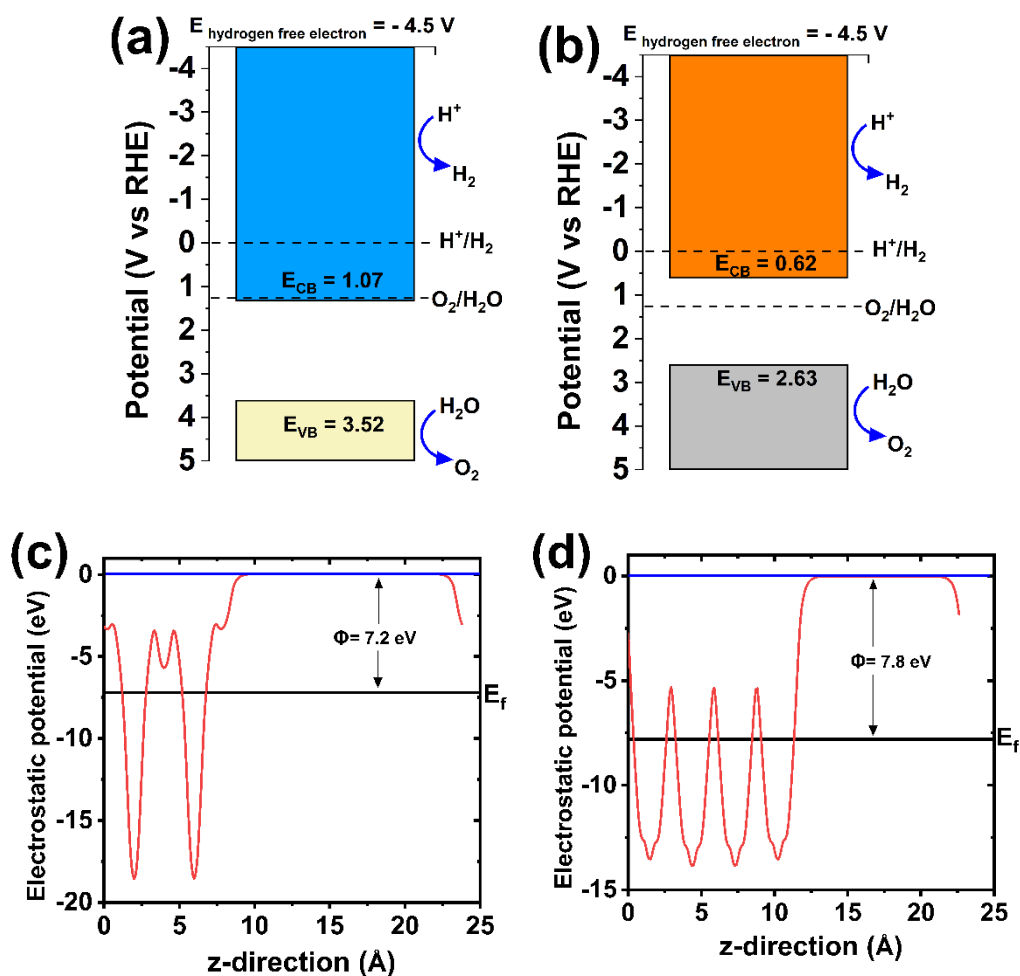


Figure 6.8. Conduction and valance band edges of (a) WO_3 , (b) BiVO_4 . Work function calculation of (c) WO_3 and (d) BiVO_4 .

CHAPTER 7

CONCLUSION

The purpose of this thesis was to develop a photoactive and stable photoanode suitable for photoelectrochemical water splitting. We successfully fabricated and evaluated thin films of WO_x , BiVO_4 , and $\text{BiVO}_4/\text{WO}_3$ heterostructures for photoelectrochemical water oxidation. To begin, each WO_x and BiVO_4 material was characterized, modified, and tested as a photoanode. Following that, a heterostructure photoanode was constructed utilizing optimal fabrication conditions for WO_x and BiVO_4 films. Specifically:

In chapter 4: the study demonstrated the influence of tungsten oxide fabrication methods and deposition parameters. The tungsten oxide film prepared by sputtering deposition was found to have better stability inside the aqueous electrolyte solution compared to that film prepared by PLD. Furthermore, different tungsten oxide phases were obtained by using DC and DC reactive sputtering techniques. Using DC sputtering magnetron, we deposited a metallic tungsten film and then transformed it into Magnéli-phase $\text{W}_{18}\text{O}_{49}$ thin film of tungsten oxide by post-annealing under an air environment. The thin films' thickness (52, 146, 290, and 550 nm) and the morphology (nanoparticles, nanosheets, nanorods, and nanopillars) were controlled by adjusting film growth time and post-annealing process. The as-derived $\text{W}_{18}\text{O}_{49}$ efficiently catalyzed the water oxidation reaction and produced 0.6 and 1.4 mA cm^{-2} photo-current at 1.23 and 1.45 V_{RHE} , respectively. In addition, the photo-electrode showed excellent stability; the performance was stable for ~ 2 h. The electrical conductivity and the charge transfer kinetics were

improved with increasing deposition time and post-annealing temperature. The photoelectrode with the lowest resistance exhibited the highest PEC performance.

Using DC reactive sputtering magnetron, we deposited a fully oxidized tungsten oxide film. We illustrated that the essential properties of WO₃ thin films could be fine-tuned by controlling deposition time and post-annealing temperature and environment. The bandgap of WO₃ can be maintained between 3.2 and 2.7 eV by adjusting the post-annealing temperature between 100 and 600 °C. It is discerned that the photoelectrocatalytic activity of WO₃ photoelectrodes increased with decreasing bandgap, and the maximum photocurrent (0.9 mA cm⁻² at 1.23 V_{RHE}) was recorded with WO₃ thin film heated at 500 °C with a bandgap of 2.85 eV. The annealing environment is also found to significantly impact the performance; the WO₃ film heated under air exhibited much better photoelectrochemical water oxidation than that of annealed under inert (argon) atmosphere. In addition to the annealing temperature and environment, the film thickness is another crucial feature that dictates the performance of WO₃. The thickness of WO₃ film can be easily controlled between ~85 and ~370 nm within a short deposition time ranging from 5 to 20 min, and the maximum photocurrent was observed when the film thickness was approximately 150 nm. The charge transfer resistance of the films annealed at 400 °C and above was significantly smaller as compared to the films annealed at 300 °C and below, which was in good agreement with the PEC trend where the crystalline WO₃ films showed higher photoelectrocatalytic activity than the amorphous films. In addition, the WO₃ photoelectrode exhibited excellent photoelectrochemical stability; the electrode was stable for the entire measurement time (120 min).

In chapter 5: the study demonstrated a novel approach to prepare Co–Pi-modified BiVO₄ films for PEC water oxidation. The BiVO₄ was derived from the Bi₂O₃ sputtered film. The transformation of Bi₂O₃ into BiVO₄ is dependent on the thickness of the Bi₂O₃ film. Microscopic images showed a morphological change from a rough Bi₂O₃ film to a porous structure of BiVO₄ film. At 420 nm, pristine BiVO₄ generated a photocurrent density of 0.9 mA cm⁻² V_{RHE} with an IPCE of 9%. This is a significantly high value in comparison with that of BiVO₄ prepared by other techniques. It is concluded that the continuous nature of the fabricated BiVO₄ film and the absence of pinholes are the main reasons for the improved PEC activity. They suppress the potential for fast surface recombination at the FTO regions exposed to the electrolyte. However, the PEC activity of BiVO₄ is still limited by the surface recombination and slow kinetics of water oxidation. After the modification of BiVO₄ with a Co-Pi layer, the photocurrent increased to 2.78 mA cm⁻² V_{RHE} with a 25% IPCE at 420 nm. The TPC study demonstrated that modifying the surface of BiVO₄ photoanodes with Co-Pi elongates the lifetime of the photogenerated holes by a factor of 9 times. The band structure properties of the BiVO₄ were obtained using DFT calculation.

In chapter 6: the study demonstrated the construction of a heterostructure photoanode composed of BiVO₄ and WO₃ in two steps. First, the WO₃ layer was deposited using DC reactive sputtering and then annealed to crystallize. Following that, Bi₂O₃ film was sputtered on top of the annealed WO₃ film and then modified it using drop-casting followed by heat treatment with the vanadium oxide precursor solution. The WO₃-based layer's thickness was optimized to increase the photoanode's PEC performance. On the surface of the BiVO₄/WO₃ film, the Co–Pi co-catalyst was electrochemically deposited and

tuned to provide a greater photocurrent density when irradiated with visible light. The photocurrent density generated by the Co–Pi/BiVO₄/WO₃ photoanode was determined to be 3.7 mA cm⁻² at 1.23 V_{RHE}, approximately 66% higher than the photocurrent generated by the bare BiVO₄/WO₃ photoanode and approximately 275% higher than the photocurrent generated by the individual BiVO₄ and WO₃ photoanodes. Additionally, at 430 nm, the Co–Pi/BiVO₄/WO₃ photoanode has an efficiency of around 25%, whereas the BiVO₄/WO₃, BiVO₄, and WO₃ photoanodes have an efficiency of approximately 16%, 7%, and 6%, respectively. The lower R_{ct} value for the BiVO₄/WO₃ heterojunction indicates a more effective electron-hole separation and faster interfacial charge transport, while the longer lifetime of the holes available for water oxidation at the Co–Pi/BiVO₄/WO₃ film's surface indicates a lower charge recombination rate and thus a higher charge transfer rate. The calculated band edges indicate that the CB and VB edges of the BiVO₄ are higher than those of the WO₃, implying that the BiVO₄/WO₃ heterostructure forms a Type-II heterostructure, resulting in effective photoexcited charge carrier separation and hence enhanced electro-photocatalytic activity.

To sum up, the synthesized photoanode (Co–Pi/BiVO₄/WO₃) exhibits superior photocatalytic performance in comparison to the majority of previously published research. In addition, it demonstrated outstanding photocurrent stability, which is one of the most important and frequently neglected factors that must be considered in the PEC. The combination of physical and chemical fabrication techniques enables us to preserve the mechanical stability of photoanode films in comparison to other wet fabrication techniques. It also allowed us to have a larger interaction surface area compared to films created only through sputtering deposition. Moreover, while the photoelectrochemical

deposition of the co-catalyst has a substantial effect on boosting the photocatalytic performance of the fabricated photoanode, fine-tuning the co-catalyst type and quantity can have a more significant effect on the $\text{BiVO}_4/\text{WO}_3$ photoanode activity. Finally, it is worthwhile to explore the possibility of depositing the co-catalyst using a physical approach in order to achieve greater photocurrent stability.

References

1. López Prol, J.; Schill, W.-P. The Economics of Variable Renewable Energy and Electricity Storage. *Annual Review of Resource Economics* **2021**, *13*, 443-467.
2. (2019), I. Global Energy & CO₂ Status Report 2019, IEA. Available online: <https://www.iea.org/reports/global-energy-co2-status-report-2019> (accessed on
3. da Silva, M.M.; Doyle. *Power and Gas Asset Management*; Springer: 2020.
4. Grimes, C.A.; Varghese, O.K.; Ranjan, S. *Light, water, hydrogen: the solar generation of hydrogen by water photoelectrolysis*; Springer: 2008; Volume 546.
5. Wismann, S.T.; Engbæk, J.S.; Vendelbo, S.B.; Bendixen, F.B.; Eriksen, W.L.; Aasberg-Petersen, K.; Frandsen, C.; Chorkendorff, I.; Mortensen, P.M. Electrified methane reforming: A compact approach to greener industrial hydrogen production. *Science* **2019**, *364*, 756-759.
6. Peláez-Peláez, S.; Colmenar-Santos, A.; Pérez-Molina, C.; Rosales, A.-E.; Rosales-Asensio, E. Techno-economic analysis of a heat and power combination system based on hybrid photovoltaic-fuel cell systems using hydrogen as an energy vector. *Energy* **2021**, *224*, 120110.
7. Alirahmi, S.M.; Assareh, E.; Chitsaz, A.; Holagh, S.G.; Jalilinasrabad, S. Electrolyzer-fuel cell combination for grid peak load management in a geothermal power plant: Power to hydrogen and hydrogen to power conversion. *International Journal of Hydrogen Energy* **2021**.
8. Gopinath, C.S.; Nalajala, N. A scalable and thin film approach for solar hydrogen generation: a review on enhanced photocatalytic water splitting. *Journal of Materials Chemistry A* **2021**, *9*, 1353-1371.
9. Peter, L.M.; Upul Wijayantha, K. Photoelectrochemical water splitting at semiconductor electrodes: fundamental problems and new perspectives. *ChemPhysChem* **2014**, *15*, 1983-1995.
10. Scott, K. Conclusions: Electrolytic Hydrogen Production and Sustainable Routes. *Electrochemical Methods for Hydrogen Production* **2019**, *25*, 392.

11. Çelik, D.; Yıldız, M. Investigation of hydrogen production methods in accordance with green chemistry principles. *International Journal of Hydrogen Energy* **2017**, *42*, 23395-23401.
12. Fujishima, A.; Honda, K. TiO₂ photoelectrochemistry and photocatalysis. *Nature* **1972**, *238*, 37-38.
13. Licht, S. Photoelectrochemical Conversion Processes. In *Springer Handbook of Electrochemical Energy*; Springer: **2017**; pp. 779-798.
14. Mayer, M.T. Photovoltage at semiconductor–electrolyte junctions. *Current Opinion in Electrochemistry* **2017**, *2*, 104-110.
15. Wang, Y.; Suzuki, H.; Xie, J.; Tomita, O.; Martin, D.J.; Higashi, M.; Kong, D.; Abe, R.; Tang, J. Mimicking natural photosynthesis: solar to renewable H₂ fuel synthesis by Z-scheme water splitting systems. *Chemical reviews* **2018**, *118*, 5201-5241.
16. Hisatomi, T.; Kubota, J.; Domen, K. Recent advances in semiconductors for photocatalytic and photoelectrochemical water splitting. *Chemical Society Reviews* **2014**, *43*, 7520-7535.
17. Kafizas, A.; Godin, R.; Durrant, J.R. Charge carrier dynamics in metal oxide photoelectrodes for water oxidation. *Semiconductors and Semimetals* **2017**, *97*, 3-46.
18. Ottone, C.; Hernández, S.; Armandi, M.; Bonelli, B. Scaling Up the Process of Photo-Electrochemical Water Splitting. In *Testing Novel Water Oxidation Catalysts for Solar Fuels Production*; Springer: **2019**; pp. 93-114.
19. Ibhaddon, A.O.; Fitzpatrick, P. Heterogeneous photocatalysis: recent advances and applications. *Catalysts* **2013**, *3*, 189-218.
20. Low, J.; Yu, J.; Jaroniec, M.; Wageh, S.; Al-Ghamdi, A.A. Heterojunction photocatalysts. *Advanced materials* **2017**, *29*, 1601694.
21. Tee, S.Y.; Win, K.Y.; Teo, W.S.; Koh, L.D.; Liu, S.; Teng, C.P.; Han, M.Y. Recent progress in energy-driven water splitting. *Advanced Science* **2017**, *4*, 1600337.
22. Beyhaqi, A.; Zeng, Q.; Chang, S.; Wang, M.; Azimi, S.M.T.; Hu, C. Construction of g-C₃N₄/WO₃/MoS₂ ternary nanocomposite with enhanced charge separation and

- collection for efficient wastewater treatment under visible light. *Chemosphere* **2020**, 247, 125784.
23. Yang, X.; Wang, D. Photocatalysis: from fundamental principles to materials and applications. *ACS Applied Energy Materials* **2018**, 1, 6657-6693.
 24. Corby, S.; Rao, R.R.; Steier, L.; Durrant, J.R. The kinetics of metal oxide photoanodes from charge generation to catalysis. *Nature Reviews Materials* **2021**, 1-20.
 25. Olea, M.A.U.; Bueno, J.d.J.P.; Pérez, A.X.M. Nanometric and surface properties of semiconductors correlated to photocatalysis and photoelectrocatalysis applied to organic pollutants—A review. *Journal of Environmental Chemical Engineering* **2021**, 106480.
 26. Modestino, M.A.; Hashemi, S.M.H.; Haussener, S. Mass transport aspects of electrochemical solar-hydrogen generation. *Energy & Environmental Science* **2016**, 9, 1533-1551.
 27. He, W.; Wang, R.; Zhang, L.; Zhu, J.; Xiang, X.; Li, F. Enhanced photoelectrochemical water oxidation on a BiVO₄ photoanode modified with multi-functional layered double hydroxide nanowalls. *Journal of Materials Chemistry A* **2015**, 3, 17977-17982.
 28. Hankin, A.; Bedoya-Lora, F.E.; Alexander, J.C.; Regoutz, A.; Kelsall, G.H. Flat band potential determination: avoiding the pitfalls. *Journal of Materials Chemistry A* **2019**, 7, 26162-26176.
 29. Gelderman, K.; Lee, L.; Donne, S. Flat-band potential of a semiconductor: using the Mott–Schottky equation. *Journal of chemical education* **2007**, 84, 685.
 30. Böer, K.W. *Introduction to space charge effects in semiconductors*; Springer: **2010**; Volume 37.
 31. Le Formal, F.; Pendlebury, S.R.; Cornuz, M.; Tilley, S.D.; Grätzel, M.; Durrant, J.R. Back electron–hole recombination in hematite photoanodes for water splitting. *Journal of the American Chemical Society* **2014**, 136, 2564-2574.
 32. 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. *Chemical Science* **2014**, 5, 2964-2973.

33. Grätzel, M. Photoelectrochemical cells. In *Materials For Sustainable Energy: A Collection of Peer-Reviewed Research and Review Articles from Nature Publishing Group*; World Scientific **2011**; pp. 26-32.
34. Sharma, B. *Metal-semiconductor Schottky barrier junctions and their applications*; Springer Science & Business Media **2013**.
35. Liu, Y.; Gu, X.; Qi, W.; Zhu, H.; Shan, H.; Chen, W.; Tao, P.; Song, C.; Shang, W.; Deng, T. Enhancing the photocatalytic hydrogen evolution performance of a metal/semiconductor catalyst through modulation of the Schottky barrier height by controlling the orientation of the interface. *ACS applied materials & interfaces* **2017**, 9, 12494-12500.
36. Hernández, S.; Hidalgo, D.; Sacco, A.; Chiodoni, A.; Lamberti, A.; Cauda, V.; Tresso, E.; Saracco, G. Comparison of photocatalytic and transport properties of TiO₂ and ZnO nanostructures for solar-driven water splitting. *Physical Chemistry Chemical Physics* **2015**, 17, 7775-7786.
37. Markowich, P.A.; Ringhofer, C.A.; Schmeiser, C. *Semiconductor equations*; Springer Science & Business Media: **2012**.
38. Butler, M. Photoelectrolysis and physical properties of the semiconducting electrode WO₂. *Journal of Applied Physics* **1977**, 48, 1914-1920.
39. Shin, Y.-S.; Lee, D.; Lee, H.-S.; Cho, Y.-J.; Kim, C.-J.; Jo, M.-H. Determination of the photocarrier diffusion length in intrinsic Ge nanowires. *Optics express* **2011**, 19, 6119-6124.
40. Belghachi, A.; Helmaoui, A. Analysis of photocurrent in the i-layer of GaAs-based n-i-p solar cell. *Solar energy materials and solar cells* **2006**, 90, 1721-1733.
41. Cendula, P.; Tilley, S.D.; Gimenez, S.; Bisquert, J.; Schmid, M.; Grätzel, M.; Schumacher, J.r.O. Calculation of the energy band diagram of a photoelectrochemical water splitting cell. *The Journal of Physical Chemistry C* **2014**, 118, 29599-29607.
42. Chakhari, W.; Naceur, J.B.; Taieb, S.B.; Assaker, I.B.; Chtourou, R. Fe-doped TiO₂ nanorods with enhanced electrochemical properties as efficient photoanode materials. *Journal of Alloys and Compounds* **2017**, 708, 862-870.

43. Chaudhary, P.; Ingole, P.P. Electrocatalytic and Photo-catalytic Water Splitting. In *Green Photocatalytic Semiconductors*; Springer: 2022; pp. 673-699.
44. Xie, S.; Zhang, Q.; Liu, G.; Wang, Y. Photocatalytic and photoelectrocatalytic reduction of CO₂ using heterogeneous catalysts with controlled nanostructures. *Chemical communications* **2016**, 52, 35-59.
45. Ge, M.; Cai, J.; Iocozzia, J.; Cao, C.; Huang, J.; Zhang, X.; Shen, J.; Wang, S.; Zhang, S.; Zhang, K.-Q. A review of TiO₂ nanostructured catalysts for sustainable H₂ generation. *international journal of hydrogen energy* **2017**, 42, 8418-8449.
46. Peleyeju, M.G.; Viljoen, E.L. WO₃-based catalysts for photocatalytic and photoelectrocatalytic removal of organic pollutants from water—A review. *Journal of Water Process Engineering* **2021**, 40, 101930.
47. Rather, R.A.; Mehta, A.; Lu, Y.; Valant, M.; Fang, M.; Liu, W. Influence of exposed facets, morphology and hetero-interfaces of BiVO₄ on photocatalytic water oxidation: A review. *International Journal of Hydrogen Energy* **2021**.
48. Wang, S.-C.; Tang, F.-Q.; Wang, L.-Z. Visible light responsive metal oxide photoanodes for photoelectrochemical water splitting: a comprehensive review on rational materials design. *Journal of Inorganic Materials* **2018**.
49. Ogden, J.M. Prospects for building a hydrogen energy infrastructure. *Annual Review of Energy and the Environment* **1999**, 24, 227-279.
50. Becquerel's, E. electrochemical actinometer. *Archives des sciences* **2005**, 58, 149-158.
51. Becquerel, M. Mémoire sur les effets électriques produits sous l'influence des rayons solaires. *Comptes rendus hebdomadaires des séances de l'Académie des sciences* **1839**, 9, 561-567.
52. Brattain, W.; Garrett, C. Experiments on the interface between germanium and an electrolyte. *Bell System Technical Journal* **1955**, 34, 129-176.
53. Salje, E.K.; Rehmann, S.; Pobell, F.; Morris, D.; Knight, K.S.; Herrmannsdörfer, T.; Dove, M.T. Crystal structure and paramagnetic behaviour of. *Journal of Physics: Condensed Matter* **1997**, 9, 6563.
54. Mardare, C.C.; Hassel, A.W. Review on the versatility of tungsten oxide coatings. *physica status solidi (a)* **2019**, 216, 1900047.

55. Vogt, T.; Woodward, P.M.; Hunter, B.A. The high-temperature phases of WO₃. *Journal of Solid State Chemistry* **1999**, *144*, 209-215.
56. Zheng, H.; Ou, J.Z.; Strano, M.S.; Kaner, R.B.; Mitchell, A.; Kalantar-zadeh, K. Nanostructured tungsten oxide—properties, synthesis, and applications. *Advanced Functional Materials* **2011**, *21*, 2175-2196.
57. Li, Y.; Tang, Z.; Zhang, J.; Zhang, Z. Enhanced photocatalytic performance of tungsten oxide through tuning exposed facets and introducing oxygen vacancies. *Journal of Alloys and Compounds* **2017**, *708*, 358-366.
58. Mirfasih, M.H.; Li, C.; Tayyebi, A.; Cao, Q.; Yu, J.; Delaunay, J.-J. Oxygen-vacancy-induced photoelectrochemical water oxidation by platelike tungsten oxide photoanodes prepared under acid-mediated hydrothermal treatment conditions. *RSC advances* **2017**, *7*, 26992-27000.
59. Srilakshmi, P.; Sivakumar, M.; Kathirvel, A.; Maheswari, A.U. Influence of annealing atmosphere for controlling oxygen vacancies of PVP-capped TiO₂ nanoparticles. *Journal of Nanoparticle Research* **2021**, *23*, 1-14.
60. Liu, Y.; Kong, L.; Guo, X.; Xu, J.; Shi, S.; Li, L. Surface oxygen vacancies on WO₃ nanoplate arrays induced by Ar plasma treatment for efficient photoelectrochemical water oxidation. *Journal of Physics and Chemistry of Solids* **2021**, *149*, 109823.
61. Kieslich, G.; Tremel, W. Magnéli oxides as promising n-type thermoelectrics. *AIMS Mater. Sci* **2014**, *1*, 184-190.
62. Bai, H.; Yi, W.; Liu, J.; Lv, Q.; Zhang, Q.; Ma, Q.; Yang, H.; Xi, G. Large-scale synthesis of ultrathin tungsten oxide nanowire networks: an efficient catalyst for aerobic oxidation of toluene to benzaldehyde under visible light. *Nanoscale* **2016**, *8*, 13545-13551.
63. Jia, C.; Zhang, X.; Matras-Postolek, K.; Huang, B.; Yang, P. Z-scheme reduced graphene oxide/TiO₂-Bronze/W₁₈O₄₉ ternary heterostructure towards efficient full solar-spectrum photocatalysis. *Carbon* **2018**, *139*, 415-426.
64. Huang, Z.-F.; Song, J.; Pan, L.; Lv, F.; Wang, Q.; Zou, J.-J.; Zhang, X.; Wang, L. Mesoporous W₁₈O₄₉ hollow spheres as highly active photocatalysts. *Chemical Communications* **2014**, *50*, 10959-10962.

65. Guo, C.; Yin, S.; Huang, Y.; Dong, Q.; Sato, T. Synthesis of $W_{18}O_{49}$ nanorod via ammonium tungsten oxide and its interesting optical properties. *Langmuir* **2011**, *27*, 12172-12178.
66. Guo, C.; Yin, S.; Yan, M.; Kobayashi, M.; Kakihana, M.; Sato, T. Morphology-controlled synthesis of $W_{18}O_{49}$ nanostructures and their near-infrared absorption properties. *Inorganic chemistry* **2012**, *51*, 4763-4771.
67. Hai, G.; Huang, J.; Jie, Y.; Cao, L.; Wang, L.; Fu, C.; Xiao, T.; Niu, M.; Feng, L. Unveiling the relationships between (010) facets-orientation growth and photocatalytic activity in $W_{18}O_{49}$ nanowires. *Journal of Alloys and Compounds* **2020**, *820*, 153127.
68. Chen, C.; Liu, X.; Long, H.; Ding, F.; Liu, Q. Preparation and photocatalytic performance of graphene Oxide/ WO_3 quantum Dots/ $TiO_2@SiO_2$ microspheres. *Vacuum* **2019**, *164*, 66-71.
69. Wang, X.; Fan, H.; Ren, P. Effects of exposed facets on photocatalytic properties of WO_3 . *Advanced Powder Technology* **2017**, *28*, 2549-2555.
70. Zhang, H.; Yang, J.; Li, D.; Guo, W.; Qin, Q.; Zhu, L.; Zheng, W. Template-free facile preparation of monoclinic WO_3 nanoplates and their high photocatalytic activities. *Applied surface science* **2014**, *305*, 274-280.
71. Li, Y.; Tang, Z.; Zhang, J.; Zhang, Z. Exposed facet and crystal phase tuning of hierarchical tungsten oxide nanostructures and their enhanced visible-light-driven photocatalytic performance. *CrystEngComm* **2015**, *17*, 9102-9110.
72. Supanantin, F.; Ponchio, C. Improvement ITO/ WO_3 photo anode electrode fabrication using electrodeposition technique for highly efficient photoelectrocatalytic insecticide degradation. *Materials Science in Semiconductor Processing* **2020**, *118*, 105212.
73. Juodkazytė, J.; Petrulėvičienė, M.; Parvin, M.; Šebeka, B.; Savickaja, I.; Pakštas, V.; Naujokaitis, A.; Virkutis, J.; Gegeckas, A. Activity of sol-gel derived nanocrystalline WO_3 films in photoelectrochemical generation of reactive chlorine species. *Journal of Electroanalytical Chemistry* **2020**, *871*, 114277.
74. Fernández-Domene, R.; Roselló-Márquez, G.; Sánchez-Tovar, R.; Cifre-Herrando, M.; García-Antón, J. Synthesis of WO_3 nanorods through anodization in the

- presence of citric acid: Formation mechanism, properties and photoelectrocatalytic performance. *Surface and Coatings Technology* **2021**, 422, 127489.
75. Shi, X.; Dong, F.; Dai, C.; Ye, X.; Yang, P.; Zheng, L.; Zheng, H. WO₃/ZnIn₂S₄ heterojunction photoanodes grafting silane molecule for efficient photoelectrochemical water splitting. *Electrochimica Acta* **2020**, 361, 137017.
 76. Ju, S.; Seok, H.-J.; Jun, J.; Huh, D.; Son, S.; Kim, K.; Kim, W.; Baek, S.; Kim, H.-K.; Lee, H. Fully blossomed WO₃/BiVO₄ structure obtained via active facet engineering of patterned FTO for highly efficient Water splitting. *Applied Catalysis B: Environmental* **2020**, 263, 118362.
 77. Limwichean, S.; Kasayapanand, N.; Ponchio, C.; Nakajima, H.; Patthanasettakul, V.; Eiamchai, P.; Meng, G.; Horprathum, M. Morphology-controlled fabrication of nanostructured WO₃ thin films by magnetron sputtering with glancing angle deposition for enhanced efficiency photo-electrochemical water splitting. *Ceramics International* **2021**.
 78. Hunge, Y.; Mahadik, M.; Kumbhar, S.; Mohite, V.; Rajpure, K.; Deshpande, N.; Moholkar, A.; Bhosale, C. Visible light catalysis of methyl orange using nanostructured WO₃ thin films. *Ceramics International* **2016**, 42, 789-798.
 79. Mohamed, A.M.; Shaban, S.A.; El Sayed, H.A.; Alanadoul, B.E.; Allam, N.K. Morphology–photoactivity relationship: WO₃ nanostructured films for solar hydrogen production. *International Journal of Hydrogen Energy* **2016**, 41, 866-872.
 80. Vidyarthi, V.S.; Hofmann, M.; Savan, A.; Sliozberg, K.; König, D.; Beranek, R.; Schuhmann, W.; Ludwig, A. Enhanced photoelectrochemical properties of WO₃ thin films fabricated by reactive magnetron sputtering. *international journal of hydrogen energy* **2011**, 36, 4724-4731.
 81. Cole, B.; Marsen, B.; Miller, E.; Yan, Y.; To, B.; Jones, K.; Al-Jassim, M. Evaluation of nitrogen doping of tungsten oxide for photoelectrochemical water splitting. *The Journal of Physical Chemistry C* **2008**, 112, 5213-5220.
 82. Marsen, B.; Miller, E.L.; Paluselli, D.; Rocheleau, R.E. Progress in sputtered tungsten trioxide for photoelectrode applications. *International Journal of Hydrogen Energy* **2007**, 32, 3110-3115.

83. Liew, S.L.; Wang, W.; Dolmanan, S.B.; Goh, G.T.W.; Chi, D. Solar water oxidation in sputter-deposited nanocrystalline WO₃ photoanodes via tuning of Ar: O₂ flow rate combinations. *Materials Chemistry and Physics* **2014**, *143*, 1171-1177.
84. Zhao, Y.; Balasubramanyam, S.; Sinha, R.; Lavrijsen, R.; Verheijen, M.; Bol, A.; Bieberle-Hütter, A. Physical and chemical defects in WO₃ thin films and their impact on photoelectrochemical water splitting. *ACS Applied Energy Materials* **2018**, *1*, 5887-5895.
85. Valerini, D.; Hernández, S.; Di Benedetto, F.; Russo, N.; Saracco, G.; Rizzo, A. Sputtered WO₃ films for water splitting applications. *Materials Science in Semiconductor Processing* **2016**, *42*, 150-154.
86. Sharp, I.D.; Cooper, J.K.; Toma, F.M.; Buonsanti, R. Bismuth vanadate as a platform for accelerating discovery and development of complex transition-metal oxide photoanodes. *ACS Energy Letters* **2017**, *2*, 139-150.
87. Li, G.; Bai, Y.; Zhang, W. Difference in valence band top of BiVO₄ with different crystal structure. *Materials Chemistry and Physics* **2012**, *136*, 930-934.
88. Park, Y.; McDonald, K.J.; Choi, K.-S. Progress in bismuth vanadate photoanodes for use in solar water oxidation. *Chemical Society Reviews* **2013**, *42*, 2321-2337.
89. 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. *Chemistry of Materials* **2009**, *21*, 547-551.
90. 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. *Chemistry of Materials* **2014**, *26*, 5365-5373.
91. Payne, D.; Robinson, M.; Egdel, R.; Walsh, A.; McNulty, J.; Smith, K.; Piper, L. The nature of electron lone pairs in BiVO₄. *Applied Physics Letters* **2011**, *98*, 212110.
92. Ma, J.; Wang, L.-W. The role of the isolated 6s states in BiVO₄ on the electronic and atomic structures. *Applied Physics Letters* **2014**, *105*, 172102.
93. Zhao, Z.; Li, Z.; Zou, Z. Electronic structure and optical properties of monoclinic clinobisvanite BiVO₄. *Physical Chemistry Chemical Physics* **2011**, *13*, 4746-4753.

94. Kudo, A.; Ueda, K.; Kato, H.; Mikami, I. Photocatalytic O₂ evolution under visible light irradiation on BiVO₄ in aqueous AgNO₃ solution. *Catalysis Letters* **1998**, *53*, 229-230.
95. Liu, X.; Liu, Y.; Su, J.; Li, M.; Guo, L. Facile preparation of BiVO₄ nanoparticle film by electrostatic spray pyrolysis for photoelectrochemical water splitting. *international journal of hydrogen energy* **2015**, *40*, 12964-12972.
96. Eisenberg, D.; Ahn, H.S.; Bard, A.J. Enhanced photoelectrochemical water oxidation on bismuth vanadate by electrodeposition of amorphous titanium dioxide. *Journal of the American Chemical Society* **2014**, *136*, 14011-14014.
97. Liang, Y.; Tsubota, T.; Mooij, L.P.; van de Krol, R. Highly improved quantum efficiencies for thin film BiVO₄ photoanodes. *The Journal of Physical Chemistry C* **2011**, *115*, 17594-17598.
98. Zhong, D.K.; Choi, S.; Gamelin, D.R. Near-complete suppression of surface recombination in solar photoelectrolysis by “Co-Pi” catalyst-modified W: BiVO₄. *Journal of the American Chemical Society* **2011**, *133*, 18370-18377.
99. 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. *Physical Chemistry Chemical Physics* **2012**, *14*, 7065-7075.
100. Alarcón-Lladó, E.; Chen, L.; Hettick, M.; Mashouf, N.; Lin, Y.; Javey, A.; Ager, J.W. BiVO₄ thin film photoanodes grown by chemical vapor deposition. *Physical Chemistry Chemical Physics* **2014**, *16*, 1651-1657.
101. Choi, S.K.; Choi, W.; Park, H. Solar water oxidation using nickel-borate coupled BiVO₄ photoelectrodes. *Physical chemistry chemical physics* **2013**, *15*, 6499-6507.
102. Madhavi, V.; Kondaiah, P.; Shaik, H.; Kumar, K.N.; Naik, T.S.K.; Rao, G.M.; Ramamurthy, P.C. Fabrication of porous 1D WO₃ NRs and WO₃/BiVO₄ hetero junction photoanode for efficient photoelectrochemical water splitting. *Materials Chemistry and Physics* **2021**, 125095.
103. Pedroni, M.; Chiarello, G.L.; Vassallo, E.; Selli, E. Multilayer WO₃/BiVO₄ Photoanodes for Solar-Driven Water Splitting Prepared by RF-Plasma Sputtering. *Surfaces* **2020**, *3*, 105-115.

104. Kodan, N.; Ahmad, M.; Mehta, B. Charge carrier separation and enhanced PEC properties of BiVO₄ based heterojunctions having ultrathin overlayers. *International Journal of Hydrogen Energy* **2021**, *46*, 189-196.
105. Cowan, A.J.; Durrant, J.R. Long-lived charge separated states in nanostructured semiconductor photoelectrodes for the production of solar fuels. *Chemical Society Reviews* **2013**, *42*, 2281-2293.
106. Kalanoor, B.S.; Seo, H.; Kalanur, S.S. Recent developments in photoelectrochemical water-splitting using WO₃/BiVO₄ heterojunction photoanode: A review. *Materials Science for Energy Technologies* **2018**, *1*, 49-62.
107. Liu, J.; Chen, W.; Sun, Q.; Zhang, Y.; Li, X.; Wang, J.; Wang, C.; Yu, Y.; Wang, L.; Yu, X. Oxygen Vacancies Enhanced WO₃/BiVO₄ Photoanodes Modified by Cobalt Phosphate for Efficient Photoelectrochemical Water Splitting. *ACS Applied Energy Materials* **2021**, *4*, 2864-2872.
108. Madhavi, V.; Kondaiah, P.; Shaik, H.; Kumar, K.N.; Naik, T.S.K.; Rao, G.M.; Ramamurthy, P.C. Fabrication of porous 1D WO₃ NRs and WO₃/BiVO₄ heterojunction photoanode for efficient photoelectrochemical water splitting. *Materials Chemistry and Physics* **2021**, *274*, 125095.
109. Zachäus, C.; Abdi, F.F.; Peter, L.M.; Van De Krol, R. Photocurrent of BiVO₄ is limited by surface recombination, not surface catalysis. *Chemical science* **2017**, *8*, 3712-3719.
110. Ma, Y.; Kafizas, A.; Pendlebury, S.R.; Le Formal, F.; Durrant, J.R. Photoinduced absorption spectroscopy of CoPi on BiVO₄: the function of CoPi during water oxidation. *Advanced Functional Materials* **2016**, *26*, 4951-4960.
111. Hegner, F.S.; Herraiz-Cardona, I.; Cardenas-Morcoso, D.; López, N.r.; Galán-Mascarós, J.-R.n.; Gimenez, S. Cobalt hexacyanoferrate on BiVO₄ photoanodes for robust water splitting. *ACS applied materials & interfaces* **2017**, *9*, 37671-37681.
112. Wang, S.; Chen, P.; Bai, Y.; Yun, J.H.; Liu, G.; Wang, L. New BiVO₄ dual photoanodes with enriched oxygen vacancies for efficient solar-driven Water Splitting. *Advanced Materials* **2018**, *30*, 1800486.

113. Fang, G.; Liu, Z.; Han, C. Enhancing the PEC water splitting performance of BiVO₄ co-modifying with NiFeOOH and Co-Pi double layer cocatalysts. *Applied Surface Science* **2020**, *515*, 146095.
114. Laskowski, F.A.; Nellist, M.R.; Qiu, J.; Boettcher, S.W. Metal oxide/(oxy) hydroxide overlayers as hole collectors and oxygen-evolution catalysts on water-splitting photoanodes. *Journal of the American Chemical Society* **2018**, *141*, 1394-1405.
115. Martin, P.M. *Handbook of deposition technologies for films and coatings: science, applications and technology*; William Andrew: **2009**.
116. Warren, B.E. *X-ray Diffraction*; Courier Corporation: **1990**.
117. Brodusch, N.; Demers, H.; Gauvin, R. *Field emission scanning electron microscopy: New perspectives for materials characterization*; Springer: **2018**.
118. Y., O. *Scanning Electron Microscopy*; Springer: Singapore, **2018**.
119. Greczynski, G.; Hultman, L. The same chemical state of carbon gives rise to two peaks in X-ray photoelectron spectroscopy. *Scientific Reports* **2021**, *11*, 1-5.
120. Stevie, F.A.; Donley, C.L. Introduction to x-ray photoelectron spectroscopy. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **2020**, *38*, 063204.
121. Haasch, R.T. X-ray photoelectron spectroscopy (XPS) and auger electron spectroscopy (AES). In *Practical Materials Characterization*; Springer: **2014**; pp. 93-132.
122. Sharma, J.; Beard, B. Fundamentals of X-ray photoelectron spectroscopy (XPS) and its applications to explosives and propellants. In *Chemistry and Physics of Energetic Materials*; Springer: **1990**; pp. 569-585.
123. Mane, A.; Patil, V. X-ray photoelectron spectroscopy of nanofillers and their polymer nanocomposites. In *Spectroscopy of Polymer Nanocomposites*; Elsevier: **2016**; pp. 452-467.
124. Tissue, B.M. Ultraviolet and visible absorption spectroscopy. *Characterization of Materials* **2002**.
125. Förster, H. UV/Vis spectroscopy. In *Characterization I*; Springer: **2004**; pp. 337-426.

126. Cazes, J. *Analytical instrumentation handbook*; CRC Press: **2004**.
127. Bard, A.J.; Faulkner, L.R. Electrochemical Methods: Fundamentals and Applications. *Surface Technology* **1983**, 20, 91-92.
128. Aikens, D. Electrochemical methods, fundamentals and applications. **1983**.
129. Fiolhais, C.; Nogueira, F.; Marques, M.A. *A primer in density functional theory*; Springer Science & Business Media: **2003**; Volume 620.
130. Jones, R.O.; Gunnarsson, O. The density functional formalism, its applications and prospects. *Reviews of Modern Physics* **1989**, 61, 689.
131. Perdew, J.P.; Wang, Y. Pair-distribution function and its coupling-constant average for the spin-polarized electron gas. *Physical Review B* **1992**, 46, 12947.
132. Heyd, J.; Scuseria, G.E. Efficient hybrid density functional calculations in solids: Assessment of the Heyd–Scuseria–Ernzerhof screened Coulomb hybrid functional. *The Journal of chemical physics* **2004**, 121, 1187-1192.
133. Becke, A.D. A new mixing of Hartree–Fock and local density-functional theories. *The Journal of chemical physics* **1993**, 98, 1372-1377.
134. Luo, W.; Wang, J.; Zhao, X.; Zhao, Z.; Li, Z.; Zou, Z. Formation energy and photoelectrochemical properties of BiVO₄ after doping at Bi³⁺ or V⁵⁺ sites with higher valence metal ions. *Physical Chemistry Chemical Physics* **2013**, 15, 1006-1013.
135. Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Physical review B* **1996**, 54, 11169.
136. Blöchl, P.E. Projector augmented-wave method. *Physical review B* **1994**, 50, 17953.
137. Chen, P.; Qin, M.; Chen, Z.; Jia, B.; Qu, X. Solution combustion synthesis of nanosized WO_x: characterization, mechanism and excellent photocatalytic properties. *RSC advances* **2016**, 6, 83101-83109.
138. Song, P.K.; Akao, H.; Kamei, M.; Shigesato, Y.; Yasui, I. Preparation and crystallization of tin-doped and undoped amorphous indium oxide films deposited by sputtering. *Japanese journal of applied physics* **1999**, 38, 5224.

139. Maillé, L.; Sant, C.; Le Paven-Thivet, C.; Legrand-Buscema, C.; Garnier, P. Structure and morphological study of nanometer W and W₃O thin films. *Thin Solid Films* **2003**, *428*, 237-241.
140. Tauc, J. Optical properties of amorphous semiconductors. In *Amorphous and liquid semiconductors*; Springer: **1974**; pp. 159-220.
141. Al-Kuhaili, M. Electromodulated transmittance of optical transitions in tungsten oxide. *Journal of Physics and Chemistry of Solids* **2020**, *139*, 109317.
142. Abdelrahman, A.; Yunus, W.; Arof, A. Optical properties of tin sulphide (SnS) thin film estimated from transmission spectra. *Journal of non-crystalline solids* **2012**, *358*, 1447-1451.
143. Vani, V.P.G.; Reddy, M.R.V.; Reddy, K. Influence of Source-Substrate Distance of Cu₄SnS₄ Thin Films Grown by Co-evaporation. In *Proceedings of the Advanced Materials Research*, **2013**; pp. 103-108.
144. Wong, H.; Zhou, J.; Zhang, J.; Jin, H.; Kakushima, K.; Iwai, H. The interfaces of lanthanum oxide-based subnanometer EOT gate dielectrics. *Nanoscale research letters* **2014**, *9*, 1-5.
145. Xie, F.; Gong, L.; Liu, X.; Tao, Y.; Zhang, W.; Chen, S.; Meng, H.; Chen, J. XPS studies on surface reduction of tungsten oxide nanowire film by Ar⁺ bombardment. *Journal of Electron Spectroscopy and Related Phenomena* **2012**, *185*, 112-118.
146. Zhong, Q.; Macharia, D.K.; Zhong, W.; Liu, Z.; Chen, Z. Synthesis of hydrophobic W₁₈O₄₉ nanorods for constructing UV/NIR-shielding and self-cleaning film. *Ceramics International* **2020**.
147. Lv, Z.; Liu, H.; Zhang, X.; Shen, X.; Liu, S.; Wu, X.; Fang, M.; Liu, Y.-g.; Min, X.; Huang, Z. Solvothermally synthesized highly porous W₁₈O₄₉ nanowires for UV, humidity and pH detection. *Physica E: Low-dimensional Systems and Nanostructures* **2020**, *117*, 113719.
148. Wang, J.; Chen, Z.; Zhai, G.; Men, Y. Boosting photocatalytic activity of WO₃ nanorods with tailored surface oxygen vacancies for selective alcohol oxidations. *Applied Surface Science* **2018**, *462*, 760-771.

149. Mohamedkhair, A.; Drmosh, Q.; Qamar, M.; Yamani, Z. Nanostructured Magnéli-Phase $W_{18}O_{49}$ Thin Films for Photoelectrochemical Water Splitting. *Catalysts* **2020**, *10*, 526.
150. Mohite, S.; Rajpure, K. Oxidative degradation of salicylic acid by sprayed WO_3 photocatalyst. *Materials Science and Engineering: B* **2015**, *200*, 78-83.
151. Dongale, T.; Mohite, S.; Bagade, A.; Kamat, R.; Rajpure, K. Bio-mimicking the synaptic weights, analog memory, and forgetting effect using spray deposited WO_3 memristor device. *Microelectronic Engineering* **2017**, *183*, 12-18.
152. Shewale, P.; Agawane, G.; Shin, S.; Moholkar, A.; Lee, J.; Kim, J.; Uplane, M. Chemical, A.B. Thickness dependent H_2S sensing properties of nanocrystalline ZnO thin films derived by advanced spray pyrolysis. *Sensors and Actuators B: Chemical* **2013**, *177*, 695-702.
153. Bouderbala, M.; Hamzaoui, S.; Amrani, B.; Reshak, A.H.; Adnane, M.; Sahraoui, T.; Zerdali, M. Thickness dependence of structural, electrical and optical behaviour of undoped ZnO thin films. *Physica B: Condensed Matter* **2008**, *403*, 3326-3330.
154. Sharma, M.; Mehra, R. Effect of thickness on structural, electrical, optical and magnetic properties of Co and Al doped ZnO films deposited by sol-gel route. *Applied Surface Science* **2008**, *255*, 2527-2532.
155. Ravikumar, P.; Taparia, D.; Alagarsamy, P.J.J.o.S.; Magnetism, N. Thickness-dependent thermal oxidation of Ni into NiO thin films. *Journal of Superconductivity and Novel Magnetism* **2018**, *31*, 3761-3775.
156. Song, P.K.; Akao, H.; Kamei, M.; Shigesato, Y.; Yasui, I. Preparation and crystallization of tin-doped and undoped amorphous indium oxide films deposited by sputtering. *Japanese Journal of Applied Physics* **1999**, *38*, 5224.
157. Ghosh, R.; Paul, G.; Basak, D. Effect of thermal annealing treatment on structural, electrical and optical properties of transparent sol-gel ZnO thin films. *Materials research bulletin* **2005**, *40*, 1905-1914.
158. Ting, C.-C.; Chen, S.-Y.; Liu, D.-M.J. Structural evolution and optical properties of TiO_2 thin films prepared by thermal oxidation of sputtered Ti films. *Journal of Applied Physics* **2000**, *88*, 4628-4633.

159. Cai, K.; Müller, M.; Bossert, J.; Rechtenbach, A.; Jandt, K.D. Surface structure and composition of flat titanium thin films as a function of film thickness and evaporation rate. *Applied Surface Science* **2005**, *250*, 252-267.
160. Zhang, M.; Xu, M.; Li, M.; Zhang, Q.; Lu, Y.; Chen, J.; Li, M.; Dai, J.; Chen, C.; He, Y. SnO₂ epitaxial films with varying thickness on c-sapphire: structure evolution and optical band gap modulation. *Applied Surface Science* **2017**, *423*, 611-618.
161. Naceur, J.B.; Gaidi, M.; Bousbih, F.; Mechiakh, R.; Chtourou, R. Annealing effects on microstructural and optical properties of nanostructured-TiO₂ thin films prepared by sol-gel technique. *Current Applied Physics* **2012**, *12*, 422-428.
162. Sagar, P.; Shishodia, P.; Mehra, R.; Okada, H.; Wakahara, A.; Yoshida, A. Photoluminescence and absorption in sol-gel-derived ZnO films. *Journal of Luminescence* **2007**, *126*, 800-806.
163. Al-Kuhaili, M. Solids, C.o. Electromodulated transmittance of optical transitions in tungsten oxide. *Journal of Physics and Chemistry of Solids* **2020**, *139*, 109317.
164. Xue, S.; Zu, X.; Zhou, W.; Deng, H.; Xiang, X.; Zhang, L.; Deng, H. Compounds. Effects of post-thermal annealing on the optical constants of ZnO thin film. *Journal of Alloys and Compounds* **2008**, *448*, 21-26.
165. Ram, J.; Singh, R.; Gupta, R.; Kumar, V.; Singh, F.; Kumar, R. Effect of annealing on the surface morphology, optical and structural properties of nanodimensional tungsten oxide prepared by coprecipitation technique. *Journal of Electronic Materials* **2019**, *48*, 1174-1183.
166. Bouhssira, N.; Abed, S.; Tomasella, E.; Cellier, J.; Mosbah, A.; Aida, M.; Jacquet, M. Influence of annealing temperature on the properties of ZnO thin films deposited by thermal evaporation. *Applied Surface Science* **2006**, *252*, 5594-5597.
167. Wong, H.; Zhou, J.; Zhang, J.; Jin, H.; Kakushima, K.; Iwai, H. The interfaces of lanthanum oxide-based subnanometer EOT gate dielectrics. *Nanoscale Research Letters* **2014**, *9*, 1-5.
168. Kalanur, S. Structural, optical, band edge and enhanced photoelectrochemical water splitting properties of tin-doped WO₃. *Catalysts* **2019**, *9*, 456.

169. Liang, Y.-C.; Chang, C.-W. Preparation of orthorhombic WO₃ thin films and their crystal quality-dependent dye photodegradation ability. *Coatings* **2019**, *9*, 90.
170. Nayak, A.K.; Ghosh, R.; Santra, S.; Guha, P.K.; Pradhan, D. Hierarchical nanostructured WO₃-SnO₂ for selective sensing of volatile organic compounds. *Nanoscale* **2015**, *7*, 12460-12473.
171. Wang, J.; Chen, Z.; Zhai, G.; Men, Y. Boosting photocatalytic activity of WO₃ nanorods with tailored surface oxygen vacancies for selective alcohol oxidations. *Applied Surface Science* **2018**, *462*, 760-771.
172. Wang, F.; Di Valentin, C.; Pacchioni, G. Electronic and structural properties of WO₃: a systematic hybrid DFT study. *The Journal of Physical Chemistry C* **2011**, *115*, 8345-8353.
173. Liu, X.; Zhou, H.; Pei, S.; Xie, S.; You, S. Oxygen-deficient WO_{3-x} nanoplate array film photoanode for efficient photoelectrocatalytic water decontamination. *Chemical Engineering Journal* **2020**, *381*, 122740.
174. Hosseini, M.G.; Sefidi, P.Y.; Aydin, Z.; Kinayyigit, S. Toward enhancing the photoelectrochemical water splitting efficiency of organic acid doped polyaniline-WO₃ photoanode by photo-assisted electrochemically reduced graphene oxide. *Electrochimica Acta* **2020**, *333*, 135475.
175. Qamar, M.; Merzougui, B.; Ahmed, M.I.; Yamani, Z.H. Broad solar spectrum-responsive and highly efficient photoanode of nonstoichiometric TiO₂ nanoplates/reduced graphene oxide. *ACS Sustainable Chemistry & Engineering* **2018**, *6*, 2112-2121.
176. Mai, M.; Ma, X.; Zhou, H.; Ye, M.; Li, T.; Ke, S.; Lin, P.; Zeng, X. Effect of oxygen pressure on pulsed laser deposited WO₃ thin films for photoelectrochemical water splitting. *Journal of Alloys and Compounds* **2017**, *722*, 913-919.
177. Chua, C.S.; Ansovini, D.; Lee, C.J.J.; Teng, Y.T.; Ong, L.T.; Chi, D.; Hor, T.A.; Raja, R.; Lim, Y.-F. The effect of crystallinity on photocatalytic performance of Co₃O₄ water-splitting cocatalysts. *Physical Chemistry Chemical Physics* **2016**, *18*, 5172-5178.
178. Xu, F.; Yao, Y.; Bai, D.; Xu, R.; Mei, J.; Wu, D.; Gao, Z.; Jiang, K. A significant cathodic shift in the onset potential and enhanced photoelectrochemical water

- splitting using Au nanoparticles decorated WO₃ nanorod array. *Journal of Colloid and Interface Science* **2015**, *458*, 194-199.
179. Trzeciński, K.; Szkoda, M.; Sawczak, M.; Lisowska-Oleksiak, A.J.E. Enhanced Photoelectrocatalytical Performance of Inorganic-Inorganic Hybrid Consisting BiVO₄, V₂O₅, and Cobalt Hexacyanocobaltate as a Perspective Photoanode for Water Splitting. *Electrocatalysis* **2020**, *11*, 180-187.
 180. Hosseini, M.G.; Sefidi, P.Y.; Aydin, Z.; Kinayyigit, S. Toward enhancing the photoelectrochemical water splitting efficiency of organic acid doped polyaniline-WO₃ photoanode by photo-assisted electrochemically reduced graphene oxide. *Electrochimica Acta* **2020**, *333*, 135475.
 181. Moniz, S.J.; Bhachu, D.; Blackman, C.S.; Cross, A.J.; Elouali, S.; Pugh, D.; Cabrera, R.Q.; Vallejos, S. A novel route to Pt–Bi₂O₃ composite thin films and their application in photo-reduction of water. *Inorganica Chimica Acta* **2012**, *380*, 328-335.
 182. Hofmann, M.; Rößner, L.; Armbrüster, M.; Mehring, M. Thin Coatings of α - and β -Bi₂O₃ by Ultrasonic Spray Coating of a Molecular Bismuth Oxido Cluster and their Application for Photocatalytic Water Purification Under Visible Light. *ChemistryOpen* **2020**, *9*, 277.
 183. 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 & Environmental Science* **2011**, *4*, 5028-5034.
 184. Sánchez, O.A.; Rodríguez, J.L.; Barrera-Andrade, J.M.; Borja-Urby, R.; Valenzuela, M.A. High performance of Ag/BiVO₄ photocatalyst for 2, 4-Dichlorophenoxyacetic acid degradation under visible light. *Applied Catalysis A: General* **2020**, *600*, 117625.
 185. 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. *Electrochimica Acta* **2016**, *195*, 51-58.

186. Liu, S.; Pan, J.; Li, X.; Meng, X.; Yuan, H.; Li, Y.; Zhao, Y.; Wang, D.; Ma, J.; Zhu, S. In situ modification of BiVO₄ nanosheets on graphene for boosting photocatalytic water oxidation. *Nanoscale* **2020**, *12*, 14853-14862.
187. Tran, F.; Blaha, P. Accurate band gaps of semiconductors and insulators with a semilocal exchange-correlation potential. *Physical review letters* **2009**, *102*, 226401.
188. Shewale, P.; Agawane, G.; Shin, S.; Moholkar, A.; Lee, J.; Kim, J.; Uplane, M. Thickness dependent H₂S sensing properties of nanocrystalline ZnO thin films derived by advanced spray pyrolysis. *Sensors and Actuators B: Chemical* **2013**, *177*, 695-702.
189. Mohamedkhair, A.K.; Drmosh, Q.A.; Qamar, M.; Yamani, Z.H. Tuning Structural Properties of WO₃ Thin Films for Photoelectrocatalytic Water Oxidation. *Catalysts* **2021**, *11*, 381.
190. Polo, A.; Grigioni, I.; Magni, M.; Facibeni, A.; Dozzi, M.V.; Selli, E. Unravelling the bulk and interfacial charge transfer effects of molybdenum doping in BiVO₄ photoanodes. *Applied Surface Science* **2021**, *556*, 149759.
191. 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. *Journal of the American Chemical Society* **2012**, *134*, 2186-2192.
192. Bhat, S.S.; Jang, H.W. Recent advances in bismuth-based nanomaterials for photoelectrochemical water splitting. *ChemSusChem* **2017**, *10*, 3001-3018.
193. Xiao, J.; Fan, L.; Zhao, F.; Huang, Z.; Zhou, S.-F.; Zhan, G. Kinetic analysis of the synergistic effect of NaBH₄ treatment and Co-Pi coating on Fe₂O₃ photoanodes for photoelectrochemical water oxidation. *Journal of Catalysis* **2020**, *381*, 139-149.
194. Zhang, L.; Reisner, E.; Baumberg, J. Al-doped ZnO inverse opal networks as efficient electron collectors in BiVO₄ photoanodes for solar water oxidation. *Energy & Environmental Science* **2014**, *7*, 1402-1408.
195. Ahmed, A.Y.; Ahmed, M.G.; Kandiel, T.A. Hematite photoanodes with size-controlled nanoparticles for enhanced photoelectrochemical water oxidation. *Applied Catalysis B: Environmental* **2018**, *236*, 117-124.

196. Dey, K.K.; Gahlawat, S.; Ingole, P.P. BiVO₄ optimized to nano-worm morphology for enhanced activity towards photoelectrochemical water splitting. *Journal of Materials Chemistry A* **2019**, *7*, 21207-21221.
197. Mohite, S.; Rajpure, K. Oxidative degradation of salicylic acid by sprayed WO₃ photocatalyst. *Materials Science and Engineering: B* **2015**, *200*, 78-83.
198. Dongale, T.; Mohite, S.; Bagade, A.; Kamat, R.; Rajpure, K. Bio-mimicking the synaptic weights, analog memory, and forgetting effect using spray deposited WO₃ memristor device. *Microelectronic Engineering* **2017**, *183*, 12-18.
199. Tokunaga, S.; Kato, H.; Kudo, A. Selective preparation of monoclinic and tetragonal BiVO₄ with scheelite structure and their photocatalytic properties. *Chemistry of Materials* **2001**, *13*, 4624-4628.
200. Zeng, Q.; Li, J.; Li, L.; Bai, J.; Xia, L.; Zhou, B. Synthesis of WO₃/BiVO₄ photoanode using a reaction of bismuth nitrate with peroxovanadate on WO₃ film for efficient photoelectrocatalytic water splitting and organic pollutant degradation. *Applied Catalysis B: Environmental* **2017**, *217*, 21-29.
201. Sun, H.; Hua, W.; Li, Y.; Wang, J.-G. Promoting photoelectrochemical activity and stability of WO₃/BiVO₄ heterojunctions by coating a tannin nickel iron complex. *ACS Sustainable Chemistry & Engineering* **2020**, *8*, 12637-12645.
202. Pyper, K.J.; Yourey, J.E.; Bartlett, B.M. Reactivity of CuWO₄ in photoelectrochemical water oxidation is dictated by a midgap electronic state. *The Journal of Physical Chemistry C* **2013**, *117*, 24726-24732.
203. Kahn, A. Fermi level, work function and vacuum level. *Materials Horizons* **2016**, *3*, 7-10.
204. Lee, M.G.; Sohn, W.; Moon, C.W.; Park, H.; Lee, S.; Jang, H.W. Conformally coated BiVO₄ nanodots on porosity-controlled WO₃ nanorods as highly efficient type II heterojunction photoanodes for water oxidation. *Nano Energy* **2016**, *28*, 250-260.
205. Ma, Z.; Song, K.; Wang, L.; Gao, F.; Tang, B.; Hou, H.; Yang, W. WO₃/BiVO₄ type-II heterojunction arrays decorated with oxygen-deficient ZnO passivation layer: a highly efficient and stable photoanode. *ACS applied materials & interfaces* **2018**, *11*, 889-897.

VITAE

Name: Amar Kamal Mohamedkhair Salih

Nationality: Sudanese

Date of Birth: 5/10/1991

Email: amarkmks@gmail.com

Address: Khartoum, Sudan

Academic Background: **Ph.D. (Physics)**
December 2021,
King Fahd University of Petroleum & Minerals,
Dhahran, Saudi Arabia.

M.Sc. (Physics)
May 2017,
King Fahd University of Petroleum & Minerals,
Dhahran, Saudi Arabia.

B.Sc. (Physics)
September 2012,
Sudan University of Science and Technology,
Khartoum, Sudan.

LIST OF PUBLICATIONS AND PATENTS

- **Growth of Co-Pi modified BiVO₄/WO₃ heterostructure photoanode for photoelectrochemical water oxidation (under progress)**
- **Pinhole-free Co-Pi /BiVO₄ thin film with interparticle porosity for improved photoelectrochemical water oxidation (submitted)**
- **Oxygen-Deficient Non-Crystalline Tungsten Oxide Thin Films for Solar-Driven Water Oxidation.** "Khan, A., Al-Muhaish, N., Mohamedkhair, A. K., Khan, M. Y., Qamar, M., Yamani, Z. H., & Drmash, Q. A. (2022). Oxygen-deficient non-crystalline tungsten oxide thin films for solar-driven water oxidation. Journal of Non-Crystalline Solids, 580, 121409"
- **Post-annealing effect on the electrochemical behavior of nanostructured magnetron sputtered W₃O films in chloride-and acid-containing environments."** Surface and Coatings Technology (2021): 127334. Adesina, Akeem Y., Q. A. Drmash, A. Madhan Kumar, and Amar K. Mohamedkhair. "
- **Plasmonic Pollen Grain Nanostructures: A Three-Dimensional Surface-Enhanced Raman Scattering (SERS)-Active Substrate."** Chemistry–An Asian Journal (2021). Drmash, Q. A., Mohammad Kamal Hossain, and Amar Kamal Mohamedkhair. "
- **Engineering the depletion layer of Au-modified ZnO/Ag core-shell films for high-performance acetone gas sensing."** Sensors and Actuators B: Chemical 338 (2021): 129851. Drmash, Q. A., Yousif Ahmed Al Wajih, Ibrahim Olanrewaju Alade, A. K. Mohamedkhair, Mohammad Qamar, Abbas Saeed Hakeem, and Z. H. Yamani. "
- **Nitrogen enriched carbon derived from albizia procera leaves.** U.S. Patent Application 16/582,748 (2021). Aziz, M.A., Mohamedkhair, A.K. and Yamani, Z.H.,
- **Tuning Structural Properties of WO₃ Thin Films for Photoelectrocatalytic Water Oxidation."** Catalysts 11, no. 3 (2021): 381. Mohamedkhair, Amar Kamal, Qasem Ahmed Drmash, Mohammad Qamar, and Zain Hassan Yamani. "
- **Fabrication and Characterization of Transparent and Scratch-Proof Yttrium/Sialon Thin Films."** Nanomaterials 10, no. 11 (2020): 2283. Mohamedkhair, Amar Kamal, Abbas Saeed Hakeem, Qasem Ahmed Drmash, Abdul Samad Mohammed, Mirza Murtuza Ali Baig, Anwar Ul-Hamid, Mohammed Ashraf Gondal, and Zain Hassan Yamani. "

- **Effect of an activating agent on the physicochemical properties and supercapacitor performance of naturally nitrogen-enriched carbon derived from *Albizia procera* leaves.**" Arabian Journal of Chemistry 13, no. 7 (2020): 6161-6173. Mohamedkhair, Amar K., Md Abdul Aziz, Syed Shaheen Shah, M. Nasiruzzaman Shaikh, Anas Karrar Jamil, Mohammed Ameen Ahmed Qasem, Ismail A. Buliyaminu, and Zain H. Yamani. "
- **Nanostructured Magnéli-Phase $W_{18}O_{49}$ Thin Films for Photoelectrochemical Water Splitting.**" Catalysts 10, no. 5 (2020): 526. Mohamedkhair, A. K., Q. A. Drmosh, Mohammad Qamar, and Z. H. Yamani. "
- **Preparation of nano- Co_3O_4 -coated *Albizia procera*-derived carbon by direct thermal decomposition method for electrochemical water oxidation.**" Arabian Journal of Chemistry 13, no. 3 (2020): 4785-4796. Buliyaminu, Ismail A., Md Abdul Aziz, Syed Shaheen Shah, A. K. Mohamedkhair, and Zain H. Yamani. "
- **Preparation and characterization of manganese oxide nanoparticles-coated *Albizia procera* derived carbon for electrochemical water oxidation.**" Journal of Materials Science: Materials in Electronics 30, no. 17 (2019): 16087-16098. Shah, Syed Shaheen, Md Abdul Aziz, Amar Kamal Mohamedkhair, Mohammed Ameen Ahmed Qasem, Abbas Saeed Hakeem, Mazen Khaled Nazal, and Zain Hasan Yamani"
- **Silver Nanoparticle-Decorated Tin Oxide Thin Films: Synthesis, Characterization, and Hydrogen Gas Sensing.**" Frontiers in materials 6 (2019): 188. Mohamedkhair, Amar K., Qasem Ahmed Drmosh, and Zain H. Yamani. "
- **Room temperature hydrogen gas sensor.**" U.S. Patent Application 15/970,575, filed November 7, 2019. Drmosh, Qasem Ahmed, Zain Hassan Yamani, Amar Kamal Mohamedkhair, and Abdulmajeed Hasan Hendi. "
- **Room temperature nitrogen dioxide gas sensor.**" U.S. Patent Application 16/000,438, filed December 5, 2019. Drmosh, Qasem Ahmed, Zain Hassan Yamani, Amar Kamal Mohamedkhair, Abdulmajeed Hasan Hendi, Mohammad Kamal Hossain, and Abdullatif Mohammed Albaser. "
- **Gold nanoparticles incorporated SnO_2 thin film: highly responsive and selective detection of NO_2 at room temperature.**" Materials Letters 214 (2018): 283-286. Drmosh, Q. A., Z. H. Yamani, A. K. Mohamedkhair, A. H. Y. Hendi, M. K. Hossain, and Ahmed Ibrahim. "
- **Room-temperature detection of hydrogen by platinum-decorated tin oxide thin films augmented by heat-treatment.**" Vacuum 156 (2018): 68-77. Drmosh, Q. A., Z. H. Yamani, A. K. Mohamedkhair, A. H. Y. Hendi, and Ahmed Ibrahim. "