

HIGH TRANSMITTANCE-n-TiO₂/ZnO BILAYER DEPOSITED BY SOL-GEL
SPIN COATING METHOD FOR ELECTRODEPOSITED-p-Cu₂O BASED
HETEROJUNCTION THIN FILM SOLAR CELL

NURLIYANA BINTI MOHAMAD ARIFIN

A thesis submitted in
fulfillment of requirement for the award of the
Doctor of Philosophy in Electrical Engineering



Faculty of Electrical and Electronic Engineering
Universiti Tun Hussein Onn Malaysia

JANUARY 2023

DEDICATION

Every challenging work need self-efforts as well as guidance of elders especially those who very close to our hearts. My humble effort I dedicate to

*My dearest husband,
Muhammad Sallehudin Bin Khalid,
Thank you for allowing me to pursue my dream.*

*My sweetheart daughter,
Nur Aisyah Wafiy Binti Muhammad Sallehudin,
Thank you for being the strength of Ummi's heart*

*My beloved mother and father,
Rahamah Binti Sumani and Mohamad Arifin Bin Sirat
For affection, love, encouragement and prays of days and nights,
Always there when thick and thin,
And this is for you, Mak and Abah.*

Alhamdulillah. Thank you.

ACKNOWLEDGMENT

In the name of Allah, the Most Gracious and the Most Merciful

Alhamdulillah, all praises to Allah for the strengths and His blessing in completing this thesis. I would like to express my gratitude and appreciation to all those who gave me the opportunity to complete this thesis. A special thanks to my project supervisor, Prof. Madya. Dr. Fariza Binti Mohamad and my co-supervisor, Prof. Madya. Ts. Dr. Rosniza Binti Hussin, whose give a lot of guidance's during coordinating my project especially in experiment and maintains project's progress in track.

I would also like to acknowledge with much appreciation to the crucial of staff of Microelectronic and Nanotechnology Shamsuddin Research Centre (MiNT-SRC), who gave the permission to use all the required machinery and the necessary material to complete the project. Thanks also to lecturers as well as the panels especially in my project presentation that has improved my presentation skill by their comment and tips.

Last but not least, my deepest gratitude goes to all my friends for their kindness and moral support during my study. To those who indirectly contributed in this project, all of your kindness means a lot to me. Thank you very much.

ABSTRACT

Metal oxide semiconductor heterojunction are gaining interest in current fundamental photovoltaic research. Copper oxide (Cu_2O) based heterojunction which consists of p- Cu_2O and n-Titanium dioxide (TiO_2) have been spotted as a potential window and absorbing layer, respectively. However, n- TiO_2 suffers low utilization in solar spectrum and high recombination rate of electron and holes. By coupling TiO_2 and Zinc oxide (ZnO) thin film, the layers are known as n- TiO_2/ZnO bilayer thin film which can enhance utilization of solar spectrum as a window layer. Due to low lattice mismatch between ZnO and Cu_2O , high crystal structure with (002) $\text{ZnO}/(111)\text{Cu}_2\text{O}$ preferred orientation plane is essential to improve the heterointerface layer. Both combination layers exhibited a similar atomic arrangement at the interface due to the crystal structure of n- ZnO and p- Cu_2O are hexagonal wurtzite and cubic, respectively. Herein, n- $\text{TiO}_2/\text{ZnO}/\text{p-Cu}_2\text{O}$ heterojunction thin film was successfully fabricated onto FTO substrate by using sol-gel spin coating and electrodeposition method. Annealing treatment affected process in fabricating n- TiO_2/ZnO bilayer thin film with different annealing temperature and time. Meanwhile, cyclic voltammetry was executed to obtain the most optimized parameter before p- Cu_2O stacking onto n- TiO_2/ZnO bilayer thin film with different bath temperature and deposition time. Based on the findings, the preferred (002)- ZnO orientation plane of thin film appeared at 34.28° in n- TiO_2/ZnO bilayer thin film when annealed for 2 hours at 500°C . High transmittance of n- TiO_2/ZnO bilayer thin film was achieved up to 80% at the edge of the visible light spectrum in the range of 450-300 nm. High crystal structure and absorbance spectrum of p- Cu_2O as absorbing layer was observed at bath temperature 40°C for 1.5 hours. P-n junction was successfully formed as indicated by significant electrical rectification properties with conversion efficiency of 0.0615%. The results prove the homogeneity, high transmittance and crystallinity of n- $\text{TiO}_2/\text{ZnO}/\text{p-Cu}_2\text{O}$ heterojunction thin film aside from enhancing the surface structure and atomic arrangement at its heterointerface which will be beneficial for solar cell application.

ABSTRAK

Semikonduktor oksida logam hetero-simpang kini menjadi minat dalam asas penyelidikan fotovoltaik. Kuprum oksida (Cu_2O) hetero-simpang terdiri dari p- Cu_2O dan n-Titanium dioksida (TiO_2) berpotensi menjadi lapisan tingkap and penyerap. Walaupun begitu, n- TiO_2 mengalami kekurangan penggunaan spektrum suria dan tinggi kadar penggabungan semula elektron dan lubang. Penggabungan TiO_2 dan Zink oksida (ZnO) saput nipis, lapisan dikenali sebagai n- TiO_2/ZnO dwilapisan saput nipis mampu meningkatkan penggunaan spektrum suria sebagai lapisan tingkap. Disebabkan tiada kesepadanan kekisi antara ZnO dan Cu_2O rendah, struktur hablur yang tinggi dengan satah orientasi pilihan (002) $\text{ZnO}/(111)\text{Cu}_2\text{O}$ adalah penting untuk meningkatkan hetero-antara muka. Gabungan dua lapisan itu mempamerkan susunan atom yang serupa kerana struktur hablur n- ZnO adalah wurtzit heksagon dan p- Cu_2O adalah kubus. Di sini, n- $\text{TiO}_2/\text{ZnO}/\text{p-Cu}_2\text{O}$ hetero-simpang saput nipis telah berjaya difabrik pada substrat FTO dengan menggunakan kaedah salutan mejam sol-gel dan elektromendapan. Penyepuhlindapan berperanan menghasilkan n- TiO_2/ZnO dwilapisan saput nipis dengan suhu dan masa penyepuhlindapan yang berbeza. Sementara itu, voltammetri berkitar dilaksanakan untuk mendapatkan parameter yang paling sesuai sebelum p- Cu_2O difabrik pada n- TiO_2/ZnO dwilapisan saput nipis dengan suhu dan masa pemendapan berbeza. Berdasarkan penemuan, satah orientasi (002)- ZnO muncul pada 34.28° dalam n- TiO_2/ZnO dwilapisan saput nipis apabila disepuhlindapan selama 2 jam pada 500°C . Kepancaran tinggi n- TiO_2/ZnO dwilapisan saput nipis dicapai sehingga 80% pada pinggir spektrum cahaya dalam julat 450-300 nm. Struktur hablur tinggi dan spektrum penyerapan p- Cu_2O sebagai lapisan penyerap diperhatikan pada suhu 40°C selama 1.5 jam. Simpang p-n berjaya dibentuk melalui sifat elektrik yang bererti dengan kecekapan penukaran sebanyak 0.0615%. Hasil menunjukkan homogen, pancaran yang tinggi dan kehabluran n- $\text{TiO}_2/\text{ZnO}/\text{p-Cu}_2\text{O}$ hetero-simpang saput nipis selain dapat mempertingkatkan struktur permukaan dan susunan atom serta bermanfaat untuk aplikasi sel suria.

CONTENTS

TITLE	i
DECLARATION	ii
DEDICATION	iii
ACKNOWLEDGMENT	iv
ABSTRACT	v
ABSTRAK	vi
CONTENTS	vii
LIST OF TABLES	xii
LIST OF FIGURES	xiv
LIST OF SYMBOLS AND ABBREVIATIONS	xxi
LIST OF APPENDICES	xxiv
 CHAPTER 1 INTRODUCTION	
1.1 Project overview	1
1.2 Problem statement	5
1.3 Research objectives	6
1.4 Scope and limitations	7
1.5 Research contribution	8
1.6 Thesis layout	8
 CHAPTER 2 LITERATURE REVIEW	
2.1 Thin film photovoltaic (PV) solar cell	10

2.1.1 Materials of thin film	12
2.2 Copper oxide (Cu_2O)	13
2.2.1 Cu_2O based homojunction thin film	14
2.2.2 Cu_2O based heterojunction thin film	15
2.3 Titanium dioxide (TiO_2)	16
2.4 Zinc oxide (ZnO)	17
2.5 TiO_2/ZnO bilayer thin film	18
2.5.1 Sol-gel spin coating method	21
2.6 $\text{ZnO}/\text{Cu}_2\text{O}$ heterojunction thin film	23
2.6.1 Electrodeposition method	28
2.7 Substrate used for fabrication of thin films	30
2.8 Cyclic Voltammetry (CV) measurement	30
2.9 Conversion efficiency of heterojunction thin film	31
2.10 Summary of chapter 2	35
CHAPTER 3 METHODOLOGY	
3.1 Fabrication of n- TiO_2/ZnO bilayer/p- Cu_2O heterojunction thin film	37
3.2 Fabrication of n- TiO_2/ZnO bilayer onto FTO coated glass substrate	41
3.2.1 Solution preparation of TiO_2 and ZnO	42
3.2.2 FTO substrate preparation	43
3.2.3 Sol-gel spin coating method process	44
3.2.4 Annealing process	45
3.3 Cyclic Voltammetry (CV) measurement of p- Cu_2O thin film onto n- TiO_2/ZnO bilayer thin film	46
3.4 Fabrication of p- Cu_2O thin film onto n- TiO_2/ZnO bilayer thin film	47

3.4.1 Solution preparation of Cu ₂ O	47
3.4.2 Substrate preparation of n-TiO ₂ /ZnO bilayer thin film	48
3.4.3 Electrodeposition method process	49
3.5 Characterization of thin film	50
3.5.1 Structural properties	50
3.5.2 Morphological properties	51
3.5.3 Optical properties	53
3.5.4 Topological properties	54
3.5.5 Electrical properties	55
3.5.6 Thickness measurement	56
3.6 Summary of chapter 3	57
CHAPTER 4 RESULTS AND DISCUSSIONS	
4.1 Fabrication of n-TiO ₂ thin film onto FTO substrate	58
4.1.1 Optimization of annealing temperature for n-TiO ₂ /FTO substrate	59
4.1.1.1 Structural properties	59
4.1.1.2 Optical properties	62
4.1.2 Optimization of annealing time for n-TiO ₂ /FTO substrate	62
4.1.2.1 Structural properties	63
4.1.2.2 Morphological properties	64
4.1.2.3 Optical properties	65
4.1.3 Summary	67
4.2 Fabrication of n-ZnO thin film onto n-TiO ₂ /FTO substrate (n-TiO ₂ /ZnO bilayer thin film)	67
4.2.1 Optimization of annealing temperature for n-ZnO thin film onto n-TiO ₂ /FTO substrate	68

4.2.1.1 Structural properties	68
4.2.1.2 Morphological properties	71
4.2.1.3 Optical properties	74
4.2.2 Optimization of annealing time for n-ZnO thin film onto n-TiO ₂ /FTO substrate	75
4.2.2.1 Structural properties	76
4.2.2.2 Morphology properties	77
4.2.2.3 Optical properties	80
4.2.3 Summary	82
4.3 Fabrication of p-Cu ₂ O thin film onto n-TiO ₂ /ZnO bilayer thin films (n-TiO ₂ /ZnO bilayer/p-Cu ₂ O heterojunction thin films	82
4.3.1 Cyclic voltammetry measurement for p-Cu ₂ O onto n-TiO ₂ /ZnO bilayer thin films	83
4.3.2 Optimization of bath temperature for p-Cu ₂ O thin film onto n-TiO ₂ /ZnO bilayer thin films	86
4.3.2.1 Structural properties	86
4.3.2.2 Morphological properties	89
4.3.2.3 Optical properties	92
4.3.3 Optimization of deposition time for p-Cu ₂ O thin film onto n-TiO ₂ /ZnO bilayer thin films	94
4.3.3.1 Structural properties	94
4.3.3.2 Morphological properties	95
4.3.3.3 Optical properties	99
4.3.3.4 Topological properties	101
4.3.4 Electrical properties of n-TiO ₂ /ZnO bilayer/p-Cu ₂ O heterojunction thin films	103
4.3.5 Summary	105
4.4 Summary of chapter 4	106

CHAPTER 5 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion	107
5.2 Recommendations	110
REFERENCES	111
APPENDICES	123



LIST OF TABLES

2.1	Summary of fabrication for n-TiO ₂ /p-Cu ₂ O bilayer thin film	16
2.2	Summary of fabrication for n-TiO ₂ /ZnO bilayer thin film	21
2.3	Summary of fabrication for ZnO/Cu ₂ O heterojunction thin film	28
2.4	Summary of conversion efficiency for TiO ₂ /Cu ₂ O heterojunction thin film	33
2.5	Summary of conversion efficiency for ZnO/Cu ₂ O heterojunction thin film	35
2.6	Summary on subtopic in literature review	37
3.1	The variation of experiment's parameters	40
3.2	Concentration and ratio of chemicals used for TiO ₂ solution	42
3.3	Concentration and ratio of chemicals used for ZnO solution	43
3.4	Concentration of chemicals used for Cu ₂ O solution	48
4.1	Fixed parameters used of the sample	59
4.2	Different annealing temperatures on n-TiO ₂ /FTO substrate for 30 minutes	60
4.3	Different annealing temperatures on n-TiO ₂ /FTO substrates for 1 hour	61
4.4	Different annealing time and FWHM for n-TiO ₂ /FTO substrate at 600°C	63
4.5	Different annealing temperatures on n-TiO ₂ /ZnO bilayer thin films for 1 hour	69
4.6	Different annealing temperatures on n-type TiO ₂ /ZnO bilayer thin films for 2 hours	70
4.7	Different annealing times for n-TiO ₂ /ZnO bilayer thin films at 500°C	77

4.8	Reduction reactions from the CV measurement for n-TiO ₂ /ZnO bilayer thin films with p-Cu ₂ O solution at different bath temperatures	84
4.9	Different deposition temperatures for p-Cu ₂ O onto n-TiO ₂ /ZnO bilayer thin films	87
4.10	Different deposition temperatures for p-type Cu ₂ O onto n-type TiO ₂ /ZnO bilayer thin films	89
4.11	Different deposition times for p-Cu ₂ O deposited at 40 °C onto n-TiO ₂ /ZnO bilayer thin films	95
4.12	The average roughness of n-TiO ₂ /ZnO bilayer/p-Cu ₂ O heterojunction thin films corresponding deposition time	102
5.1	Summary on enhancements to achieve the objectives	109



PTTA AUTHM
PERPUSTAKAAN TUNKU TUN AMINAH

LIST OF FIGURES

1.1	Photovoltaic technology status and prospect [5]	2
2.1	Illustration of semiconductor thin film photovoltaic cell [45]	11
2.2	Crystal structure of copper oxide (Cu_2O) [49]	14
2.3	Crystal structure of TiO_2 (a) anatase, (b) rutile and (c) brookite [62]	17
2.4	Crystal structure of ZnO [64]	18
2.5	Schematic diagrams of band alignmnet and charge recombination in the cells with (a) TiO_2 or ZnO single layer and (b) TiO_2/ZnO bilayer (c) ZnO/TiO_2 bilayer as the compact layer, respectively [38]	19
2.6	Illustration of spin coater [72]	22
2.7	Atomic structure of hexagonal wurtzite for ZnO and cubic for Cu_2O [74]	23
2.8	Orientation plane in the atomic structure of ZnO and Cu_2O [75]	24
2.9	Illustration of atomic arrangements for (a) hexagonal (002)- ZnO and (b) (111)- Cu_2O orientation plane [74].	25
2.10	Illustrations of (a) right-angle triangle in cubic structure, (b) hard sphere model for Cu_2O (111)-orientation plane and (c) face diagonal in cubic structure [79]	26
2.11	Illustration of different lattice parameters of (002) ZnO and (111) Cu_2O orientation planes	26
2.12	Illustration of three electrodes in an electrodeposition system [43]	29
2.13	Cyclic voltammetry for Cu_2O depositions in electrolyte bath of pH 12.5 at 60 °C [91]	31
3.1	Flowchart for fabrication of n- TiO_2/ZnO bilayer/p- Cu_2O heterojunction thin films	39
3.2	Illustration of fabrication layer for (a) n- TiO_2/ZnO bilayer onto FTO substrate and (b) n- TiO_2/ZnO bilayer/p- Cu_2O heterojunction thin film	40

3.3	Flowchart for fabrication of n-TiO ₂ /ZnO bilayer thin film onto FTO substrate	41
3.4	Chemical used to prepare TiO ₂ solution (a) titanium (IV) butoxide, (b) n-butanol and (c) acetic acid glacial	42
3.5	Chemical used to prepare ZnO solution (a) zinc acetate, (b) iso-propyl alcohol and (c) diethanolamine (DEA)	43
3.6	a) FTO glass substrate with dimension of 2.5 cm x 1.5 cm and (b) Masked FTO substrate	44
3.7	(a) Spin coating process and (b) pre-heated process for deposition of n-TiO ₂ /ZnO bilayer thin films	45
3.8	(a) Sample was placed on alumina before annealing process and (b) Protherm furnace used to anneal n-TiO ₂ /ZnO bilayer thin film	45
3.9	Annealing temperature profile	46
3.10	Flowchart for the stacking of p-Cu ₂ O layer onto n-TiO ₂ /ZnO bilayer thin film	47
3.11	Chemicals used to prepare copper acetate-based solution (a) Copper (II) acetate monohydrate; (b) Lactic acid; (c) Potassium hydroxide	48
3.12	Masked FTO substrate with deposition area of 1 cm x 1 cm	49
3.13	Electrodeposition set up for p-Cu ₂ O deposition onto TiO ₂ /ZnO bilayer thin film	49
3.14	X-Ray Diffraction (XRD) Spectroscopy located at MiNT- SRC, UTHM	51
3.15	Field Emission-Scanning Electron Microscopy (FE-SEM) located at MiNT-SRC, UTHM	52
3.16	Illustration of sample stage for FE-SEM observation	52
3.17	The control panel of (a) sample stage and (b) operation stage, respectively	53
3.18	UV-Vis Absorption Spectroscopy located at MiNT- SRC, UTHM	54
3.19	(a) Sample compartment and (b) illustration of the operation of UV-Vis Absorption Spectroscopy	54
3.20	Atomic Force Microscopy located at MiNT-SRC, UTHM	55
3.21	Solar simulator located at MiNT- SRC, UTHM	55
3.22	Surface Profiler located at MiNT- SRC, UTHM	57

3.23 Illustration of thickness measurement concept by using Surface Profiler	57
4.1 The XRD patterns of (a) FTO, (b) as-deposited n-TiO ₂ /FTO, n-TiO ₂ /FTO substrate annealed at (c) 400 °C, (d) 500 °C and 600 °C for 30 minutes, respectively	60
4.2 The XRD patterns of (a) FTO, (b) as deposited n-TiO ₂ /FTO substrate, n-TiO ₂ /FTO substrate annealed at (c) 400 °C, (d) 500 °C and I 600 °C for 1 hour, respectively	61
4.3 The transmittance spectrum of n-TiO ₂ /FTO substrate annealed for 1 hour at (a) 400 °C, (b) 500 °C, (c) 600 °C, respectively	62
4.4 The XRD patterns of (a) FTO, (b) as-deposited n-TiO ₂ /FTO substrate, n-TiO ₂ /FTO substrate annealed at 600 °C for (c) 30 minutes, (d) 1 hour and (e) 2 hours, respectively	64
4.5 Top view images of n-TiO ₂ /FTO substrates annealed at 600 °C for (a) 1 hour, (b) 2 hours and (c) cross-sectional image of n-TiO ₂ /FTO substrate annealed at 600 °C for 1 hour	65
4.6 The transmittance spectrum of n-TiO ₂ /FTO substrate annealed at 600 °C for (a) 30 minutes, (b) 1 hour and (c) 2 hours, respectively	66
4.7 The extrapolated band gap for n-TiO ₂ /FTO substrate annealed for 1 hour at 600 °C	67
4.8 The XRD patterns of (a) n-TiO ₂ /FTO substrate annealed at 600 °C and n-TiO ₂ /ZnO bilayer thin film annealed at (b) 400 °C (c) 500 °C, (d) 600 °C for 1 hour, respectively	69
4.9 The XRD patterns of (a) TiO ₂ /FTO substrate annealed at 600 °C for 1 hour and n-TiO ₂ /ZnO bilayer thin films annealed at (b) 400 °C, (c) 500 °C, (d) 600 °C for 2 hours, respectively	70
4.10 Top view images of TiO ₂ /ZnO bilayer thin films annealed at 400 °C for 1 hour under magnifications of (a) 50,000x and (b) 100,000x	71
4.11 Top view images of TiO ₂ /ZnO bilayer thin films annealed at 500 °C for 1 hour under magnifications of (a) 50,000x and (b) 100,000x	72
4.12 Top view images of TiO ₂ /ZnO bilayer thin films annealed at 600 °C for 1 hour under magnifications of (a) 50,000x and (b) 100,000x	72

4.13	Top view images of TiO ₂ /ZnO bilayer thin films annealed at 400 °C for 2 hours under magnifications of (a) 50,000x and (b) 100,000x	73
4.14	Top view images of TiO ₂ /ZnO bilayer thin films annealed at 500 °C for 2 hours under magnifications of (a) 50,000x and (b) 100,000x	73
4.15	Top view images of TiO ₂ /ZnO bilayer thin films annealed at 600 °C for 2 hours under magnifications of (a) 50,000x and (b) 100,000x	73
4.16	The transmittance spectrum of n-TiO ₂ /ZnO bilayer thin films annealed at (a) 400 °C, (b) 500 °C, (c) 600 °C for 1 hour, respectively	74
4.17	The transmittance spectrum of n-TiO ₂ /ZnO bilayer thin films annealed at (a) 400 °C, (b) 500 °C, (c) 600 °C for 2 hours, respectively	75
4.18	The XRD patterns for (a) n-TiO ₂ /FTO substrate annealed at 600 °C for 1 hour, n-TiO ₂ /ZnO bilayer thin films annealed at 500 °C for (b) 1 hour, (c) 1.5 hours, (d) 2 hours and (e) 2.5 hours	77
4.19	Top view images of TiO ₂ /ZnO bilayer thin film annealed at 500 °C for 1 hour under magnifications of (a) 50,000x and (b) 100,000x	78
4.20	Top view images of TiO ₂ /ZnO bilayer thin film annealed at 500 °C for 1.5 hours under magnifications of (a) 50,000x and (b) 100,000x	78
4.21	Top view images of TiO ₂ /ZnO bilayer thin film annealed at 500 °C for 2 hours under magnifications of (a) 50,000x and (b) 100,000x	79
4.22	Top view images of TiO ₂ /ZnO bilayer thin film annealed at 500 °C for 2.5 hours under magnifications of (a) 50,000x and (b) 100,000x	79
4.23	Cross-sectional images of n-TiO ₂ /ZnO bilayer thin films annealed at 500 °C for (a) 1 hour, (b) 1.5 hours, (c) 2 hours and (b) 2.5 hours	80
4.24	The transmittance spectrum of (a) n-TiO ₂ /FTO substrate and n-TiO ₂ /ZnO bilayer thin films annealed for (b) 1 hour (c) 1.5 hour (d) 2 hours and (e) 2.5 hours at 500 °C, respectively	81
4.25	The extrapolated band gap for n-TiO ₂ /ZnO bilayer thin film annealed for 2 hours at 500 °C	81
4.26	Cyclic voltammetry for deposition of p-Cu ₂ O onto n-TiO ₂ /ZnO bilayer thin film at 30 °C	84

4.27	Cyclic voltammetry for deposition of p-Cu ₂ O onto n-TiO ₂ /ZnO bilayer thin film at 40 °C	85
4.28	Cyclic voltammetry for deposition of p-Cu ₂ O on n-TiO ₂ /ZnO bilayer thin film at 50 °C	85
4.29	Cyclic voltammetry for deposition of p-Cu ₂ O on n-TiO ₂ /ZnO bilayer thin film at 60 °C	86
4.30	The XRD patterns showed for (a) n-TiO ₂ /ZnO bilayer thin film, n-TiO ₂ /ZnO/p-Cu ₂ O heterojunction thin films deposited for 1 hour at bath temperature of (b) 30 °C (c) 40 °C and (d) 50 °C, respectively	87
4.31	The XRD patterns showed for (a) n-TiO ₂ /ZnO bilayer thin film, n-TiO ₂ /ZnO/p-Cu ₂ O heterojunction thin films deposited for 2 hours at bath temperature of (b) 30 °C, (c) 40 °C and (d) 50 °C, respectively	88
4.32	Top-view images of n-TiO ₂ /ZnO/p-Cu ₂ O heterojunction thin film deposited at bath temperature of 30 °C for 1 hour under magnifications of (a) 10,000x and (b) 25,000x	90
4.33	Top-view images of n-TiO ₂ /ZnO/p-Cu ₂ O heterojunction thin film deposited at bath temperature of 40 °C for 1 hour under magnification of (a) 5,000x and (b) 10,000x	90
4.34	Top-view images of n-TiO ₂ /ZnO/p-Cu ₂ O heterojunction thin film deposited at bath temperature of 50 °C for 1 hour under magnifications of(a) 5,000x and (b) 10,000x	90
4.35	Different top-view images of n-TiO ₂ /ZnO/p-Cu ₂ O heterojunction thin film deposited at bath temperature of (a) 30, (b) 40, (c) 50 °C for 1 hour	91
4.36	Top-view images of n-TiO ₂ /ZnO/p-Cu ₂ O heterojunction thin film deposited for 2 hours at bath temperature of 30 °C under magnifications of (a) 5,000x and (b) 10,000x	91
4.37	Top-view images of n-TiO ₂ /ZnO/p-Cu ₂ O heterojunction thin film deposited for 2 hours at bath temperature of 40 °C under magnifications of (a) 5,000x and (b) 10,000x	92
4.38	Top-view images of n-TiO ₂ /ZnO/p-Cu ₂ O heterojunction thin film deposited for 2 hours at bath temperature of 50 °C under magnifications of (a) 5,000x and (b) 10,000x	92

4.39	The absorbance spectrum n-TiO ₂ /ZnO/p-Cu ₂ O heterojunction thin films deposited at bath temperatures of (a) 30 °C, (b) 40 °C and (e) 50 °C, respectively	93
4.40	The XRD patterns showed for (a) n-TiO ₂ /ZnO bilayer thin film, TiO ₂ /ZnO/p-Cu ₂ O heterojunction thin films deposited at bath temperature 40 °C for (b) 0.5, (c) 1, (d) 1.5 and (e) 2 hours, respectively	95
4.41	Top view images of n-TiO ₂ /ZnO/p-Cu ₂ O heterojunction thin film deposited at bath temperature of 40 °C for 30 minutes under magnifications of (a) 10,000x and (b) 25,000x	97
4.42	Top-view images of n-TiO ₂ /ZnO/p-Cu ₂ O heterojunction thin film deposited at bath temperature of 40 °C for 1 hour under magnifications of (a) 5,000x and (b) 10,000x	97
4.43	Top-view images of n-TiO ₂ /ZnO/p-Cu ₂ O heterojunction thin films deposited at bath temperature of 40 °C for 1.5 hours under magnifications of (a) 5,000x and (b) 10,000x	97
4.44	Top-view images of n-TiO ₂ /ZnO/p-Cu ₂ O heterojunction thin film deposited at bath temperature of 40 °C for 2 hours under magnifications of (a) 5,000x and (b) 10,000x	98
4.45	Cross-sectional images of stacked p-Cu ₂ O on n-TiO ₂ /ZnO bilayer thin films at bath temperature of 40 °C for (a) 0.5, (b) 1, (c) 1.5 and (d) 2 hours, respectively	99
4.46	The absorbance spectrum of n-TiO ₂ /ZnO bilayer/p-Cu ₂ O heterojunction thin films deposited at bath temperature 40 °C for (a) 0.5 (b) 1 (c) 1.5 and (d) 2 hours, respectively	100
4.47	The extrapolated band gap of n-TiO ₂ /ZnO bilayer/p-Cu ₂ O heterojunction thin film deposited at bath temperature 40 °C for 1.5 hours	101
4.48	The 3D and 2D images of the topological surface of p n-TiO ₂ /ZnO/p-Cu ₂ O heterojunction thin films deposited for (a) 0.5, (b) 1, (c) 1.5 and (d) 2 hours, respectively	102

4.49 I-V measurement of n-TiO₂/ZnO bilayer/p-Cu₂O heterojunction thin film (a) in the dark and (b) under illumination. The inset shows illustration of the device

105



PTTA UTHM
PERPUSTAKAAN TUNKU TUN AMINAH

LIST OF SYMBOLS AND ABBREVIATIONS

3D	-	Three dimensional
l_{Cu_2O}	-	Lattice parameter of Cu ₂ O
l_{ZnO}	-	Lattice parameter of ZnO
A	-	Surface area
AFM	-	Atomic Force Microscopy
Ag/AgCl	-	Silver/silver chloride
AZO	-	Zinc/Aluminium doped
bcc	-	Body-centered cubic
BiVO	-	Bismuth vanadate
Cds	-	Cadmium sulphide
CdTe	-	Cadmium telluride
CE	-	Counter electrode
CIGS	-	Copper Indium Gallium Selenide
cm	-	centimetre
CO ₂	-	Carbon dioxide
Cu	-	Copper
Cu ₂ O	-	Copper oxide
CV	-	Cyclic voltammetry
CZTS	-	Copper zinc tin sulphide
D ₂	-	Deuterium
DC	-	Direct current
DEA	-	Diethanolamine
E	-	Irradiance
E _g	-	Band gap
eV	-	Electron volt
fcc	-	Face-centered cubic

Fe_2O_3	-	Hematite
FE-SEM	-	Field Emission Scanning Electron Microscopy
FF	-	Fill factor
FTO	-	Fluorine doped tin oxide
FWHM	-	Half-width at full maximum
h	-	Planck constant
H_2O	-	Hydrogen
HCP	-	Close-pack hexagonal
IEA	-	International Energy Agency
I_{\max}	-	Maximum current
I_{sc}	-	Short circuit current
ITO	-	Indium tin oxide
I-V	-	Current-voltage
LSV	-	Linear Sweep Voltammetry
M	-	mol
mm	-	millimetre
MoO_3	-	molybdenum oxide
mV/s	-	Millivolt/seconds
nm	-	nanometre
pH	-	Potential of hydrogen
PLD	-	Pulsed laser deposition
P_{\max}	-	Maximum power point
Pt	-	Platinum
PV	-	Photovoltaic
RE	-	Reference electrode
RF	-	Radio Frequency
rpm	-	Revolutions per minutes
SiO	-	Silicon monoxide
SnO_2	-	Tin oxide
sso	-	Sample surface offset
TCO	-	Transparent Conducting Oxide
TiO_2	-	Titanium dioxide
UV	-	Ultra-violet

UV-Vis	-	Ultraviolet-Visible Absorption Spectroscopy
V _{max}	-	Maximum voltage
V _{oc}	-	Open circuit voltage
vs	-	versus
WD	-	Working distance
WE	-	Working electrode
WO ₃	-	Tungsten trioxide
XRD	-	X-Ray Diffraction
ZnO	-	Zinc oxide
ZnTiO ₃		Zinc Titanate
α	-	Absorbance spectra
α -Si	-	Amorphous silicon
η	-	Conversion efficiency
μm	-	micrometre



PTT AUTHM
PERPUSTAKAAN TUNKU TUN AMINAH

LIST OF APPENDICES

A	List of Publications	123
---	----------------------	-----



PTTA UTHM
PERPUSTAKAAN TUNKU TUN AMINAH

CHAPTER 1

INTRODUCTION

This chapter deliberated on the introduction of the project. It consists of several subtopics including project overview, problem statement, research objectives, scope and limitations as well as the research contribution of the project.

1.1 Project overview

According to International Energy Agency (IEA), renewable energy technologies seem to have started growing in 2017 and have been paid attention by various industries. Several modern renewable energy technologies have been established as mainstream and cost-competitive sources of energy such as hydropower, bioenergy, geothermal power, fossil fuels and solar. However, fossil fuels are still at the highest percentage of consumption at 79.5% of the total final energy consumption [1]. This had been a challenge to researchers and industries since fossil fuels are some of the major sources that can cause pollution by carbon dioxide (CO_2) emission. CO_2 is one of the gases that can cause climate change and rise global temperature. Based on the growing rate of fossil fuel consumption, the concentration of CO_2 is foreseen to reach a dangerous level at 750 ppm by 2050. Since there is no natural decomposition of CO_2 in the atmosphere, the pollution effect can take 500 to 2000 years to reduce [2]. Thus, modern renewable technologies have received attention including solar photovoltaics (PV) which undergo natural processes by using sun as the main source which is much more environmentally friendly [2].

Based on a roadmap technologies statistics conducted by IEA, crystalline silicon technologies represent 85% to 90% of PV modules performance at world

REFERENCES

- [1] D. Hales, *Renewables 2018 global status report*. 2018.
- [2] S. Lewis and G. Nocera, “Powering the planet : Chemical challenges in solar energy utilization,” *PNAS*, vol. 103, no. 43, 2006.
- [3] N. Binti Mohamad Arifin, F. Mohamad, C. Hui Ling, N. Binti Zinal, A.S. Binti Mohd Hanif, N.H.B. Muhd Nor, M. Izaki, “Growth mechanism of copper oxide fabricated by potentiostatic electrodeposition method,” *Mater. Sci. Forum*, vol. 890 MSF, pp. 303–307, 2017.
- [4] N. Tanaka, *Technology Roadmap Solar photovoltaic energy*. 2010.
- [5] N. Asim, K. Sopian, S. Ahmadi, K. Saeedfar, M.A. Alghoul, O. Saadatian, H. Z. Saleem, “A review on the role of materials science in solar cells,” *Renew. Sustain. Energy Rev.*, vol. 16, no. 8, pp. 5834–5847, 2012.
- [6] V. Avrutin, N. Izyumskaya, and H. Morkoç, “Semiconductor solar cells: Recent progress in terrestrial applications,” *Superlattices Microstruct.*, vol. 49, no. 4, pp. 337–364, Apr. 2011, doi: 10.1016/j.spmi.2010.12.011.
- [7] P. Paulson and V. Dutta, “Thin-Film Solar Cells: An Overview,” *Prog. Photovolt. Res. Appl.*, vol. 12, no. March, pp. 69–92, 2004, doi: 10.1002/pip.541.
- [8] K. L. Chopra, P. D. Paulson, and V. Dutta, “Thin-film solar cells: An overview,” *Prog. Photovoltaics Res. Appl.*, vol. 12, no. 2–3, pp. 69–92, 2004, doi: 10.1002/pip.541.
- [9] M. Pavan, S. Ruhle, A. Ginsburg, D. A. Keller, H-N Barad, P. M. Sberna, D. Nunes, R. Martins, A. Y, Anderson, A. Zaban, E. Forunato, “ TiO_2/Cu_2O all-oxide heterojunction solar cells produced by spray pyrolysis,” *Sol. Energy Mater. Sol. Cells*, vol. 132, pp. 549–556, 2015.
- [10] M. K. S. Bin Rafiq *et al.*, “WS₂: A New Window Layer Material for Solar Cell Application,” *Sci. Rep.*, vol. 10, no. 1, pp. 1–11, 2020, doi: 10.1038/s41598-020-57596-5.

- [11] F. Mohamad, N. M. Arifin, A. Z. M. Ismail, N. Ahmad, M. N. N. Hisyamudin, and M. Izaki, “Cu₂O-based homostructure fabricated by electrodeposition method,” *Acta Phys. Pol. A*, vol. 135, no. 5, pp. 911–914, 2019, doi: 10.12693/APhysPolA.135.911.
- [12] N. Mohamad, F. Mohamad, L. Sheng, A. Ismail, N.. Ahmad, N. Nor, M. Izaki, “Construction of Nanorod-TiO₂/p-Cu₂O Heterostructure Thin Films for Solar Cell Application,” *Int. J. Adv. Trends Comput. Sci. Eng.*, vol. 9, no. 1, pp. 304–310, 2020.
- [13] E. Güneri, F. Göde, M. Ari, and B. Saatçi, “The effect of Cu₂O layer on characteristic properties of n-CdS/p-Cu₂O heterojunction,” *J. Mol. Struct.*, vol. 1241, pp. 2–7, 2021, doi: 10.1016/j.molstruc.2021.130679.
- [14] M. Ma, E. Lei, Z. Dan, X. Ying, W. Xiangfeng, M. Yue, L. Zhifeng, “The p-n heterojunction of BiVO₄/Cu₂O was decorated by plasma Ag NPs for efficient photoelectrochemical degradation of Rhodamine B,” *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 633, no. September 2021.
- [15] M. I. Khan, K. A. Bhatti, R. Qindeel, L. G. Bousiakou, N. Alonizan, and Fazal-e-Aleem, “Investigations of the structural, morphological and electrical properties of multilayer ZnO/TiO₂ thin films, deposited by sol-gel technique,” *Results Phys.*, vol. 6, pp. 156–160, 2016, doi: 10.1016/j.rinp.2016.01.015.
- [16] M. I. Khan, S. Imran, Shahnawaz, M. Saleem, and S. Ur Rehman, “Annealing effect on the structural, morphological and electrical properties of TiO₂/ZnO bilayer thin films,” *Results Phys.*, vol. 8, pp. 249–252, 2018, doi: 10.1016/j.rinp.2017.12.030.
- [17] R. Hussin, K. L. Choy, and X. H. Hou, “Fabrication of multilayer ZnO/TiO₂/ZnO thin films with enhancement of optical properties by atomic layer deposition (ALD),” *Appl. Mech. Mater.*, vol. 465–466, pp. 916–921, 2014, doi: 10.4028/www.scientific.net/AMM.465-466.916.
- [18] Y. Z. Gu, H. L. Lu, Y. Geng, Z. Y. Ye, Y. Zhang, Q. Q. Sun, S. J. Ding, D. W. Zhang, “Optical and microstructural properties of ZnO/TiO₂ nanolaminates prepared by atomic layer deposition,” *Nanoscale Res. Lett.*, vol. 8, no. 1, pp. 1–5, 2013.
- [19] M. I. Khan, K. A. Bhatti, R. Qindeel, N. Alonizan, and H. S. Althobaiti, “Characterizations of multilayer ZnO thin films deposited by sol-gel spin coating technique,” *Results Phys.*, vol. 7, pp. 651–655, 2017, doi:

- 10.1016/j.rinp.2016.12.029.
- [20] I. Saurdi, M. H. Mamat, and M. Rusop, "Electrical and structural properties of ZnO/TiO₂ nanocomposite thin films by RF magnetron co-sputtering," *Adv. Mater. Res.*, vol. 667, pp. 206–212, 2013, doi: 10.4028/www.scientific.net/AMR.667.206.
 - [21] W. Y. Kim, S. W. Kim, D. H. Yoo, E. J. Kim, and S. H. Hahn, "Annealing effect of ZnO seed layer on enhancing photocatalytic activity of ZnO/TiO₂ nanostructure," *Int. J. Photoenergy*, vol. 2013, no. 130541, pp. 1–7, 2013, doi: 10.1155/2013/130541.
 - [22] W. Johansson, A. Peralta, B. Jonson, S. Anand, L. Österlund, and S. Karlsson, "Transparent TiO₂ and ZnO Thin Films on Glass for UV Protection of PV Modules," *Front. Mater.*, vol. 6, no. October, 2019, doi: 10.3389/fmats.2019.00259.
 - [23] C. M. Firdaus, M. S. B. Shah Rizam, M. Rusop, and S. Rahmatul Hidayah, "Characterization of ZnO and ZnO:TiO₂ thin films prepared by sol-gel spray-spin coating technique," *Procedia Eng.*, vol. 41, pp. 1367–1373, 2012, doi: 10.1016/j.proeng.2012.07.323.
 - [24] B. Mohamad Fariza, J. Sasano, T. Shinagawa, H. Nakano, S. Watase, and M. Izaki, "Electrochemical Growth of (0001)-n-ZnO Film on (111)-p-Cu₂O Film and the Characterization of the Heterojunction Diode," *J. Electrochem. Soc.*, vol. 158, no. 10, p. D621, 2011, doi: 10.1149/1.3623776.
 - [25] N. Bai, X. Liu, Z. Li, X. Ke, K. Zhang, and Q. Wu, "High-efficiency TiO₂/ZnO nanocomposites photocatalysts by sol–gel and hydrothermal methods," *J. Sol-Gel Sci. Technol.*, vol. 99, no. 1, pp. 92–100, 2021, doi: 10.1007/s10971-021-05552-8.
 - [26] R. A. Rahman, M. A. H. Zulkefle, W. F. H. Abdullah, M. Rusop, and S. H. Herman, "Characteristics of TiO₂/ZnO bilayer film towards pH sensitivity prepared by different spin coating deposition process," *AIP Conf. Proc.*, vol. 1733, 2016, doi: 10.1063/1.4948877.
 - [27] A. Karapetyan, R. Anna, G. Suzanne, F. Carole, S. Laszlo, N. Serge, N. Manuk, G. Vladimir, M. Wladimir, "Cuprous oxide thin films prepared by thermal oxidation of copper layer. Morphological and optical properties," *J. Lumin.*, vol. 159, pp. 325–332, 2015.

- [28] T. J. Song Huaibing, Zhan Xiaojun, Li Dengbing, Zhou Ying, Yang Bo, Zeng Kai, Zhong Jie, Miao Xiangshui, “Rapid thermal evaporation of Bi_2S_3 layer for thin film photovoltaics,” *Sol. Energy Mater. Sol. Cells*, vol. 146, pp. 1–7, Mar. 2016, doi: 10.1016/j.solmat.2015.11.019.
- [29] J. F. Wang Y., Ghanbaja, J., Soldera F., Migot S., Boulet P., Horwat D., Mücklich F., Pierson, “Tuning the structure and preferred orientation in reactively sputtered copper oxide thin films,” *Appl. Surf. Sci.*, vol. 335, pp. 85–91, Apr. 2015, doi: 10.1016/j.apsusc.2015.02.028.
- [30] B. Mohamad, J. Sasano, T. Shinagawa, S. Watase, and M. Izaki, “Light-assisted electrochemical construction of (111) $\text{Cu}_2\text{O}/(0001)$ ZnO heterojunction,” *Thin Solid Films*, vol. 520, no. 6, pp. 2261–2264, 2012, doi: 10.1016/j.tsf.2011.09.022.
- [31] A. R. Abdelwahed, “Potentiostatic Deposition and Characterization of Cuprous Oxide Thin Films,” *Hindawi Publ. Corp.*, vol. 2013, pp. 1–5, 2013.
- [32] A. Sasha, F. Mohamad, and R. Zafiruddin, “Cyclic Voltammetry measurement for n-type Cu_2O Thin Film using copper acetate-based solution,” *J. Eng. Appl. Sci.*, vol. 19, no. 10, pp. 8562–8568, 2015.
- [33] R. Akbari, G. Godeau, M. Mohammadizadeh, F. Guittard, and T. Darmanin, “The influence of bath temperature on the one-step electrodeposition of non-wetting copper oxide coatings,” *Appl. Surf. Sci.*, vol. 503, no. April 2019, p. 144094, 2020, doi: 10.1016/j.apsusc.2019.144094.
- [34] W. Septina, I. Shigeru, K. A. Alam, H. Takeshi, H. Takashi, M. Michio, P. M. Laurence, “Potentiostatic electrodeposition of cuprous oxide thin films for photovoltaic applications,” *Electrochim. Acta*, vol. 56, no. 13, pp. 4882–4888, 2011.
- [35] M. H. Tran, J. Y. Cho, S. Sinha, M. G. Gang, and J. Heo, “ $\text{Cu}_2\text{O}/\text{ZnO}$ heterojunction thin-film solar cells: the effect of electrodeposition condition and thickness of Cu_2O ,” *Thin Solid Films*, vol. 661, no. April, pp. 132–136, 2018, doi: 10.1016/j.tsf.2018.07.023.
- [36] R. Hussin, K. L. Choy, and X. Hou, “Enhancement of crystallinity and optical properties of bilayer TiO_2/ZnO thin films prepared by atomic layer deposition,” *J. Nanosci. Nanotechnol.*, vol. 11, no. 9, pp. 8143–8147, 2011, doi: 10.1166/jnn.2011.5086.
- [37] M. I. Khan, K. A. Bhatti, R. Qindeel, L. G. Bousiakou, and N. Alonizan,

- “Investigations of the structural , morphological and electrical properties of multilayer ZnO /TiO₂ thin films , deposited by sol–gel technique,” *Results Phys.*, vol. 6, pp. 156–160, 2016, doi: 10.1016/j.rinp.2016.01.015.
- [38] X. Xu *et al.*, “Highly efficient planar perovskite solar cells with a TiO₂/ZnO electron transport bilayer,” *J. Mater. Chem. A*, vol. 3, no. 38, pp. 19288–19293, 2015, doi: 10.1039/c5ta04239a.
 - [39] N. S. Zulkiflee, R. Hussin, J. Halim, M. I. Ibrahim, M. Z. Zainal, S. Nizam, S. A. Rahman, “Characterization of TiO₂, ZnO, and TiO₂/ZnO thin films prepared by sol-gel method,” *ARPEN J. Eng. Appl. Sci.*, vol. 11, no. 12, pp. 7633–7637, 2016.
 - [40] S. Wang, B. Kavaipatti, S. J. Kim, X. Pan, R. Ramesh, J. W. Ager, L. W. Wang, “Atomic and electronic structures of lattice mismatched Cu₂O/TiO₂ interfaces,” *Appl. Phys. Lett.*, vol. 104, no. 21, pp. 1–5, 2014.
 - [41] M. Zamzuri, F. B. Mohamad, and M. Izaki, “Electrodeposited (111)-oriented Cu₂O Photovoltaic Device with Al:ZnO,” *J. Surf. Finish. Soc. JapanJournal Surf. Finish. Soc. Japan*, vol. 66, no. 11, pp. 544–545, 2015, doi: 10.4139/sfj.66.544.
 - [42] M. Y. Abdu, “Copper (I) Oxide (Cu₂O) Based Solar Cells - A Review,” *Bayero J. Pure Appl. Sci.*, vol. 2, no. 2, pp. 8–12, 2009.
 - [43] A. Maren and A. Fyhn, “Electrodeposition of Metal Oxides for Solar Cell Applications,” 2012.
 - [44] P. Würfel, “Physics of Solar Cells,” *WILEY-VCH Verlag GmbH & Co. KGaA*, pp. 37–84, 2005.
 - [45] Y. Abdu and A. Musa, “Copper (I) oxide (Cu₂) based solar cells - a review,” *Bayero J. Pure Appl. Sci.*, vol. 2, no. 2, 2011, doi: 10.4314/bajopas.v2i2.63717.
 - [46] M. Zeman, “Thin-film silicon PV technology,” *J. Electr. Eng.*, vol. 61, no. 5, pp. 271–276, 2010, doi: 10.2478/v10187-010-0039-y.
 - [47] T. D. Lee and A. U. Ebong, “A review of thin film solar cell technologies and challenges,” *Renew. Sustain. Energy Rev.*, vol. 70, no. September 2015, pp. 1286–1297, 2017, doi: 10.1016/j.rser.2016.12.028.
 - [48] L. J. Lewis, “Fifty years of amorphous silicon models: the end of the story?,” *J. Non. Cryst. Solids*, vol. 580, no. December 2021, p. 121383, 2022, doi: 10.1016/j.jnoncrysol.2021.121383.

- [49] A. S. Zoolfakar, R. A. Rani, A. J. Morfa, A. P. O'Mullane, and K. Kalantari-Zadeh, "Nanostructured copper oxide semiconductors: A perspective on materials, synthesis methods and applications," *J. Mater. Chem. C*, vol. 2, no. 27, pp. 5247–5270, 2014, doi: 10.1039/c4tc00345d.
- [50] T. Mahalingam, J. S. P. Chitra, S. Rajendran, M. Jayachandran, and M. J. Chockalingam, "Galvanostatic deposition and characterization of cuprous oxide thin films," vol. 216, pp. 304–310, 2000.
- [51] J. K. D. S. J. K.M.D.C. Jayathileke, W. Siripala, "Electrodeposition of p-type , n-type and p-n Homojunction Cuprous Oxide Thin Films," *Sri Lanka J. Phys.*, vol. 9, pp. 35–46, 2008, doi: 10.4038/sljp.v9i0.2509.
- [52] A. Mittiga, E. Salza, F. Sarto, M. Tucci, and R. Vasanthi, "Heterojunction solar cell with 2% efficiency based on a Cu₂O substrate," *Appl. Phys. Lett.*, vol. 88, no. 16, pp. 16–18, 2006, doi: 10.1063/1.2194315.
- [53] J. Hou, C. Yang, H. Cheng, S. Jiao, O. Takeda, and H. Zhu, "High-performance p-Cu₂O/n-TaON heterojunction nanorod photoanodes passivated with an ultrathin carbon sheath for photoelectrochemical water splitting," *Energy Environ. Sci.*, vol. 7, no. 11, pp. 3758–3768, 2014, doi: 10.1039/c4ee02403f.
- [54] L. Cheng, Y. Tian, and J. Zhang, "Construction of p-n heterojunction film of Cu₂O/α-Fe₂O₃ for efficiently photoelectrocatalytic degradation of oxytetracycline," *J. Colloid Interface Sci.*, vol. 526, pp. 470–479, 2018, doi: 10.1016/j.jcis.2018.04.106.
- [55] P. Sawicka-Chudy, Sibiński. M., Pawełek R., Wisz G., Cieniek B., Potera P., Szczepan P., Adamiak S., Cholewa M., Głowa L., "Characteristics of TiO₂, Cu₂O, and TiO₂/Cu₂O thin films for application in PV devices," *AIP Adv.*, vol. 9, no. 5, 2019.
- [56] M. Fariza, N. Ahmad, F. N. Fahrizal, Z. Anis, M. K. Ahmad, A. Talib, N. Ahmad, H. M. N. Nik, I. Masanobu, "Fabrication of Nanorods-TiO₂ for Heterojunction Thin Film Application with Electrodeposit-p-Cu₂O Absorbing Layer," *Materials Today: Proceedings*, vol. 18. pp. 468–472, 2019.
- [57] T. Ghrib, A. K. Nouf, A. Aishah, E. A. Abdelhafeez, B. Sami, B. Khaoula, E. A. Khaled, "Annealing effect on the microstructural, optical, electrical, and thermal properties of Cu₂O/TiO₂/Cu₂O/TiO₂/Si heterojunction prepared by sol-gel technique," *Superlattices Microstruct.*, no. September, p. 107119, 2021.
- [58] J. L. Chen, M. M. Liu, S. Y. Xie, L. J. Yue, F. L. Gong, K. M. Chai, Y. H.

- Zhang, “Cu₂O-loaded TiO₂ heterojunction composites for enhanced photocatalytic H₂ production,” *J. Mol. Struct.*, vol. 1247, p. 131294, 2022, doi: 10.1016/j.molstruc.2021.131294.
- [59] M. Rani and S. K. Tripathi, “Electron transfer properties of organic dye sensitized ZnO and ZnO/TiO₂ photoanode for dye sensitized solar cells,” *Renew. Sustain. Energy Rev.*, vol. 61, pp. 97–107, 2016, doi: 10.1016/j.rser.2016.03.012.
- [60] M. K. Hossain, A. A. Mortuza, S. K. Sen, M. K. Basher, M. W. Ashraf, S. Tayyaba, M. N. H. Mia, M. J. Uddin, “A comparative study on the influence of pure anatase and Degussa-P25 TiO₂ nanomaterials on the structural and optical properties of dye sensitized solar cell (DSSC) photoanode,” *Optik (Stuttgart)*, vol. 171, no. May, pp. 507–516, 2018.
- [61] F. I. M. Fazli, M. K. Ahmad, C. F. Soon, N. Nafarizal, A. B. Suriani, A Mohamed, M. H. Mamat, M. F. Malek, M. Shimomura, K. Murakami, “Dye-sensitized solar Cell using pure anatase TiO₂ annealed at different temperatures,” *Optik (Stuttgart)*, vol. 140, pp. 1063–1068, 2017.
- [62] F. Scarpelli, T. F. Mastropietro, T. Poerio, and N. Godbert, “Mesoporous TiO₂ Thin Films: State of the Art,” *Titan. Dioxide - Mater. a Sustain. Environ.*, no. June 2018, 2018, doi: 10.5772/intechopen.74244.
- [63] J. Tian, L. Chen, J. Dai, X. Wang, Y. Yin, and P. Wu, “Preparation and characterization of TiO₂, ZnO, and TiO₂/ZnO nanofilms via sol – gel process,” *Ceram. Int.*, vol. 35, pp. 2261–2270, 2009, doi: 10.1016/j.ceramint.2008.12.010.
- [64] S. Baruah and J. Dutta, “Hydrothermal growth of ZnO nanostructures,” *Sci. Technol. Adv. Mater.*, vol. 10, no. 1, 2009, doi: 10.1088/1468-6996/10/1/013001.
- [65] P. L. Gareso, Musfitasari, and E. Juarlin, “Optical and Structural Characterization of ZnO/TiO₂ Bilayer Thin Films Grown by Sol-Gel Spin Coating,” *J. Phys. Conf. Ser.*, vol. 979, no. 1, pp. 012060, 1–7, 2018, doi: 10.1088/1742-6596/979/1/012060.
- [66] V. J. Garcia, C. M. Pelicano, and H. Yanagi, “Low temperature-processed ZnO nanorods-TiO₂ nanoparticles composite as electron transporting layer for perovskite solar cells,” *Thin Solid Films*, vol. 662, no. July, pp. 70–75, 2018, doi: 10.1016/j.tsf.2018.07.039.

- [67] S. Pitchaiya, E. Nandhakumar, N. Muthukumarasamy, S. Agilan, R. Venkatraman Madurai, A. Vijayshankar, P. Pavithrakumar, P. Balraju, K. Ananthi, V. Dhayalan, "Interfacing green synthesized flake like-ZnO with TiO₂ for bilayer electron extraction in perovskite solar cells," *New J. Chem.*, vol. 44, no. 20, pp. 8422–8433, 2020.
- [68] R. Hussin, N. S. Zulkiflee, Z. Kamdi, A. R. Ainuddin, Z. Harun, and M. N. Mohamed Hatta, "Photocatalytic activity of bilayer TiO₂/ZnO and ZnO/TiO₂ thin films," *Mater. Sci. Forum*, vol. 1010 MSF, pp. 411–417, 2020, doi: 10.4028/www.scientific.net/MSF.1010.411.
- [69] N. Naseri, M. Yousefi, and A. Z. Moshfegh, "A comparative study on photoelectrochemical activity of ZnO/TiO₂ and TiO₂/ZnO nanolayer systems under visible irradiation," *Sol. Energy*, vol. 85, no. 9, pp. 1972–1978, 2011, doi: 10.1016/j.solener.2011.05.002.
- [70] S. Moradi, P. Aberoomand-azar, and S. Raeis-farshid, "The effect of different molar ratios of ZnO on characterization and photocatalytic activity of TiO₂/ZnO nanocomposite," *J. Saudi Chem. Soc.*, vol. 20, no. 4, pp. 373–378, 2016, doi: 10.1016/j.jscs.2012.08.002.
- [71] R. Asmatulu, *Nanocoatings for corrosion protection of aerospace alloys*. Woodhead Publishing Limited, 2012.
- [72] M. D. Tyona, "A theoretical study on spin coating technique," *Adv. Mater. Res.*, vol. 2, no. 4, pp. 195–208, 2013, doi: 10.12989/amr.2013.2.4.195.
- [73] S. S. Jeong, A. Mittiga, E. Salza, A. Masci, and S. Passerini, "Electrodeposited ZnO/Cu₂O heterojunction solar cells," *Electrochim. Acta*, vol. 53, no. 5, pp. 2226–2231, 2008, doi: 10.1016/j.electacta.2007.09.030.
- [74] R. Kumar, O. Al-Dossary, G. Kumar, and A. Umar, "Zinc oxide nanostructures for NO₂ gas-sensor applications: A review," *Nano-Micro Lett.*, vol. 7, no. 2, pp. 97–120, 2015, doi: 10.1007/s40820-014-0023-3.
- [75] Y. S. Chen, C. H. Liao, C. L. Chueh, C. C. Lai, L. Y. Chen, A. K. Chu, C. K. Kuo, H. C. Wang, "High performance Cu₂O/ZnO core-shell nanorod arrays synthesized using a nanoimprint GaN template by the hydrothermal growth technique," *Opt. Mater. Express*, vol. 4, no. 7, p. 1473, 2014.
- [76] S. H. Jeong and E. S. Aydil, "Heteroepitaxial growth of Cu₂O thin film on ZnO by metal organic chemical vapor deposition," *J. Cryst. Growth*, vol. 311, no. 17, pp. 4188–4192, 2009, doi: 10.1016/j.jcrysgr.2009.07.020.

- [77] A. Kiani, K. Dastafkan, A. Obeydavi, and M. Rahimi, "Solid solutions of gadolinium doped zinc oxide nanorods by combined microwave-ultrasonic irradiation assisted crystallization," *Solid State Sci.*, vol. 74, pp. 152–167, 2017, doi: 10.1016/j.solidstatesciences.2017.10.002.
- [78] R. Kara, H. Lahmar, L. Mentar, R. Siab, F. Kadirgan, and A. Azizi, "Electrochemical growth and characterization of Cu₂O:Na/ZnO heterojunctions for solar cells applications," *J. Alloys Compd.*, vol. 817, no. December 2018, pp. 2–8, 2020, doi: 10.1016/j.jallcom.2019.152748.
- [79] K. Akimoto, S. Ishizuka, M. Yanagita, Y. Nawa, G. K. Paul, and T. Sakurai, "Thin film deposition of Cu₂O and application for solar cells," *Sol. Energy*, vol. 80, pp. 715–722, 2006, doi: 10.1016/j.solener.2005.10.012.
- [80] H. Lahmar, F. Seti, A. Azizi, G. Schmerber, and A. Dinia, "On the electrochemical synthesis and characterization of p-Cu₂O/n-ZnO heterojunction," *J. all*, vol. 718, pp. 36–45, 2017, doi: 10.1016/j.jallcom.2017.05.054.
- [81] M. H. Tran, J. Y. Cho, S. Sinha, M. G. Gang, and J. Heo, "Cu₂O/ZnO heterojunction thin-film solar cells : the effect of electrodeposition condition and thickness of Cu₂O," *Thin Solid Films*, vol. 661, no. April, pp. 132–136, 2018, doi: 10.1016/j.tsf.2018.07.023.
- [82] T. Özdal and H. Kavak, "Fabrication and characterization of ZnO/Cu₂O heterostructures for solar cells applications," *Superlattices Microstruct.*, vol. 146, no. May, 2020, doi: 10.1016/j.spmi.2020.106679.
- [83] J. Chen, Y. Jia, W. Wang, J. Fu, H. Shi, and Y. Liang, "Morphology selective electrodeposition of Cu₂O microcrystals on ZnO nanotube arrays as efficient visible-light-driven photo-electrode," *Int. J. Hydrogen Energy*, vol. 45, no. 15, pp. 8649–8658, 2020, doi: 10.1016/j.ijhydene.2020.01.114.
- [84] D. C. Perng, M. H. Hong, K. H. Chen, and K. H. Chen, "Enhancement of short-circuit current density in Cu₂O/ZnO heterojunction solar cells," *J. Alloys Compd.*, vol. 695, pp. 549–554, 2017, doi: 10.1016/j.jallcom.2016.11.119.
- [85] Y. C. Zhou and J. A. Switzer, "Galvanostatic electrodeposition and microstructure of copper (I) oxide film," *Mater. Res. Innov.*, vol. 2, no. December, pp. 1–2, 1997.
- [86] S. K. B. B.G. Streetman, *Solid State Electronic Devices 6th ed. Pearson int. ed.* 2010.

- [87] L. Chen, S. Sudhakar, T. Houwen, W. Heli, D. Todd, Y. Yanfa, T. John, A. Mowafak, “Electrochemical deposition of copper oxide nanowires for photoelectrochemical applications,” *J. Mater. Chem.*, vol. 20, no. 33, pp. 6962–6967, 2010.
- [88] S. T. Wei-min, Chao, Wen-how, Lan, Shao-yi Lee, Yi-chun Chou, Chun-wei Tsai, Ming-chang Shih, Yi-da Wu, “Investigation into the influence of the CuInSe₂ device with ITO and FTO layer,” in *17th Opto-Electronics and Communications Conference (OECC 2012)*, 2012, no. July, pp. 671–672.
- [89] A. J. B. L. R. Faulkner, *Electrochemical methods Fundamentals and Applications*. 2001.
- [90] H. Lee, J.-H. Lee, Y.-H. Hwang, and Y. Kim, “Cyclic voltammetry study of electrodeposition of CuGaSe₂ thin films on ITO-glass substrates,” *Curr. Appl. Phys.*, vol. 14, no. 1, pp. 18–22, Jan. 2014, doi: 10.1016/j.cap.2013.10.001.
- [91] T. H. Wilman Septinaa, Shigeru Ikedaa, M. Alam Khana, Takeshi Hiraia and L. M. P. Michio Matsumuraa, “Potentiostatic electrodeposition of cuprous oxide thin films for photovoltaic applications,” *Electrochim. Acta*, vol. 56, no. 13, pp. 4882–4888, 2011, doi: 10.1016/j.electacta.2011.02.075.
- [92] F. Dincer and M. E. Meral, “Critical Factors that Affecting Efficiency of Solar Cells,” *Smart Grid Renew. Energy*, vol. 01, no. 01, pp. 47–50, 2010, doi: 10.4236/sgre.2010.11007.
- [93] M. Ichimura and Y. Kato, “Fabrication of TiO₂/Cu₂O heterojunction solar cells by electrophoretic deposition and electrodeposition,” *Mater. Sci. Semicond. Process.*, vol. 16, no. 6, pp. 1538–1541, 2013, doi: 10.1016/j.mssp.2013.05.004.
- [94] N. Ahmad, M. Fariza, T. Azman, A. M. Khairul, M. I. A. Zafirah, and M. A. Nurliyana, “Fabrication and Characterization of p-Cu₂O on n-TiO₂ Layer by Electrodeposition Method for Heterojunction Solar Cells Development,” *J. Human, Earth, Futur.*, vol. 2, no. 4, pp. 334–344, 2021, doi: 10.28991/hef-2021-02-04-02.
- [95] C. Sujuan, L. Lin, J. Liu, L. Peiwei, W. Xiaoping, Z. Weifeng, Q. Yan, L. Fachun, “An electrochemical constructed p-Cu₂O/n-ZnO heterojunction for solar cell,” *J. Alloys Compd.*, vol. 644, pp. 378–382, 2015.
- [96] M. Abd-Ellah, J. P. Thomas, L. Zhang, and K. T. Leung, “Enhancement of solar cell performance of p-Cu₂O/n-ZnO-nanotube and nanorod heterojunction devices,” *Sol. Energy Mater. Sol. Cells*, vol. 152, pp. 87–93, 2016, doi:

- 10.1016/j.solmat.2016.03.022.
- [97] B. D. Cullity, *Elements of X-ray diffraction*. 1978.
- [98] A. B. Suriani, Muqoyyanah, A. Mohamed, M. H. Mamat, N. Hashim, I. M. Isa, M. F. Malek, M. I. Kairi, A. R. Mohamed, M. K. Ahmad, “Improving the photovoltaic performance of DSSCs using a combination of mixed-phase TiO₂ nanostructure photoanode and agglomerated free reduced graphene oxide counter electrode assisted with hyperbranched surfactant,” *Optik (Stuttg.)*, vol. 158, no. 2010, pp. 522–534, 2018, doi: 10.1016/j.ijleo.2017.12.149.
- [99] S. V. Litvinenko, A. V. Kozinetz, and V. A. Skryshevsky, “Concept of photovoltaic transducer on a base of modified p-n junction solar cell,” *Sensors Actuators, A Phys.*, vol. 224, pp. 30–35, 2015, doi: 10.1016/j.sna.2015.01.014.
- [100] J. A. N. T. Soares, “Introduction to Optical Characterization of Materials,” in *Practical Materials Characterization*, 2014, p. 51.
- [101] S. M. Shahrestani, “Electrodeposition Of Cuprous Oxide For Thin Film Solar Cell Applications,” 2013.
- [102] J. P. R. Abbott and H. Zhu, “3D optical surface profiler for quantifying leaf surface roughness,” *Surf. Topogr. Metrol. Prop.*, vol. 7, no. 4, 2019, doi: 10.1088/2051-672X/ab4cc6.
- [103] N. S. Zulkiflee and R. Hussin, “Effect of Temperature on TiO₂/ZnO Nanostructure Thin Films,” *Mater. Sci. Forum*, vol. 840, pp. 262–266, 2016, doi: 10.4028/www.scientific.net/MSF.840.262.
- [104] M.-B. Kuhu Sarkar Erik, V. Braden, Thomson, Froschi Nicola, Husing Peter, “Spray-deposited zinc titanate films obtained via sol–gel synthesis for application in dye-sensitized,” *J. Mater. Chem. A*, pp. 15008–15014, 2014, doi: 10.1039/c4ta02031f.
- [105] L. S. Cavalcante, M. Anicete-Santos, M. F. M. Pontes, F. M. I. A. Souza, I. A. L. P.S. Santos, I. L.V. Rosa, M. R.M.C. Santos, L. S. Santos-Júnior, E. R. Leite, E. Longo, “Effect of annealing time on morphological characteristics of Ba(Zr,Ti)O₃ thin films,” *J. Alloys Compd.*, vol. 437, no. 1–2, pp. 269–273, 2007.
- [106] S. J. Nurani, A. Islam, A. Sadat, S. Rahman, and G. Mowla, “Electrodeposition and Dependency of Optical Properties on Operating Voltage and Bath Temperature of Copper Oxide (II) Thin Films for Photovoltaic Applications,” in *IEEE International Conference on Telecommunication and Photonics (ICTP)*,

- 2015, p. 5.
- [107] L. De Los Santos Valladares *et al.*, “Crystallization and electrical resistivity of Cu₂O and CuO obtained by thermal oxidation of Cu thin films on SiO₂/Si substrates,” *Thin Solid Films*, vol. 520, no. 20, pp. 6368–6374, 2012, doi: 10.1016/j.tsf.2012.06.043.
- [108] C. H. Kuo and M. H. Huang, “Facile synthesis of Cu₂O nanocrystals with systematic shape evolution from cubic to octahedral structures,” *J. Phys. Chem. C*, vol. 112, no. 47, pp. 18355–18360, 2008, doi: 10.1021/jp8060027.
- [109] O. Messaoudi, I. Ben Assaker, M. Gannouni, A. Souissi, H. Makhlouf, A. Bardaoui, R. Chtourou, “Structural, morphological and electrical characteristics of electrodeposited Cu₂O: Effect of deposition time,” *Appl. Surf. Sci.*, vol. 366, pp. 383–388, 2016.
- [110] L. Xiong, S. Huang, X. Yang, M. Qiu, Z. Chen, and Y. Yu, “Electrochimica Acta p-Type and n-type Cu₂O semiconductor thin films: Controllable preparation by simple solvothermal method and photoelectrochemical properties,” *Electrochim. Acta*, vol. 56, no. 6, pp. 2735–2739, 2011, doi: 10.1016/j.electacta.2010.12.054.
- [111] L. C. Wang, N. R. De Tacconi, C. R. Chenthamarakshan, K. Rajeshwar, and M. Tao, “Electrodeposited copper oxide films: Effect of bath pH on grain orientation and orientation-dependent interfacial behavior,” *Thin Film Solid*, vol. 515, pp. 3090–3095, 2007, doi: 10.1016/j.tsf.2006.08.041.
- [112] M. Voinea, C. Vladuta, C. Bogatu, and A. Duta, “Surface properties of copper based cermet materials,” *Mater. Sci. Eng. B*, vol. 152, pp. 76–80, 2008, doi: 10.1016/j.mseb.2008.06.020.
- [113] N. S. Zulkiflee and R. Hussin, “Effect of temperature on TiO₂/ZnO nanostructure thin films,” *Mater. Sci. Forum*, vol. 840, pp. 262–266, 2016, doi: 10.4028/www.scientific.net/MSF.840.262.
- [114] R. P. Wijesundera, L. K. A. D. D. S. Gunawardhana, and W. Siripala, “Solar Energy Materials & Solar Cells Electrodeposited Cu₂O homojunction solar cells: Fabrication of a cell of high short circuit photocurrent,” *Sol. Energy Mater. Sol. Cells*, vol. 157, pp. 881–886, 2016, doi: 10.1016/j.solmat.2016.07.005.

APPENDIX A

LIST OF PUBLICATIONS

Year	Articles	Scopus/ISI
2022	<p>Arifin, N.M., Mohamad, F., Hussin, R., Ismail, A.Z.M., Ramli, S.A., Ahmad, N., Nor, N.H.M., Sahdan, M.Z., Zain, M.Z.M., Izaki, M., Annealing Treatment on Homogenous n-TiO₂/ZnO Bilayer Thin Film Deposition as Window Layer for p-Cu₂O Based Heterostructure Thin Film. <i>Coatings</i>. <i>(Accepted on 07 November 2022)</i></p>	Q2 (IF 3.236)
2021	<p>Arifin, N.M., Mohamad, F., Hussin, R., Ismail, A.Z.M., Ramli, S.A., Ahmad, N., Nor, N.H.M., Sahdan, M.Z., Zain, M.Z.M., Izaki, M., Development of homogenous n-TiO₂/ZnO bilayer/p-Cu₂O heterostructure thin film. <i>J Sol-Gel Sci Technol</i> 100, 224–231 (2021). https://doi.org/10.1007/s10971-021-05650-7</p>	Q1 (IF 2.422)
2020	<p>N. Mohamad, F. Mohamad, L. Sheng, A. Ismail, N. Ahmad, N. Nor, M. Izaki, “Construction of Nanorod-TiO₂/p-Cu₂O Heterostructure Thin Films for Solar Cell Application,” <i>Int. J. Adv. Trends Comput. Sci. Eng.</i>, vol. 9, no. 1, pp. 304–310, 2020. https://doi.org/10.30534/ijatcse/2020/5391.12020</p>	Scopus

- 2019 F. Mohamad, **N. M. Arifin**, A. Z. M. Ismail, N. Ahmad, M. N. N. Hisyamudin, and M. Izaki, “Cu₂O-based homostructure fabricated by electrodeposition method,” *Acta Phys. Pol. A*, vol. 135, no. 5, pp. 911–914, 2019. Q4
(IF 0.536)
- https://doi: 10.12693/APhysPolA.135.91*



PTT AUTHM
PERPUSTAKAAN TUNKU TUN AMINAH