PERFORMANCE ANALYSIS OF ZINC OXIDE NANOROD FOR DSSC SOLAR CELL

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This report is submitted in partial fulfilment of the requirements for the degree of Bachelor of Electronic Engineering with Honours

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DECLARATION

I declare that this report entitled “PERFORMANCE ANALYSIS OF ZINC OXIDE NANOROD FOR DSSC SOLAR CELL” is the result of my own work except for quotes as cited in the references.

Signature :

Author : Mohd Syafiq Farhan Mohd Radzuan

Date : 3 July 2020

APPROVAL

I hereby declare that I have read this thesis and in my opinion this thesis is sufficient in terms of scope and quality for the award of Bachelor of Electronic Engineering with Honours.

Signature :

Supervisor Name : Dr Muhammad Idzdihar

Date : 3 / 7 / 2020

DEDICATION

Firstly, I am grateful to Allah for all the blessings in terms of healthy life and wellbeing for completing this thesis. I dedicated this thesis to my supervisor, my supportive parents, my family, and to all my fellow friends for their encouragements and doa's.

ABSTRACT

A solar cell is known as a photovoltaic cell that can convert light energy to electrical energy through the photovoltaic effect. A dye-sensitized solar cell (DSSC) is the third generation of solar cells and has the potential to generate green energy attributed to its low cost of the fabrication process, high stability, environmental friendliness, and easy fabrication. This project presents the investigation of zinc oxide (ZnO) nanorod as an electron transport layer. ZnO has high electron mobility. The electron transport layer supports dye molecules and has possession of encouraging energy to receive the photogenerated electrons from the excited state of the natural dye. Furthermore, the photoanode is an important part of DSSC to sustain stability and increase efficiency. The main objective of this project is to analyze the performance of zinc oxide nanorods after control of the seeding phase and growth process. These two processes important part of the performance of ZnO nanorods. The seeding phase to control the thickness of the nanorod and growth process using the hydrothermal method at an annealing temperature of 90Celsius. Design of project for seeding phase created to get the trend from variables input of procedure. The characterization result is to determine the performance of ZnO nanorod. A scanning electron microscope (SEM) was performed to observe and examine the structure of ZnO nanorod with different range areas and magnification for structural characterization. In addition, X-Ray diffraction measurement with data analysis was used to identify the crystalline phase of materials and to reveal information about unit cell dimensions. Furthermore, UV-Vis Spectroscopy used to determine the wavelength and absorption of light from ZnO nanorods. The performance of DSSC is determined by analyzing results of characterization. The best performance obtain is Sample 4 with no cycles ten times during seeding with solution filtered and the growth process is facing down position of the sample. This method is to achieve the best performance in term of characterizaation ZnO nanorods for DSSC. The outcome of this research and design of experiments that create could be a stepping stone in ZnO nanorod performance for DSSC solar cells to get the best and higher efficiency. In addition, COMSOL Multiphysics software used to simulate the propagation of light, scattering section, and absorption between cylindrical geometry as a reference to nanorod shape. This simulation experiment analyzes the relationship between nanorod with zinc oxide material and light beam to obtain the electric field. The output from this simulation, can be analyzed and prove the effect of zinc oxide nanorod and electric field reaction.

ABSTRAK

Sel solar dikenali sebagai sel fotovoltaik yang dapat menukar tenaga cahaya menjadi tenaga elektrik melalui kesan fotovoltaik. Sel solar peka pewarna (DSSC) adalah generasi ketiga sel suria dan berpotensi menghasilkan tenaga hijau yang disebabkan oleh kos proses fabrikasinya yang rendah, kestabilan tinggi, keramahan alam sekitar, dan pembuatan yang mudah. Projek ini mengemukakan penyelidikan nanorod zink oksida (ZnO) sebagai lapisan pengangkutan elektron. ZnO mempunyai mobiliti elektron yang tinggi. Lapisan pengangkutan elektron menyokong molekul pewarna dan mempunyai tenaga yang menggalakkan untuk menerima elektron fotogenerasi dari keadaan pewarna semulajadi yang teruja. Selanjutnya, photoanode adalah bahagian penting DSSC untuk mengekalkan kestabilan dan meningkatkan kecekapan. Objektif utama projek ini adalah untuk menganalisis prestasi nanorod zink oksida setelah kawalan fasa pembenihan dan proses pertumbuhan. Kedua-dua proses ini merupakan bahagian penting dalam prestasi nanorod ZnO. Fasa pembenihan untuk mengawal ketebalan nanorod dan proses pertumbuhan menggunakan kaedah hidrotermal pada suhu penyepuhlindapan 90Celsius. Reka bentuk projek untuk fasa pembenihan dibuat untuk mendapatkan tren dari input prosedur pemboleh ubah. Pencirian adalah hasil untuk menentukan prestasi nanorod ZnO. Mikroskop elektron imbasan (SEM) dilakukan untuk memerhatikan dan memeriksa struktur nanorod ZnO dengan kawasan julat yang berbeza dan pembesaran untuk pencirian struktur. Selain itu, pengukuran difraksi sinar-X dengan analisis data digunakan untuk mengenal pasti fasa kristal bahan dan untuk mengungkapkan maklumat mengenai dimensi sel unit. Selanjutnya, Spektroskopi UV-Vis digunakan untuk menentukan panjang gelombang dan penyerapan cahaya dari nanorod ZnO. Prestasi DSSC ditentukan dengan menganalisis semua hasil pencirian. Prestasi terbaik yang diperoleh adalah Sampel 4 tanpa putaran sepuluh kali semasa penyemaian dengan larutan disaring dan proses pertumbuhan menghadap ke bawah sampel. Kaedah ini adalah untuk mencapai analisis terbaik dari SEM, XRD, dan hasil pencirian UV-Vis untuk mencapai prestasi terbaik nanorod ZnO. Hasil penyelidikan dan reka bentuk eksperimen yang dibuat ini dapat menjadi batu loncatan dalam prestasi nanorod ZnO untuk sel solar DSSC untuk mendapatkan kecekapan terbaik dan lebih tinggi. Selain itu, perisian Multiphysics COMSOL digunakan untuk mensimulasikan penyebaran cahaya, bahagian hamburan, dan penyerapan antara geometri silinder sebagai rujukan kepada bentuk nanorod. Eksperimen simulasi ini menganalisis hubungan antara nanorod dengan bahan zink oksida dan pancaran cahaya untuk mendapatkan medan elektrik. Hasil dari simulasi ini, dapat dianalisis dan membuktikan kesan tindak balas zink oksida nanorod dan medan elektrik..

ACKNOWLEDGMENTS

First and foremost, I want to express my gratitude towards Allah the Most Gracious, the Most Merciful. This work isn't possible without all the support of various people who supported me along the way. My heartfelt appreciation goes to my main supervisor, Dr. Muhammad Idzdihar for all their inspiration and positive input on this journey. I am very grateful that despite my supervisor's tight schedule, he always made their time for me. Lastly, much obliged to all my relatives, lecturers, and friends who become a helping hand for me to finish this thesis successfully.

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LIST OF SYMBOLS AND ABBREVIATIONS

DSSC	:	Dye sensitized solar cell
ZnO	:	Zinc oxide
ZnA	:	Zinc acetate
TiO_2	:	Titanium dioxide
CBD	:	Chemical Bath Deposition
CVD	:	Chemical Vapour Deposition
ITO	:	Indium Tin Oxide
SEM	:	Scanning electron Microscope
XRD	:	X-ray Diffraction

CHAPTER 1

INTRODUCTION

This chapter explains the subject matter and problem statement, objectives, scope of work, and significance of the project. The project background and problem statement introduced in this chapter regarding the challenges for fabrication dye-sensitized solar cells by using zinc oxide nanorods. The organization of the thesis summary is included by the end of the chapter.

1.1 Project background

Dye-Sensitized Solar Cell (DSSC) is known as one of the promising third-generation types of solar cell which are being developed nowadays. DSSC performance can be enhanced by modifying the morphology of the photoanode. Apart from the main challenge of the development of DSSC is to increase solar-electricity conversion efficiency. This project is to fabricate dye-sensitized solar cells and study the performance of Zinc oxide nanorod with solar cells. ZnO-based DSSC is interesting to be developed due to its higher position of the conduction band allowing the possibility to generate higher photovoltage In this study, synthesis of zinc oxide nanorod controlled by several testing syntheses of the nanoparticle to study the growth of zinc oxide. This can be done by varying methods for the seed layer during synthesis. Analysis performance can be done by using a Scanning Electron Microscope (SEM) and to get the visual images of samples. For the solar cell fabrication part, there are important step which preparation of paste, deposition to glass, stain with dye, prepare counter electrode, assemble solar cell, and analyzing performance. Therefore, the methodology for this study based on the Design of Experiment (DOE) to related the process is done with output obtains.

1.2 Problem Statement

Currently, apart from reducing the cost, further development of solar cells is focussing on improving efficiency stability and durability. To improve, four dominant functions which are photoanodes, dye, electrolyte, and counter electrodes need to be optimized. Recently, zinc oxide (ZnO) has attracted much attention as an alternative photoanode material because it exhibits a similar bandgap and electron injection process. Because of their unique, multifunctional properties, zinc oxide (ZnO) nanostructures are promising materials to use to create photoanodes for DSSCs. Furthermore, the electron mobility of ZnO is higher than TiO2. Therefore, ZnO is expected to be a promising photoanode material to improve the conversion efficiency of DSSCs.

Zinc oxide nanorod is yet a challenging undertaking based on DSSC. It needs to be optimized to higher to get the best result of zinc oxide nanorod that works for solar cells. The growth of zinc oxide nanorod needs to control to get the high surface area and it the challenge for this project.

1.3 Objective

Several objectives that need to be achieved after completing this project which are:

1) To study the synthesis of Zinc Oxide nanorod for dye-sensitized solar cells based on the seed layer and performance growth analysis
2) To analyze the characterization of Zinc Oxide nanorod.
3) To study, design and simulate light propagation beam on nanorods

Based on the objective stated above, the purpose of this project is to synthesis and analyze the performance of zinc oxide nanorod for dye-sensitized solar cells. Furthermore, this project also to study the light beam propagation on nanorods from a simulation by using COMSOL software.

1.4 Scope of work

The scope of work for the project needs to be identified to achieve this project objective. This project focused on:

1) At the beginning of this project, it more focuses on the procedure to synthesis ZnO nanorod and analyzed the performance of zinc oxide nanorod.
2) Optimize relationship seed layer and growth based on Design of Experiment (DOE)
3) Analyze seed layer and particle growth from the synthesis process by using Scanning Electron Microscope (SEM), X-ray Diffraction (XRD), UV-Vis Spectroscopy

1.5 Thesis organization

Chapter 1, the project overview which the motivation, problem statement, scope of work, and objectives are briefly discussed to give the readers an understanding of the initiation of the project.

Chapter 2, Literature review from other articles relating to this case study is included in this study. This chapter reviews other articles and journals from the work of others. The associated topic is also taken as a reference to ensure that this project receives as much information as possible.

Chapter 3, is about the project's research methodology. This chapter describes the methods or approaches used in project development based on the literature review.

Chapter 4, briefly discuss the observations, outcomes, and analysis of the project achieved during project development. This chapter also includes the project's final results and defines the project function.

Chapter 5, which is a conclusion and recommendation part, a short conclusion for readers to understand the findings, and the results of this study are explained in general and specifically. Discussion of the entire thesis and project contents and recommendations for improvement in the future study.

CHAPTER 2

LITERATURE REVIEW

This chapter covered the literature review of the project. This chapter discussed the literature review that includes the information gathered to get knowledge and ideas for the project's completion. Several sources, such as books, thesis, and journals have been taken as a resource for this project. Method and approaches that can be used also take from the resource as reference and guideline.

2.1 Solar Cell

A solar cell is a solid electrical device that converts solar energy directly to electricity. There are two fundamental functions of solar cells: photo-generation of charge carriers (electrons and holes) in a light-absorbing material and separation of the charge carriers to a conductive interaction to transmit electricity. Adding to the wide range of solar cells, hybrid solar cells based on inorganic and organic compounds are a promising renewable energy source.

2.1.1 Generation of solar cell

Solar cells can be classified into first, second, and third-generation cells. The first generation cells—also called conventional, traditional, or wafer-based cells—are made of crystalline silicon, the commercially predominant PV technology, that includes materials such as polysilicon and monocrystalline silicon. Second generation cells are thin-film solar cells, that include amorphous silicon, CdTe, and CIGS cells and are commercially significant in utility-scale photovoltaic power stations, building-integrated photovoltaics or in a small standalone power system. The third generation of solar cells includes several thin-film technologies often described as emerging photovoltaics—most of them have not yet been commercially applied and are still in the research or development phase.

First Generation	• Monocrystalline • Polycrystalline • Amorphous Silicon
Second Generation	• Cadmium Telluride • Copper Indium Selenide • Copper Indium Gallium Diselenide
Third Generation	• Dye-sensitized (DSSC) • Perovskite cell • Organic (OPV)

Table 1 Generation of solar cell

2.1.2 The efficiency of solar cell

The efficiency of solar cells is one of the greatest limiting factors for solar cells. The portfolio of solar cells consists of many established and emerging technologies, employs different semiconductive and photosensitive materials, and involves three generations of which the updated best research-cell efficiencies are plotted in the below figure.

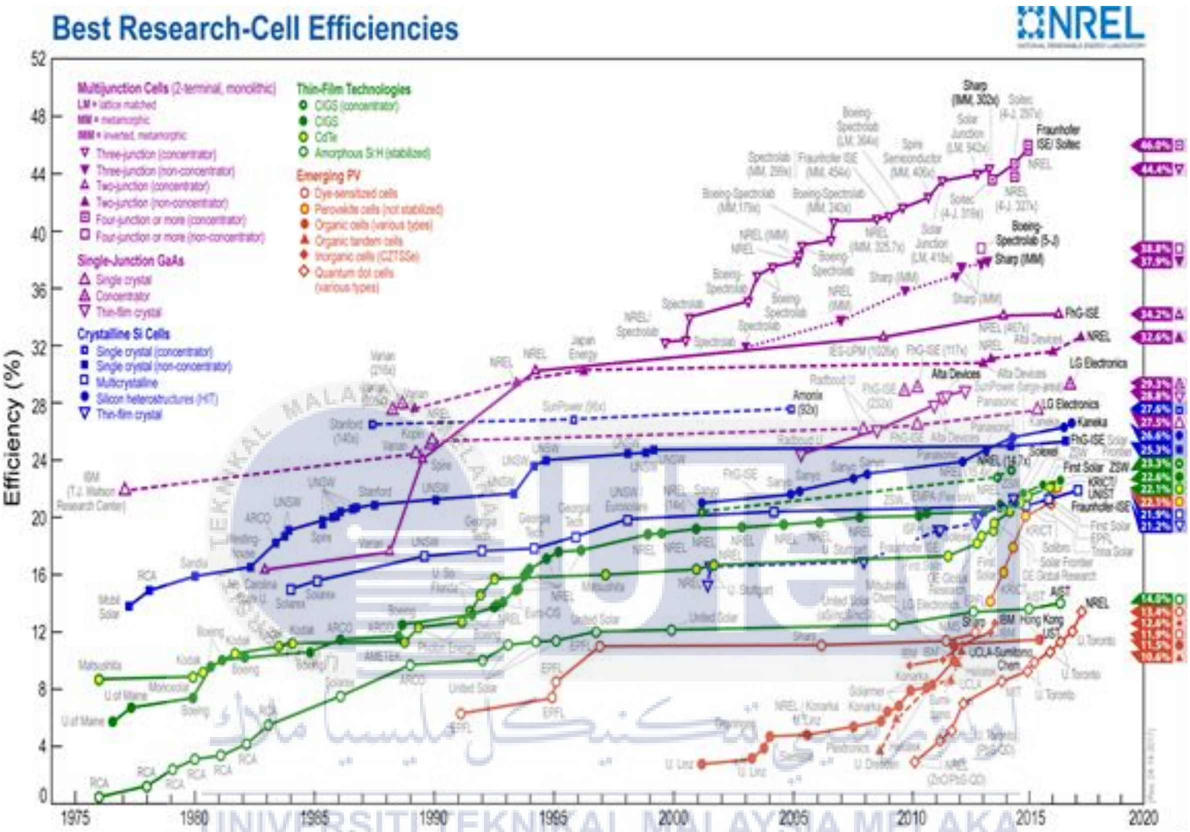


Figure 1 Solar cell latest research efficiency from start development until 2020, DSSC start from 2000, highest efficiency 13%

Solar cells based on silicon, that come in wafer-like monocrystalline, polycrystalline, and amorphous forms, are categorized as the first generation. Solar cells doped with phosphorus and boron in a P-N junction to achieve high-efficient charge separation of electron-hole pairs. These solar cells demonstrate good performance with more than 20% of the power conversion efficiency (PCE) as well as high stability, which currently dominate the markets, accounting for around 80% of the global share.

The excellent efficiency of the second-generation solar cells is as high as 20 percent PCE. This is constructed from layers of semiconductive materials with a thickness of only a few micrometers that can make electronics lightweight and reduce the cost of production.

2.2 Dye-Sensitized Solar Cell

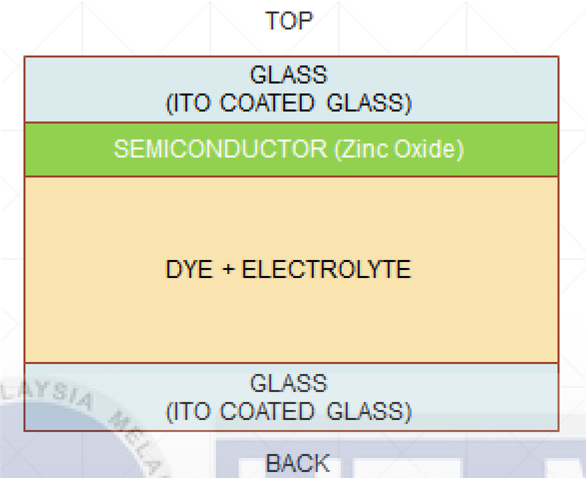


Figure 2 Structure of DSSC, coverd with top and back contact, semiconductor and dye as photoandode

Invented in 1991 by Grätzel, the latest version of a dye-sensitized solar cell is a low-cost solar cell belonging to thin-film solar cells. DSSC offered an alternative design that was technologically and economically viable to present-day p-n photovoltaic junction systems. DSSC divides these two functions into two distinct materials, unlike traditional solar cell systems in which semiconductors serve as both photon absorber and charge carrier.

Based on the NREL statistics, the DSSCs' highest reported laboratory output to date is about 12 percent. Although their efficiencies are still lower than first- and second-generation cells, DSSC manufacturing is cost-effective by using inexpensive and abundant wide-bandgap semiconductive materials such as Titania (TiO_2) and Zinc oxide (ZnO) in photoanodes.

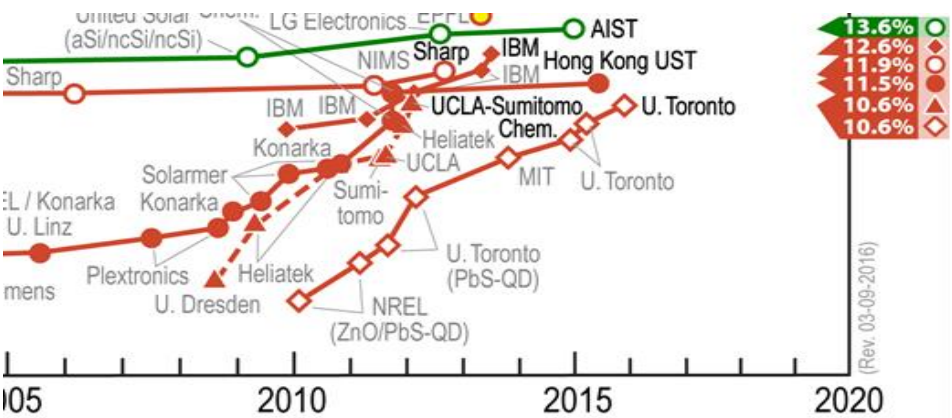


Figure 3 Latest Third Gen efficiency DSSC

2.2.1 Working principle of DSSC

The semiconductor layer is between two transparent fluorine-doped tin oxide glass layers and the left serves as the anode and the right serves as the cathode. The cathode layer has graphite on its layer. Photo absorbent dye is bonded to the semiconductor oxide and when light hits the cell it is absorbed by the dye used in the DSSC. Photon excites the TiO2 particles causes them to release electrons. These electrons exit the cells through the anode, travel through a load and return to the cells through the cathode. At the anode, iodide electrolyte oxidized to form triiodide and then reduced at the cathode to form iodide again. To transform solar illumination into electric energy, this whole cycle is repeated several times.

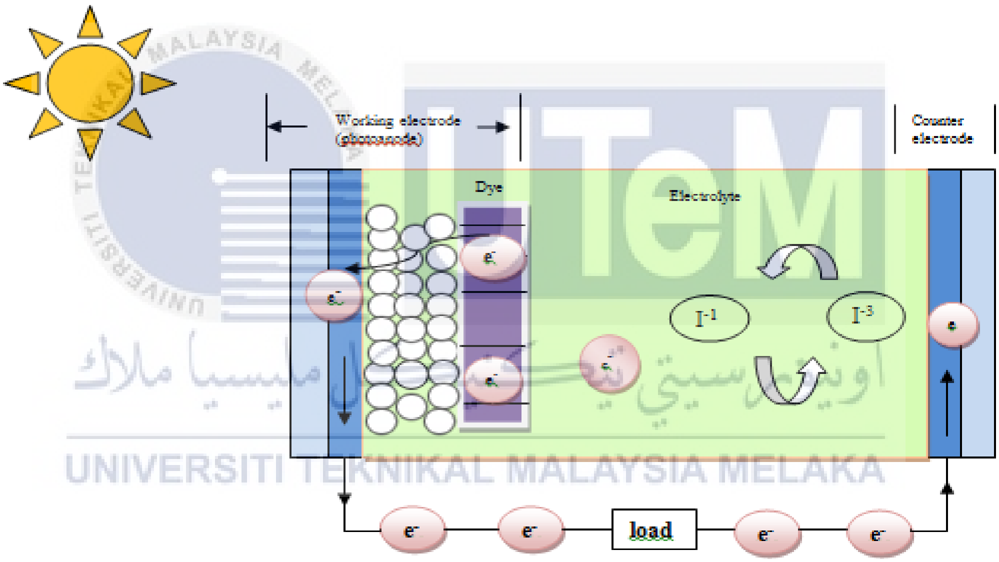


Figure 4 DSSC Schematic Diagram on energy flow for DSSC

2.2.2 Efficiency of DSSC

The overall performance of coloring sensitized solar cells depends on optimization and compatibility between TiO2 semiconductor and Dye molecules. The high surface area and the thickness of the TiO2 semiconductor film are a very important factor, which contributes to increased color loading and enhanced electron transport. Also, the DSSC's spectral response, such as the relative efficiency of the DSSC in light detection and photon absorption, depends on the absorption properties of the color used. Thus, the device's efficiency is measured through the quantum yield for the overall charge injection process and is referred to as the Incident Photon to Electrical Conversion Efficiency (IPCE). This quantity can be experimentally calculated according to the formula:

$$Isc = \int_0^\infty IPCE\ (\lambda).Isum\lambda\ d\lambda$$

$$IPCE = 1240(\frac{Isc}{\lambda p})$$

Where:

I_{sum}: is the incident irradiance as a function of λ

I_{sc}: is the current at short circuit

Thus for efficiency can be express as overall conversion efficiency of DSSC as:

$$\eta = \frac{Pmax}{Pin} = \frac{Isc.Voc.FF}{Pin}$$

Where:

FF: fill factor

P_{in}: solar power input

Voc: voltage across the point

2.3 Zinc oxide Nanorod

The ZnO was a semiconductor with great properties such as a small bandgap and strong binding exciton energy. At present, ZnO nanostructures such as nanoparticles, nanotube, nanowires, and nanorods have been extensively researched in various applications such as thermoelectric chips, solar cells, and chemical sensors due to their high potential. ZnO nanostructure can be obtained by various approaches such as chemical vapor deposition (CVD), metal-organic chemical vapor deposition (MOCVD), molecular beam epitaxy (MBE), the vapor-liquid-solid mechanism (VLS), thermochemical processes at various growth temperatures and thermal evaporation and condensation compliant with the desire applications. Nanorods provide unprecedented opportunities to explore the new physical properties within all nanostructures.

DSSC's basic function depends on the absorption of the incident light, the generation of electron-hole pairs, and the transfer of charge carriers to counter-electrodes. As most of the semiconductor oxide used in DSSC like TiO2 and ZnO are responsive to UV light only due to their corresponding wide energy bandgap. Another novel design of DSSC as described in (Chen et al., 2008), where the ZnO nanorods are grown on the top of a ZnO film to eliminate the heterogeneous junction interface. The contribution of this work is the growth of ZnO nanorods on ZnO film, in addition to expanding the concept of removing the heterogeneous interface between FTO and nanorods in cooperation with the growth of ZnO / ZnP composite nanorods at the top of ZnO film. The updated concept of composite nanostructure on ZnO film removes the heterogeneous interface and results in DSSC performance and conversion efficiency significantly improved.

2.3.1 Comparison of Zinc oxide (ZnO) and Titanium Dioxide (TiO_2)

From the characteristic of TiO_2 which has low electron mobility, it also has a low electron transport rate. Nevertheless, another oxide, which is ZnO, has high electron mobility and high potential as transparent anode candidates. Nevertheless, the efficiency of power conversion with ZnO is still lower than TiO2, and this relates to the low internal surface area. Due to low-cost preparation methods, nanoparticle TiO2 still maintains a favorable choice at DSSC. The mobility of TiO2 electron is small and influences the rate of electron transport, which means the rate at which the photogenerated electrons are transferred from the photoanode film to the external contact in the photoanode film, resulting in a decrease in the efficiency of the collection of photogenerated electrons.

2.4 Seed layer

The seed layer is an important factor in growing vertically aligned ZnO nanorods because the seed affects the growth alignment of ZnO nanorods. A study found the thickness of the seed layer influenced the alignment and morphology of the resulting ZnO nanorods. Additionally, the thickness of the ZnO seed layer affected the output of the dye-sensitized solar cell based on ZnO nanorods. Furthermore, reported that ZnO nanorods morphology was affected by the ZnO seed layer and a higher seed layer's concentration would lead to a longer thickness of ZnO nanorods.

Meanwhile, also has a study about the seed layer was deposited through a spin coating method because of its simplicity. Multiple spin coating treatments were conducted to improve the thickness of the seed layer. Therefore, for the growth of high-quality ZnO nanorod, the seed layer is very important and plays a major role in the high surface area of glass substrates.

2.5 Growth process

The growth process is a process to grow nanorod from the seed layer that creates from the seeding phase. The growth process shows the result of how crystalline, shape, length of nanorod been synthesized. The growth process has many methods such as CVD, CBD, Hydrothermal is among the most used technique been used for many researchers. The difference from approaches and methods used for the growth process is in terms of temperature used and thermal evaporation. For CVD, CBD used a high temperature compared to hydrothermal approaches.

2.6 Research Summary

Table show some recent research about synthesis zinc oxide nanorods. Dye-sensitized solar cells based on zinc oxide nanorod got much interest from researchers because the output result from this topic can be a stepping stone to get them out of the best of DSSC performance. From 2015 till now, the approaches that been made come from many methods such as focusing on seed layer thickness, control diameter of the seed layer, and many more.

In 2015, ZnO Nanorod efficiency obtained from control seed layer thickness by using the Chemical Bath deposition method. The highest efficiency is 0.42% from the 100mm thickness of the seed layer. Furthermore, the control diameter and length of nanorod by using a simple hydrothermal method also has been done. The result summary shows that average diameter increase by increasing the precursor. In addition, research about seed layer thickness been controlled from the sputtering method also been done in 2017. The results from this research stated that the thickness of the seed layer affects the grain size of nanorods which is 10mm thickness and grain size is 9.76nm.

Furthermore, for growth process study also show that various deposition time for the growth process affects the length of ZnO nanorods. It shows that growth time can control the length of ZnO nanorods. This research used the Chemical Bath Deposition method.

Years	References	Approaches	Results
2017	Influence of seed layer thickness on well-aligned ZnO nanorods via hydrothermal method. [9]	ZnO seed layers with different thicknesses 10, 20, 30, and 40 nm on silicon (100) substrate were prepared by dc-magnetron sputtering.	Thickness and grain size 10mm = 9.76nm 20mm = 11.57nm 30mm = 14.68nm 40mm = 14.89nm
2016	Fabrication and Photovoltaic Properties of ZnO Nanorods/Perovskite Solar Cells [Yasuhiro Shirahata]	Using Chemical Bath Deposition Various deposition time for growth	Lengths of the ZnO nanorods could be controlled by deposition time of ZnO seed layer
2015	Controlling Diameter, Length and Characterization of ZnO Nanorods by Simple Hydrothermal Method for Solar Cells [Ahmed H. Kurda]	Alteration in the immersion time at a given concentration can control the length of the ZnO nanorods. The solution concentration was varied from 15 to 35 mM for controlling the ZnO nanorods.	The average diameter of ZnO nanorods are increasing as the precursor concentration increases

2015	Recent improvements in dye-sensitized solar cells [Sugathan]	ZnO NR efficiency based on seed layer thickness Using Chemical Bath Depositon	10mm = 0.38% 20mm = 0.39% 50mm = 0.40% 75mm = 0.42% 100mm = 0.42%

Table 2 Recent Latest Research Summary about ZnO Nanorod including method and result obtained.

CHAPTER 3

Methodology

. This chapter provides the guideline in implementing the information and data gathered using a specific method to obtain and attain the required project objectives. The basic flowchart of this study also is illustrated in this section to give us a better idea of the progress of this project. This chapter presented an overview of the method that used that covers the whole segment of this project. Furthermore, it explains about procedures used for this project step by step.

3.1 Introduction

This section explains the procedure and method used in the synthesis process of ZnO Nanorods and analyzes performance on it for DSSC. There are three mains procedures in this zinc oxide nanorod project, which are the synthesis of zinc oxide nanorods and characterization, analysis performance, and simulation for light beam nanorod

In the synthesis process, zinc oxide nanorods are grow based on research journals. During synthesis, seed layer thickness to control the zinc oxide nanorods growth. The effect of the seed layer and ZnO nanorods growth can be to study the performance.

For the growth process, there are two methods used which is facing up the sample, and facing down sample. The position of the sample is variable to get the analysis of the effect of the exposed sample to the solution with ZnO nanorod growth.

In addition, simulation about light beam propagation in zinc oxide nanorod been simulated the get the result about light propagation in nanorod and electric field effect. The result simulation has been analyzed.

3.2 Synthesis Zinc oxide nanorods

The synthesis process is a method to produce nanoparticles by a combination of materials that break up bulk materials into atoms or ions. For zinc oxide nanorods, the Hydrothermal method used as a method to grow the nanorods. Hydrothermal can be defined as a chemical reaction of single crystals that depends on the solubility of minerals in hot water under high pressure.

The flow of the synthesis process can be referred to as the figure below, as which cleaning process be done first. Then, the seeding phase to make seed layer zinc oxide on the glass. From the seed layer, nanorods can grow by using a hydrothermal reaction.

In addition, for this project seed layer thickness be controlled to get the ideal zinc oxide nanorods. Based on research, seed layer thickness gave affect the growth of nanorods.

Figure 5 Flow process of zinc oxide nanorods synthesis start with clean ito glass, seed layer used spin coat, and hydrothermal growth

3.2.1 Flowchart Synthesis Zinc Oxide Nanorod

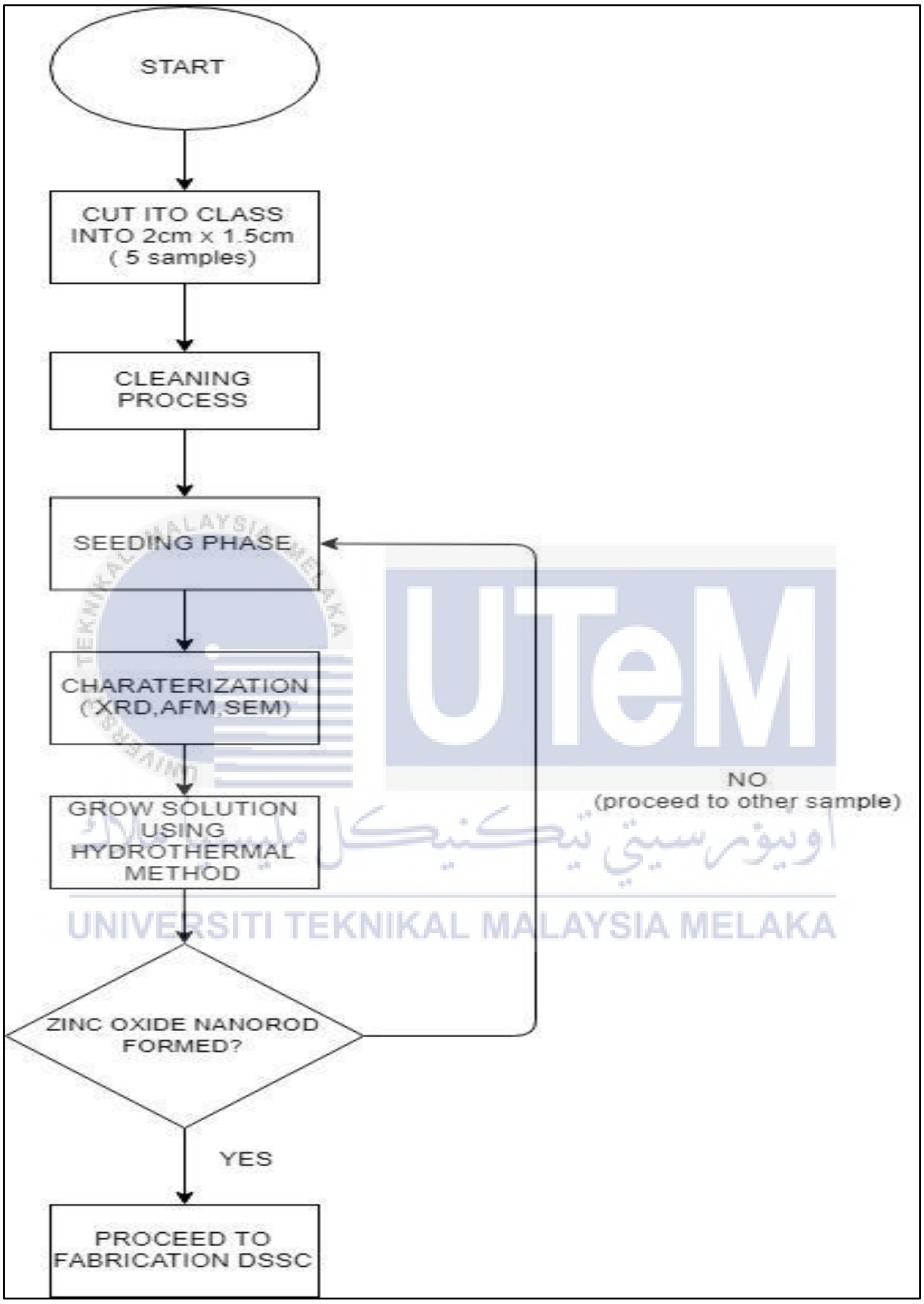


Figure 6 Flowchart of synthesis ZnO NR's

3.2.2 Materials and equipment

All of the materials used for this process be more on chemical reactions based on zinc oxide.

i. Zinc acetate
ii. Zinc nitrate
iii. Ethanol
iv. Deionized water
v. Iodine

For equipment, it placed in Lab PV and Thin Film and ready to use for this project development

i. Spin coater for seeding phase

Figure 7 Spin Coater Used For Seed layer on glass substrate with different speed and time

ii. Ultrasonic bath use for cleaning equipment

Figure 8 Ultrasonic bath used for clean equipment and sonicate

iii. Hot plate Magnetic stirrer to stir the solution till dissolved

Figure 9 Hot Plate To Stir The Solution To Dissolved in Solution

iv. Oven use for heat treatment and growth process

Figure 10 Oven For Annealing Growth Process

v. ITO coated glass cut into size to be sample and holder

Figure 11 ITO Coated Glass that conduct electricity used as electrode and holder for this project

3.2.3 Cleaning process

The cleaning process purposely to remove dust and stain on the glass. Dust and stain are very sensitive and affected the surface of glass if not remove. Glass substrate firstly was cleaned by using soap, then immersed with IPA, ethanol, and rinsed with deionized water. Ultrasonic bath used for this process to sonicate while immersing the glass. Make sure glass not overlapping each other.

Figure 12 Sonicate process for equipment to clean equipment experiment. Sonicate in 15minutes with Di water in equipment

3.2.4 Seeding phase

A seed layer solution was made by mixing 1mM zinc acetate(Zn) and ethanol dissolved together. The prepared seed layer solution was coated on the ITO glass substrate by spin coater. The unit mole (M) for 1 mM of zinc acetate dihydrate and 1 mM of sodium hydroxide needs to be converted in gram as it is easier to be implemented. The formula for converting from mole to gram is shown below

Mass (g)= Molecular mass (gmol) x Concentration x Volume of solution

The concentration of a solution is based on ZnA that be used and can be referred from the product of ZnA. In this process, the volume of the solution is used 60ml of ethanol. So the mass obtained is 0.0312gram.

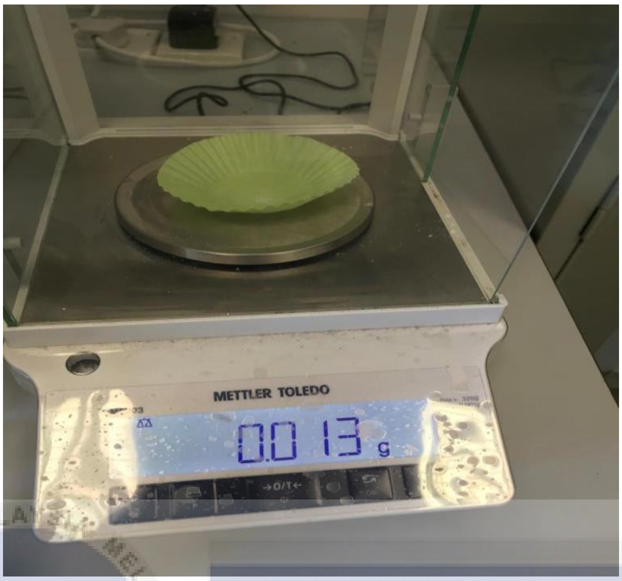


Figure 13 Mass of zinc acetate with 0.013gram

The resulting seed layer solution was a drop on ITO glass then spin coat at 3000rpm in 20seconds. The spin coating method was used to deposit the seed solution on ITO glass substrates and followed by thermal treatment at 70°C for 5 minutes by using a hot plate. This step count as one cycle process and no cycles were decided as the variables respectively to control the thickness seed layer. Lastly, anneal the ITO glass with a high temperature in a furnace for 250°C in 5hours.

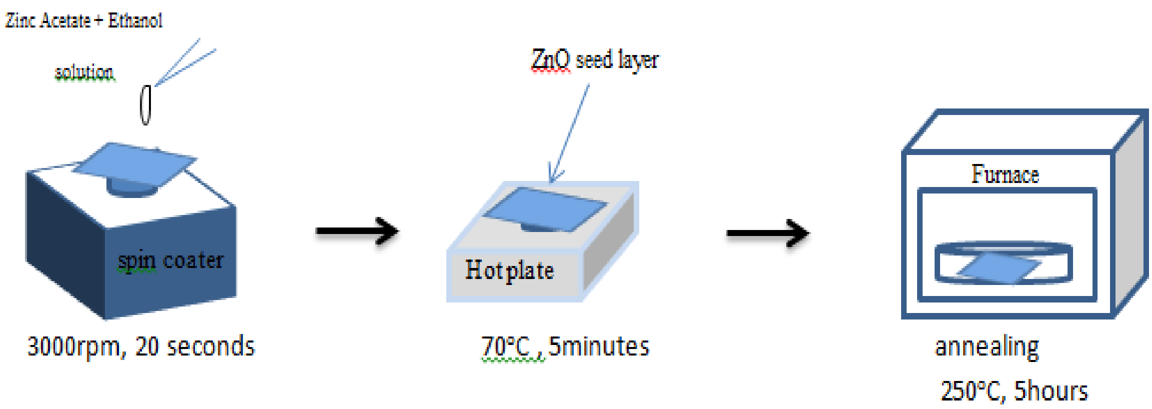


Figure 14 Flow process for seeding phase, Sample on the top spin coat for 3000rpm and 20seconds, annealing using a hot plate and furnace

Annealing process be done by using furnace at Fakulti Kejuruteraan Pembuatan (FKP).

Figure 15 Furnace for annealing 250celsius for 5hours

3.2.5 Design of experiment (DOE)

Design of experiment (DOE) is designed for this project to focus on controlling zinc oxide nanorod by seed layer thickness. DOE function is to create a trend that can help to analyze performance based on trends or graphs that obtain. DOE also can use to solve the problem for this project.

For this project, DOE creates to control no of cycles of spin coating and heat treatment. From the figure below, no cycles various from 10, 20, and 30 for a different sample. The other two samples not use a spin coat for deposition and use one drop of seed layer solution. From table DOE, the project organized properly and objectives can be achieved. It also can track the problem during the process of this project

Sample	No of cycles	Spin coating (3000rpm, 20seconds)	Heating Treatment (70°C, 5 minutes)
1	10	Yes	Yes
2	20	Yes	Yes
3	30	Yes	Yes
4	10	No (filtered solution)	Yes

Table 3 Design of experiment to control the seed layer using 5 sample with different approach of spin coant and heat treatment.

3.2.6 Growth of nanorods

The growth solution for ZnO nanorods fabrication made by mixing an equimolar solution containing 10 mM of Zinc nitrate with hexamethylenetetramine in deionized water. Firstly, ITO glass with the seeded sample was set up facing down with holder 2mm thickness to make a gap between surface and ITO glass.

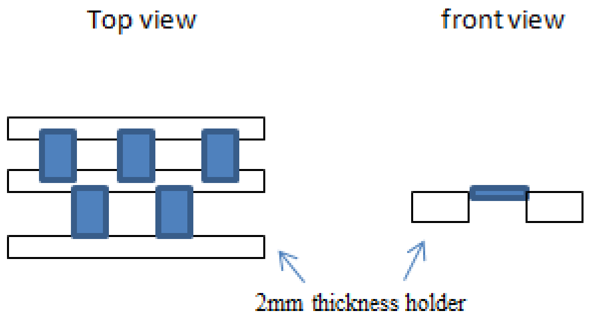


Figure 16 Diagram View for Growth Sample and Holder position than placed in a beaker.

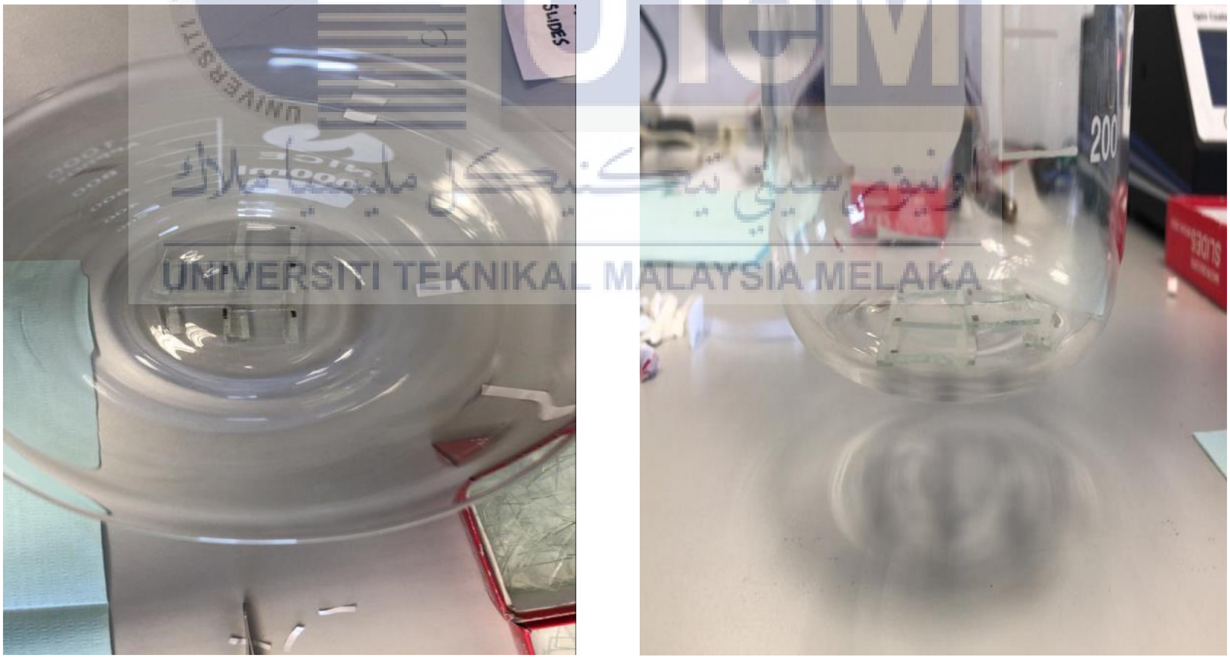


Figure 17 Growth Process During Experiment in Lab

Same as the seeding process, for chemical solution for growth process also converted into gram from 10mM. The solution is 400ml as 100ml for the first step then change the solution for every 5hours.

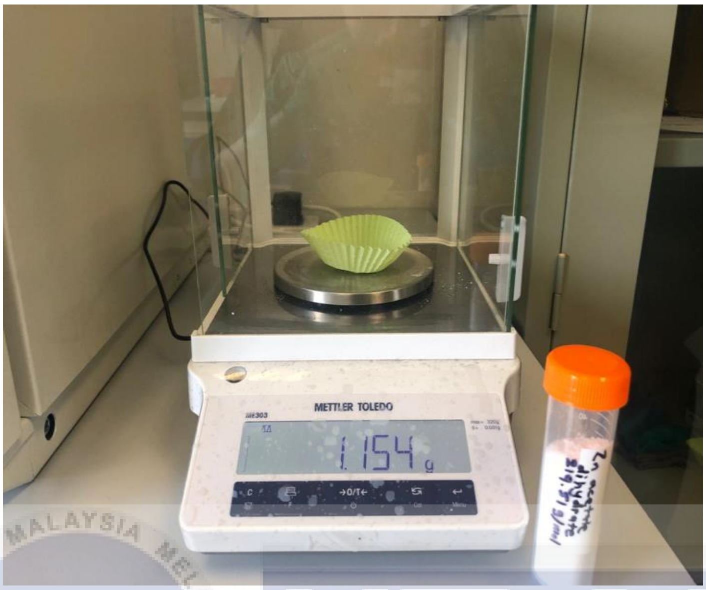


Figure 18 Mass of Zinc Nitrate

Then, the seeded sample placed and beaker and pour growth solution into the beaker. The samples need to immerse completely with the growth solution. For the growth process, the oven was used as a heating element. Beaker with the seeded sample placed in oven and heat 90°C for 15hours. The solution was replaced every 5 hours with a new precursor solution to maintain a steady rate of growth of ZnO nanorods.

Furthermore, it avoids the degradation of the chemical during the growth process. The sample was rinsed with DI water at the end of the process and dried in the furnace at 350 ° C for 1 hour.

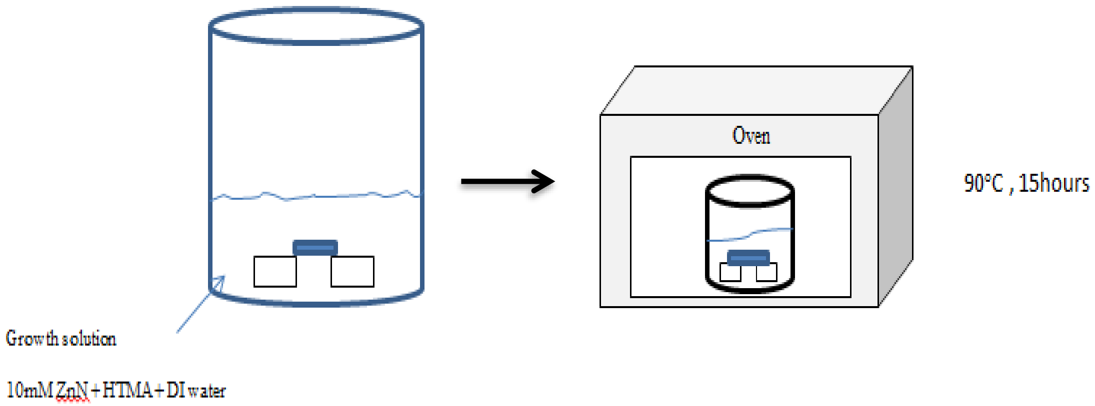


Figure 19 Flow Process For Growth Process, Start with sample immersed with solution then heat treatment in oven 90celsius for 15hours

Characterization used to analyze the results of performance. Characterization used to scan zinc oxide nanorod quality. Quality of zinc oxide nanorods can be categorized in terms of crystalline, properties, size, and density of nanorods. Three types of equipment used for this project:-

i. Scanning Electron Microscope (SEM)
   - produces images of a sample by scanning the surface with a focused beam of electron

ii. Atomic Force Microscope (AFM)
   - produces images of a sample by scanning the surface with a focused beam of electron

iii. X-ray Diffraction
   - Determine crystalline of zinc oxide nanorods

iv. UV Vis spectroscopy
   - To measure wavelength and absorption of light from zinc oxide nanorods.

Results image from characterization being analyzed and discuss the sample images. It can be used as a reference for the next sample or reference for further studies.

3.3 Simulation using COMSOL Multiphysics software

COMSOL is a software for the simulation of finite elements, solver, and multiphysics across platforms. It makes user interface based on traditional physics as a workflow for electrical, mechanical, fluid, acoustics, and chemical applications. For this project, COMSOL software used to study the wave optical affected on nanorod and scattering section of one rod. It can define the result of zinc oxide confinements in a cylinder shape.

The wave mechanics principles used for modeling, and the electromagnetic waves being analyzed in the frequency domain. This interface is used to solve electromagnetic field distributions with time-harmonies. It also solves the Electric field time-harmonic wave equation.

3.3.1 Flowchart Simulation Experiment

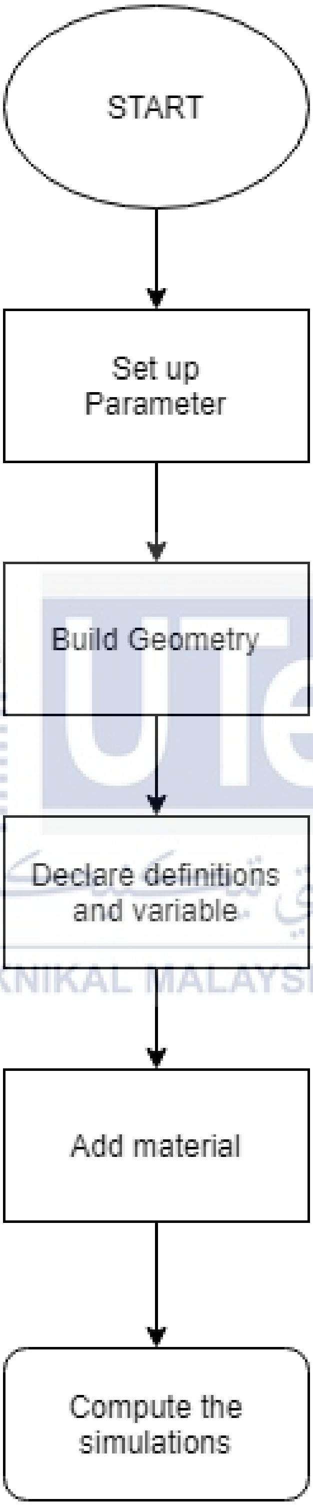
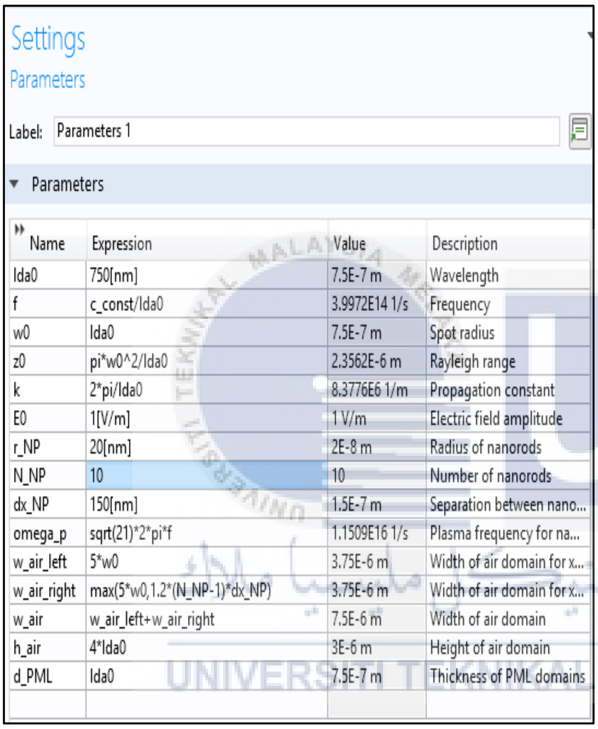


Figure 20 Flowchart for Simulation Using COMSOL

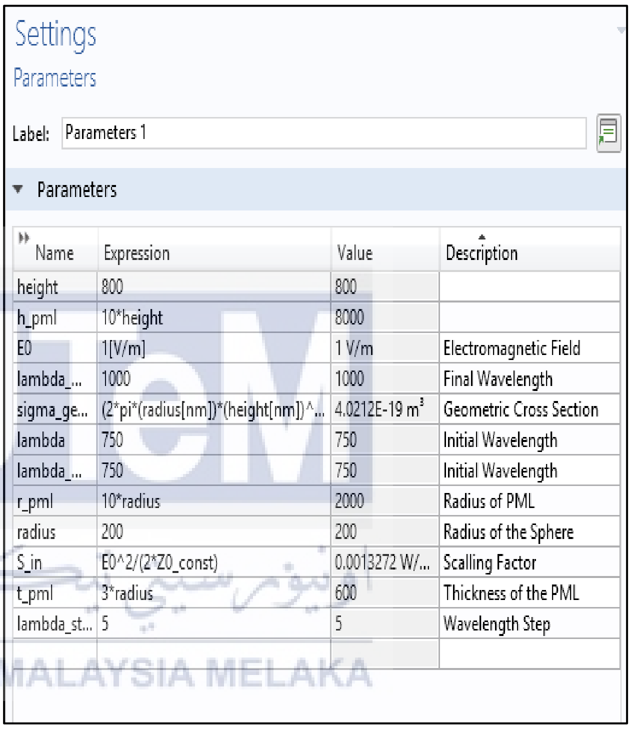
3.3.2 Simulation parameter

Parameters are the most important part of COMSOL software. In parameter settings, all the variables, properties, and definitions need to be declared to compute the study based on electromagnetic waves. This parameter effect the other setting that needs to be set to run the simulation. In parameters, it includes the geometry settings, the integration, and expression for the simulation study.



Settings
Parameters
Label: Parameters 1
Parameters

Name	Expression	Value	Description
lda0	750[nm]	7.5E-7 m	Wavelength
f	c_const/lda0	3.9972E14 1/s	Frequency
w0	lda0	7.5E-7 m	Spot radius
z0	pi*w0^2/lda0	2.3562E-6 m	Rayleigh range
k	2*pi/lda0	8.3776E6 1/m	Propagation constant
E0	1[V/m]	1 V/m	Electric field amplitude
r_NP	20[nm]	2E-8 m	Radius of nanorods
N_NP	10	10	Number of nanorods
dx_NP	150[nm]	1.5E-7 m	Separation between nano...
omega_p	sqrt(21)*2*pi*f	1.1509E16 1/s	Plasma frequency for na...
w_air_left	5*w0	3.75E-6 m	Width of air domain for x...
w_air_right	max(5*w0,1.2*(N_NP-1)*dx_NP)	3.75E-6 m	Width of air domain for x...
w_air	w_air_left+w_air_right	7.5E-6 m	Width of air domain
h_air	4*lda0	3E-6 m	Height of air domain
d_PML	lda0	7.5E-7 m	Thickness of PML domains



Settings
Parameters
Label: Parameters 1
Parameters

Name	Expression	Value	Description
height	800	800	
h_pml	10*height	8000	
E0	1[V/m]	1 V/m	Electromagnetic Field
lambda_...	1000	1000	Final Wavelength
sigma_ge...	(2*pi*(radius[nm])*(height[nm])^...	4.0212E-19 m^3	Geometric Cross Section
lambda	750	750	Initial Wavelength
lambda_...	750	750	Initial Wavelength
r_pml	10*radius	2000	Radius of PML
radius	200	200	Radius of the Sphere
S_in	E0^2/(2*Z0_const)	0.0013272 W/...	Scalling Factor
t_pml	3*radius	600	Thickness of the PML
lambda_st...	5	5	Wavelength Step

Figure 21 Parameter Setting to set up the run of simulation such as height and radius of nanorod.

3.3.3 Geometry Build Up

Geometry set up is used to set up the shape of an object or sample to simulate. Geometry setting includes the width, length, radius already declare in the parameter. Furthermore, it also depends on the space dimension selected. For this simulation, space dimensions in 2D and 3D choose to be computed. For example in 2D, it used a rectangle as base and circle as reference for one nanorod. In 3D, the cylinder used as a physical domain and perfected match layer.

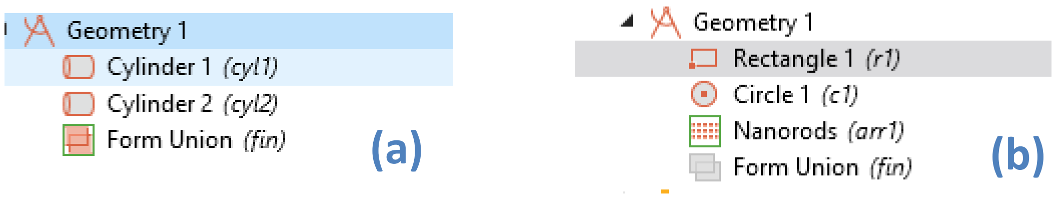


Figure 22 a) Geometry Set up For 3D cylinder b) Geometry setting for 2D simulation

3.3.4 Definitions declaration

In column Definitions, there are variables and selections to be set up to get the ideal parameters. In variables, integration for simulation to compute the solution set in terms of expressions. For selections, the layer or surface from geometry selected to choose which boundary or domain to be set up and declarations.

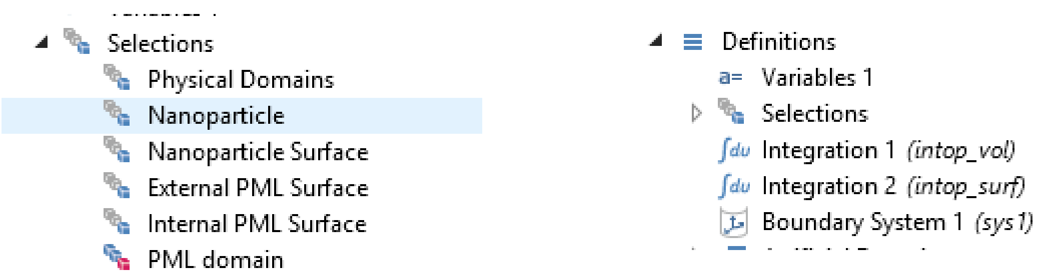


Figure 23 Domains and Boundary Parameter Setting For Nanoparticle and PML

3.3.5 Material properties

The main materials used are "Air" and Zinc oxide. Air used for a physical domain that occupies all the space in geometry building. For zinc oxide, it added to zinc oxide nanorod based on geometry entity selections.

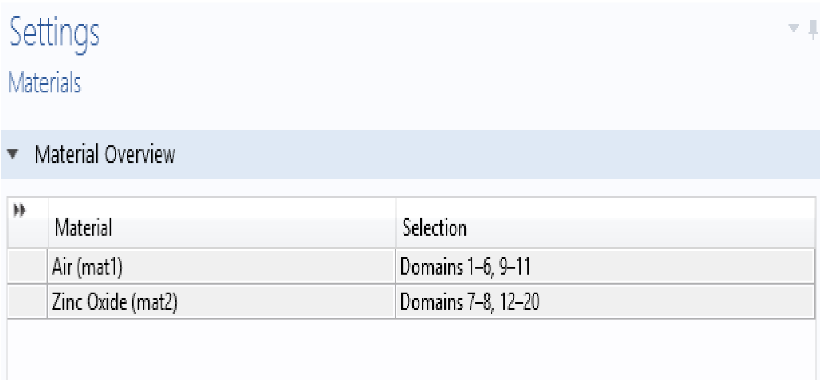


Figure 24 Materials Properties of Nanorod, material used in simulation for nanorod

Zinc oxide has its properties based on semiconductor materials content. It also includes based on the wave equation for electric and displacement of electric material content. The data parameters set to be variables based on other research in terms of semiconductor material of zinc oxide.

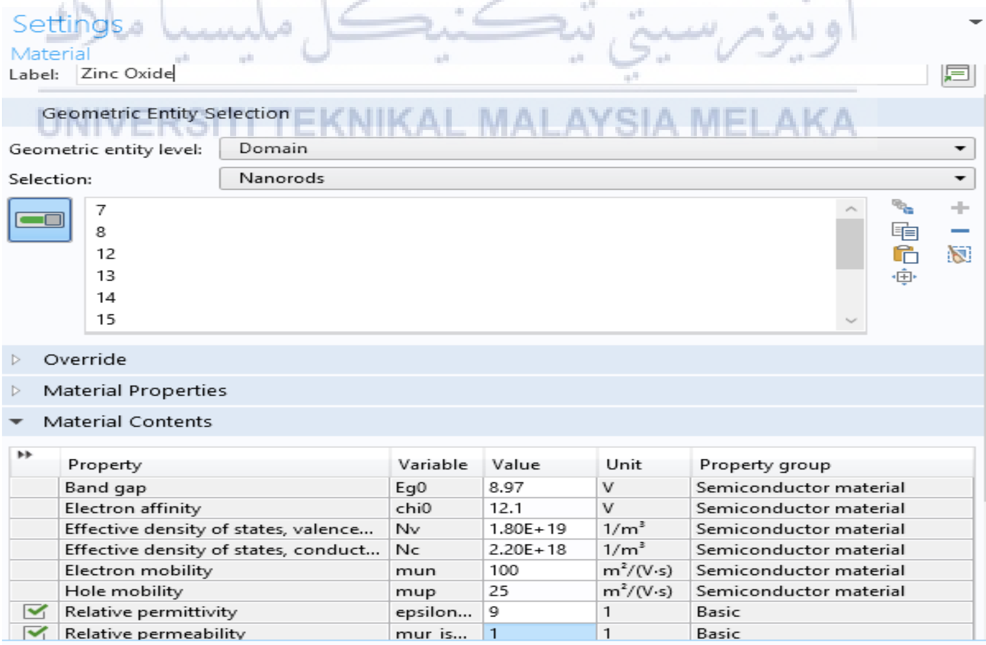


Figure 25 ZnO semiconductor material properties and contents

CHAPTER 4

RESULT AND DISCUSSION

This chapter provides the result obtained. The result obtained is analyzed and presented in the discussion part of this chapter. Experimental results consist of five samples with different designs of experiments. Then, the characterization results obtained observed and analyzed.

4.1 Introduction

This chapter pursues the result and performance analysis of the method for the project. At first, the synthesis method approach is presented with zinc oxide nanorod from the seeding phase and growth process. The best sample method is chosen based on the analysis performance of results from characterization.

4.2 Characterization of zinc oxide nanorod

4.2.1 Scanning Electron Microscope (SEM)

A scanning electron microscope (SEM) is a machine that produces images of a sample by scanning the surface with a focused beam of the electron. SEM uses a focused beam of high-energy electrons to generate a variety of signals at the surface of a solid sample. It also used for observation and analysis in various fields. It depends on the release of the electron to clarify an object on the surface of the sample. In a scanning mode, the area ranging from SEM can be set by adjusting the magnification ranging and spatial resolution.

In this project, SEM was used to identify the morphology of zinc oxide nanorod after done synthesis process. The image of zinc oxide nanorod been analyzing in terms of uniformly and crystalline of shape zinc oxide nanorod. Diameter and length of one nanorod in each image calculated from SEM.

Five samples with different no of cycles during the seeding phase performed observation and analysis. Then all samples continued with the growth of ZnO nanorod with two methods which is facing up and facing down the position of the sample.

Sample	No of cycles	Spin coating (3000rpm, 20seconds)	Heating Treatment (70°C, 5 minutes)
1	10	Yes	Yes
2	20	Yes	Yes
3	30	Yes	Yes
4	10	No (filtered solution)	Yes
5	10	No (no filter)	Yes

Figure 26 Design of Project to create a trend for analyzing the seed layer results

The result of five different samples with a facing down method be observed as shown in the figure below. The SEM images have two different ranging areas and magnification to get the best analysis around the samples.

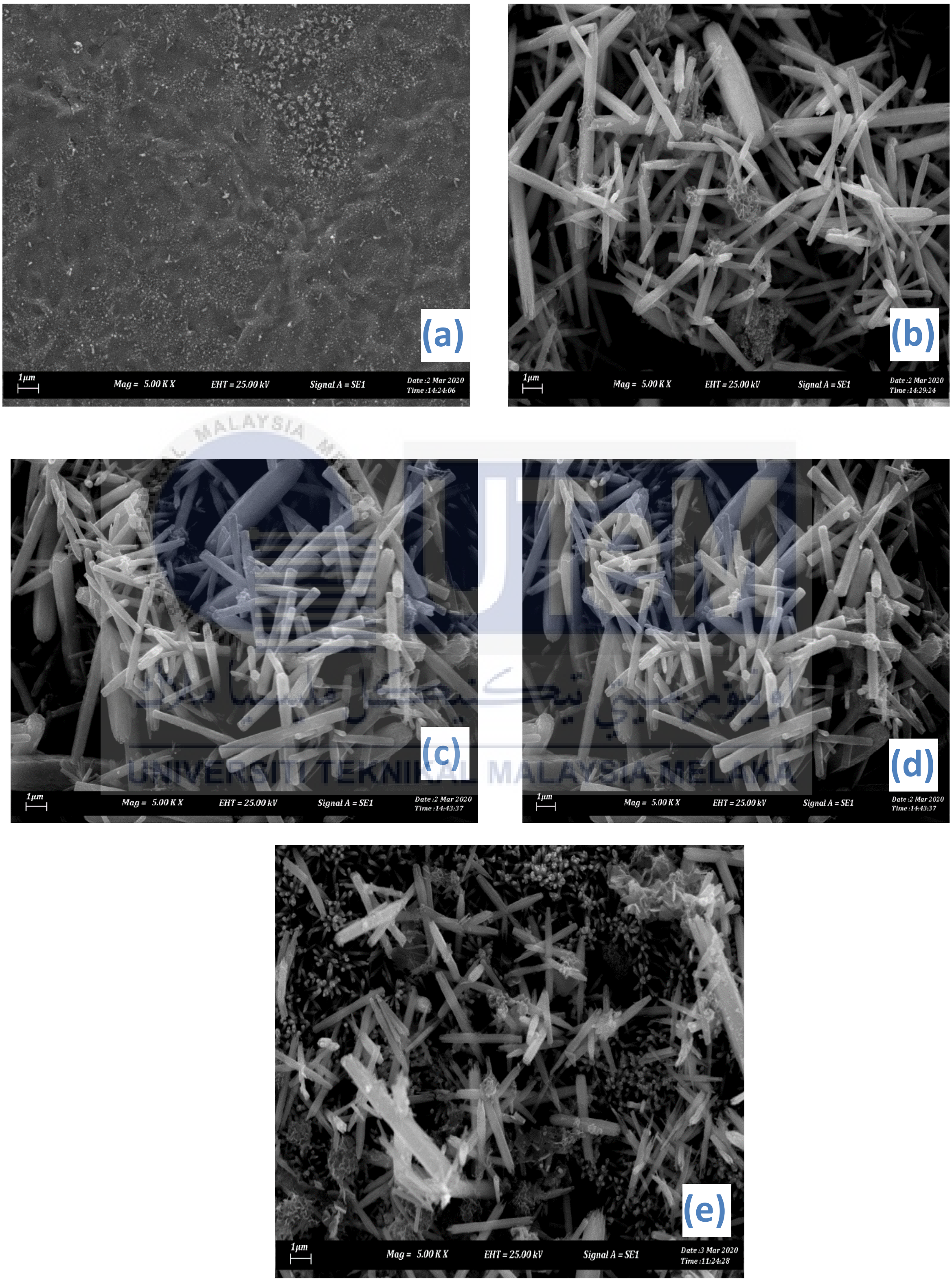


Figure 27 Magnification 5.0kX (facing down method)

(a) Sample 1 (b) Sample 2 (c) Sample 3 (d) Sample 4 (e) Sample 5

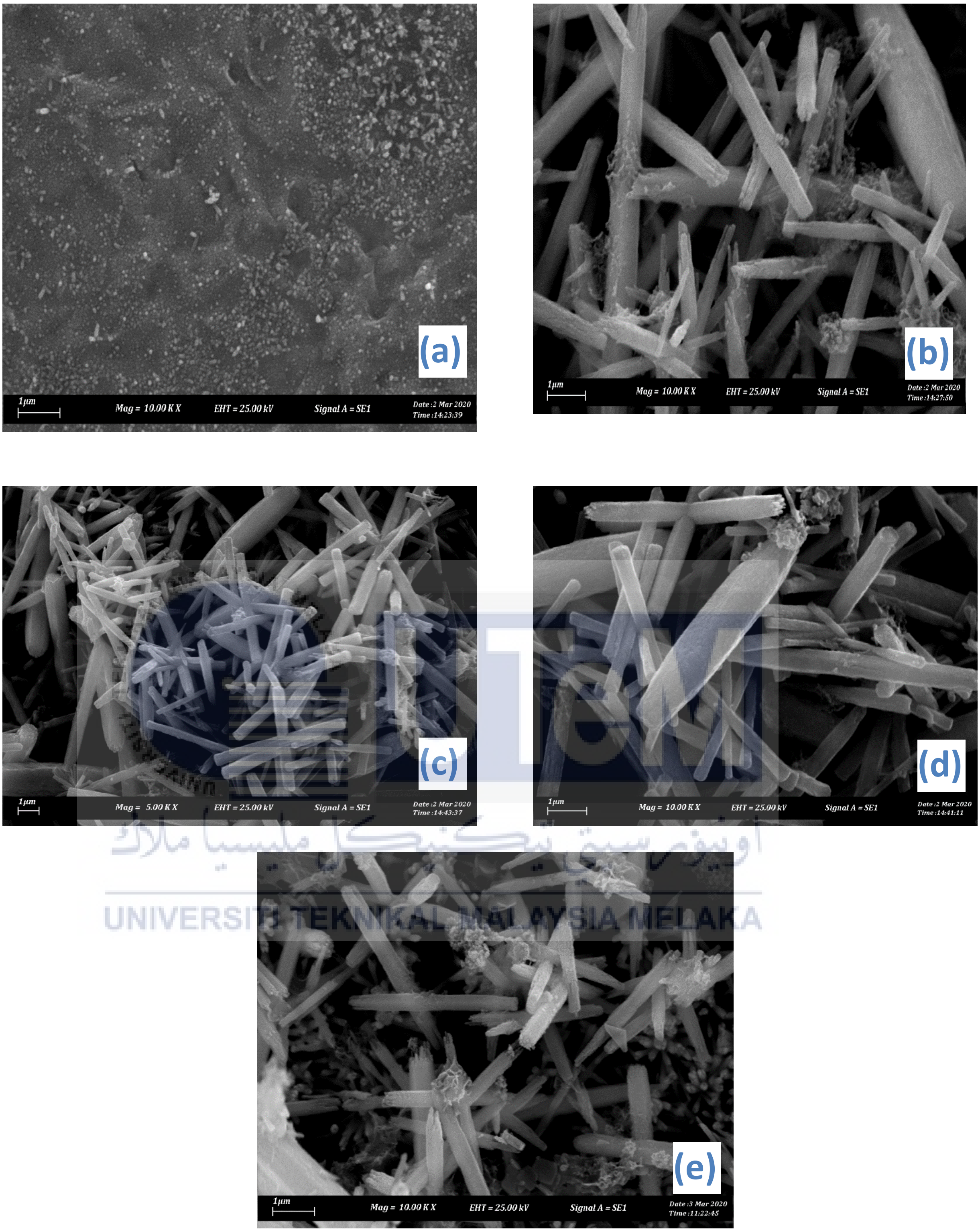


Figure 28 Magnification 10.0kX (facing down)

(a) Sample 1 (b) Sample 2 (c) Sample 3 (d) Sample 4 (e) Sample 5

As we can analyze and observe the image from the result of the SEM facing down method above., there are two different magnification for each sample. Firstly, magnification with 5.0kX showed that the more surrounding of each sample than 10.0kX than zoom for a certain part for nanoparticle. The ideal result from this method is Sample 2, Sample 3, Sample 4, and Sample 5. The SEM results show that the image of nanorod shapes and crystalline the nanorod in the sample. As for Sample 1, the sample show image that no presence of nanorod in the sample for both magnification

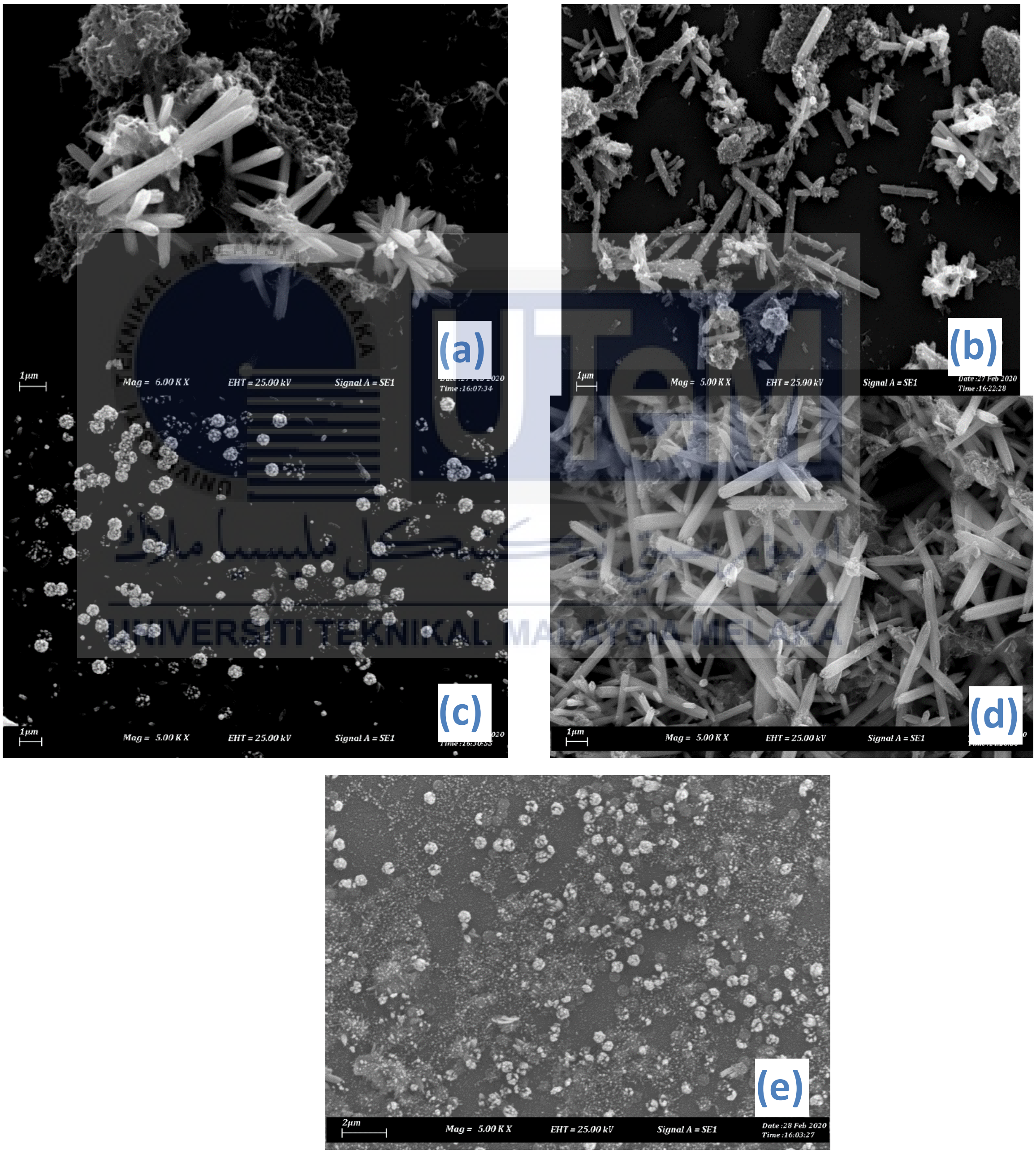


Figure 29 Magnification 5.0kX (facing up method)

(a) Sample 1 (b) Sample 2 (c) Sample 3 (d) Sample 4 (e) Sample 5

For the facing up method, from observation SEM image results analysis that can be made is most of the sample not achieve crystalline of nanorod in image result. Both magnifications show that nanorod grows randomly in the sample and not uniformly or vertically grows. Analysis can be made is facing up make sample fail to grow the nanorods on the sample.

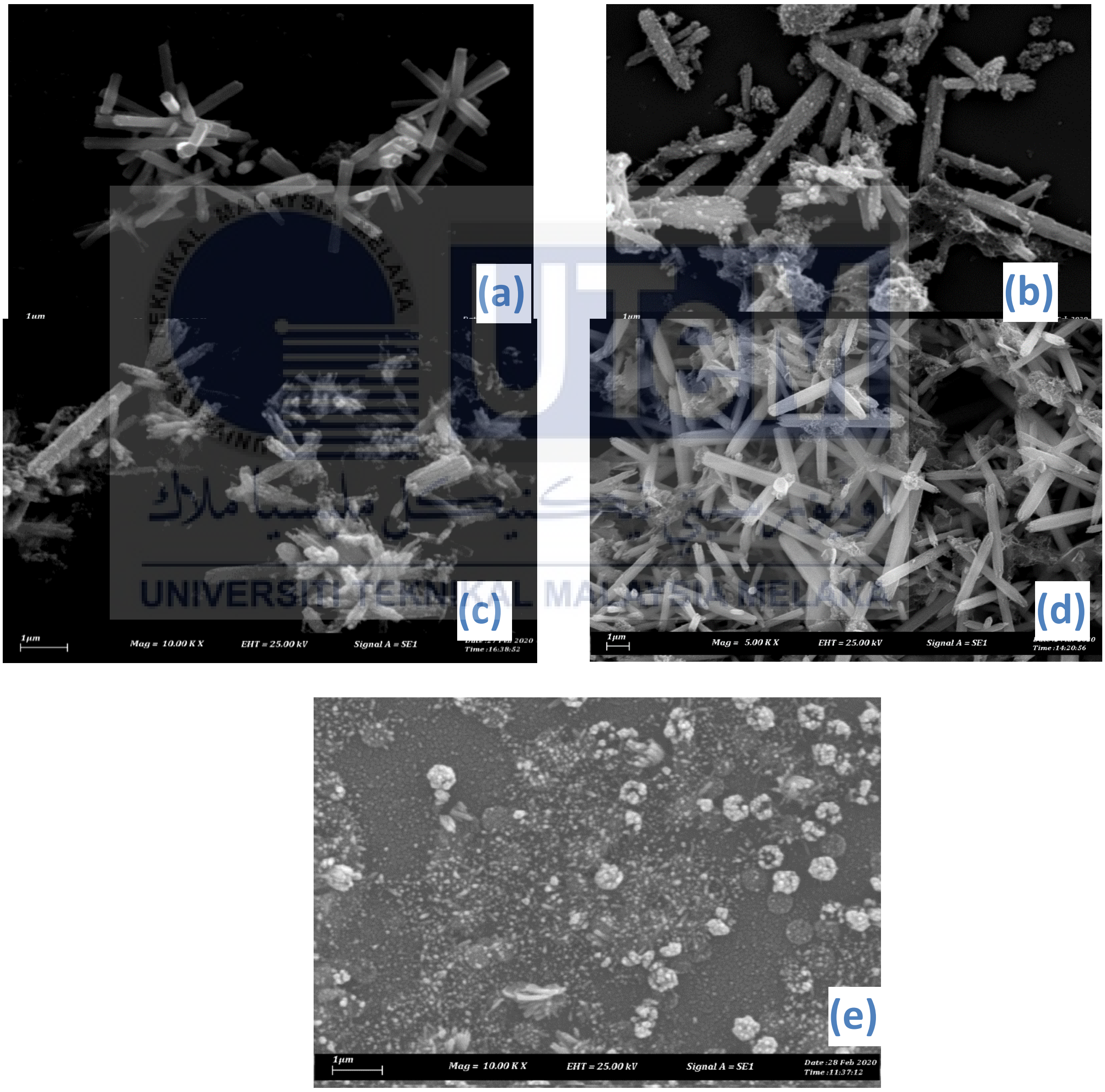


Figure 30 Magnification 10.0kX (facing up method)

(a) Sample 1 (b) Sample 2 (c) Sample 3 (d) Sample 4 (e) Sample 5

4.2.2 X-ray Diffraction (XRD)

X-Ray Diffraction (XRD) was utilized for the physical construction of the ZnO thin films. X-ray diffraction measurement with data analysis was used to classify the crystalline phase of the materials and to disclose details on unit cell measurements. Cathode ray tube and filter produced by X-ray generate monochromatic radiation and concentrate directly on the sample. X-ray diffraction peaks are created by constructive interference of a monochromatic X-ray beam scattered at a particular angle

XRD pattern of the crystal structure and orientation of the nanocrystalline ZnO nanorods deposited on glass substrate using spin coating at 3000 rpm, pre-heated at 90˚C and annealed in air at 250˚C. X-ray Diffraction (XRD) profiles of the ZnO nanorods, glass facing up, and glass facing down during growth process respectively. It can be seen that the XRD profiles of the two structures are considerably different. Another factor to be considered is the number of cycle spin coating during the seeding process. From the XRD pattern, one can clearly observe a diffraction peak at 2θ, and the height for facing up sample is slightly higher than facing downsample. Strong preferential growth is observed along the c-axis, suggesting that the prepared ZnO nanorods have the wurtzite structure.

The graph below shows the diffraction of a peak for each sample for both methods which is facing down and facing up. The graph shows the relationship between intensity for the y-axis and the scattering angle for the x-axis. From the result below, all sample facing down methods show the presence of zinc oxide and zinc acetate in the sample. This can be analyzed from the peak structure along the c-axis based on the wurtzite structure. Meanwhile, for all sample facing up did not show any peak of diffraction of any structure.

a) XRD Facing Down Method

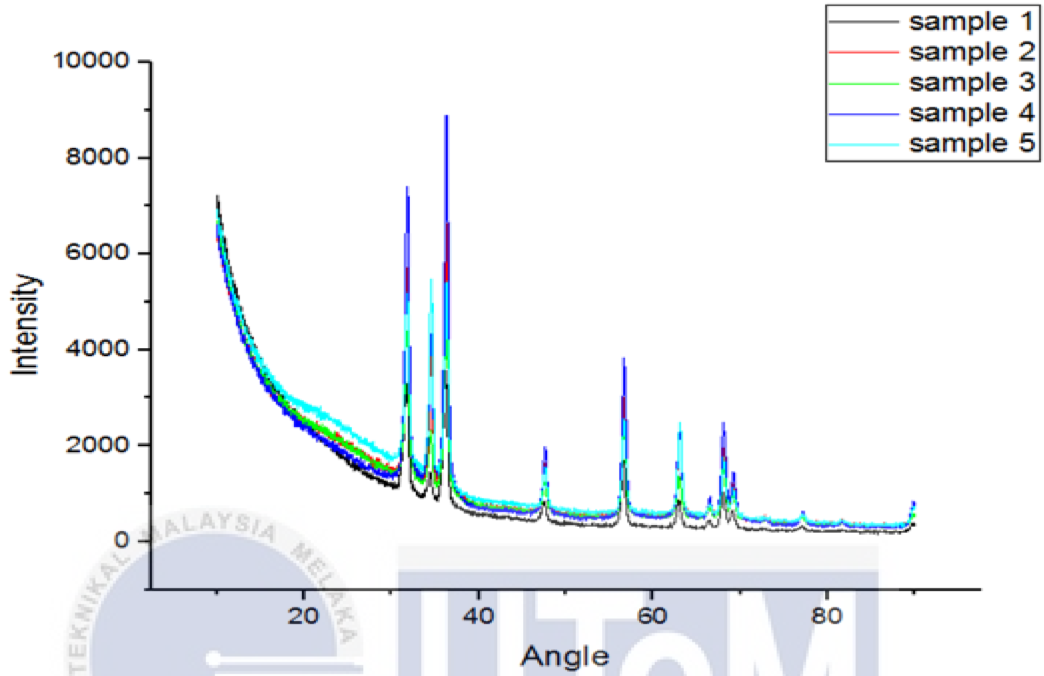


Figure 31 XRD pattern for facing down method ZnO nanorods

b) XRD Facing Up Method

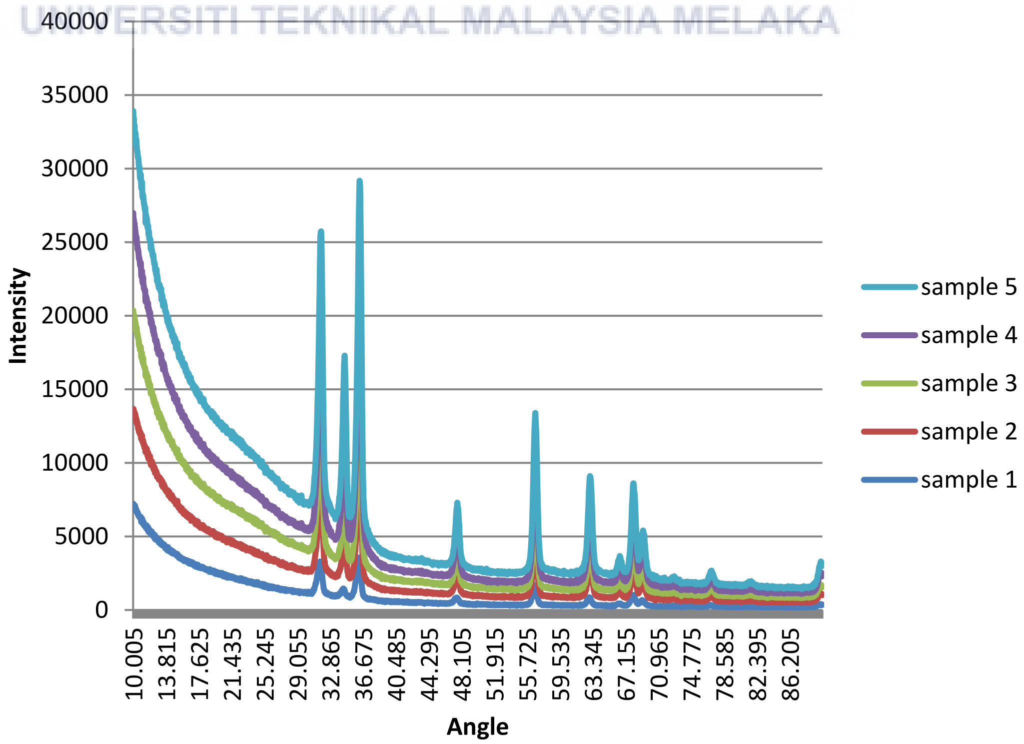


Figure 32XRD pattern for facing up method ZnO nanorods

The scan range is between 10° to 90°. The XRD pattern in sample1 and 2 is normal. However, the peak intensity of sample 2 is higher than sample 1 and the amount of zinc oxide powder in sample 2 is well balanced. Sample 3 has the highest peak intensity and the electron density variation for this sample also the highest that the other samples. The XRD pattern fits well with a wurtzite structure. The height of the peak higher if any preferred crystal orientation is existing but if crystals are arranged in a chaotic or random, the peak below. As the electron density variation is increased, the intensity for the plane reflected in the XRD pattern also increases. The peak intensity represents the atomic position in the crystal structure. I take the powder or chemical of the sample and measure with XRD again, the intensity is probably decrease.

4.2.3 UV-VIS Graph

UV-Vis refers to absorption spectroscopy or reflectance spectroscopy in part of the ultraviolet and the full, adjacent visible spectral region. UV-visible absorption spectroscopy is widely being used technique to examine the optical properties of nanoparticles.

The UV and visible light range between 400 nm to 700 nm in the test tube generally do the electronic transitions where the molecules can absorb the light in the UV and visible region. As the electronic transition can go from lower energy state to higher energy state. Increasing the distance in the energy band required more energy to be absorbed by the ZnO nanorod as the range of optical absorption of ZnO nanorod wavelengths can be controlled by adjusting scale.

a) Facing down method

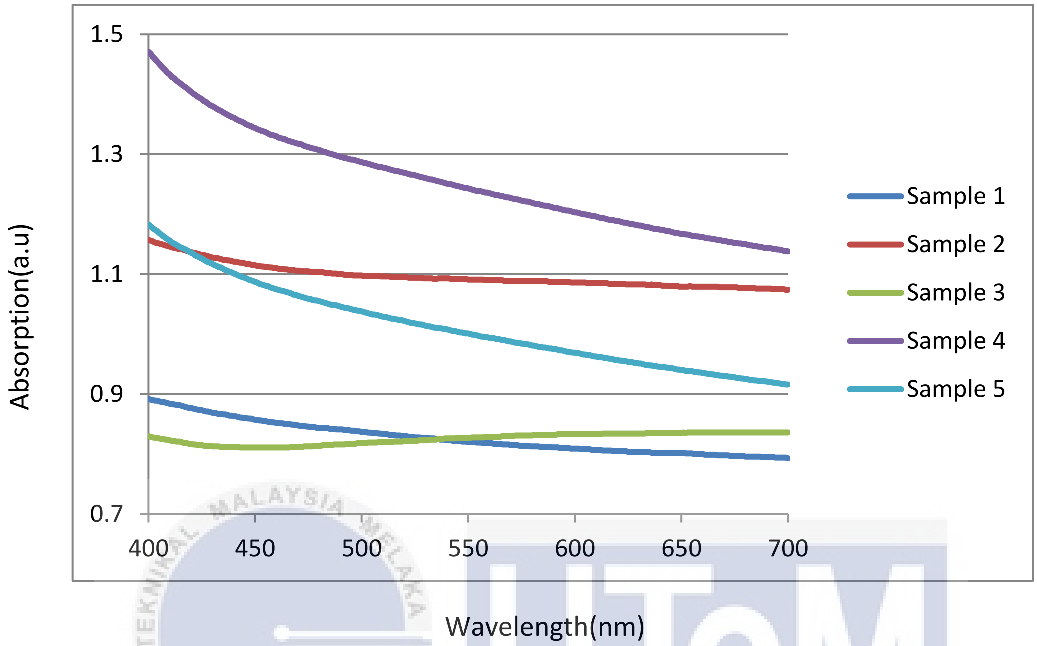


Figure 33 UV Vis graph facing down

Based on the graph result from characterization by using UV-Vis, it shows the absorption of light from each sample. Sample 4 shows the higher absorption at wavelength 400nm than other samples. Sample 3 shows the lower absorption light. The higher the absorption shows the good performance of the sample because it shows that it absorbs more light at a certain wavelength.

For facing up method, it shows all sample in a linear graph from the initial wavelength to the final wavelength. The higher number of absorption is 0.4 a.u is lower than the facing down method. It shows that it less absorption of the light for the sample facing up method.

b) Facing up method

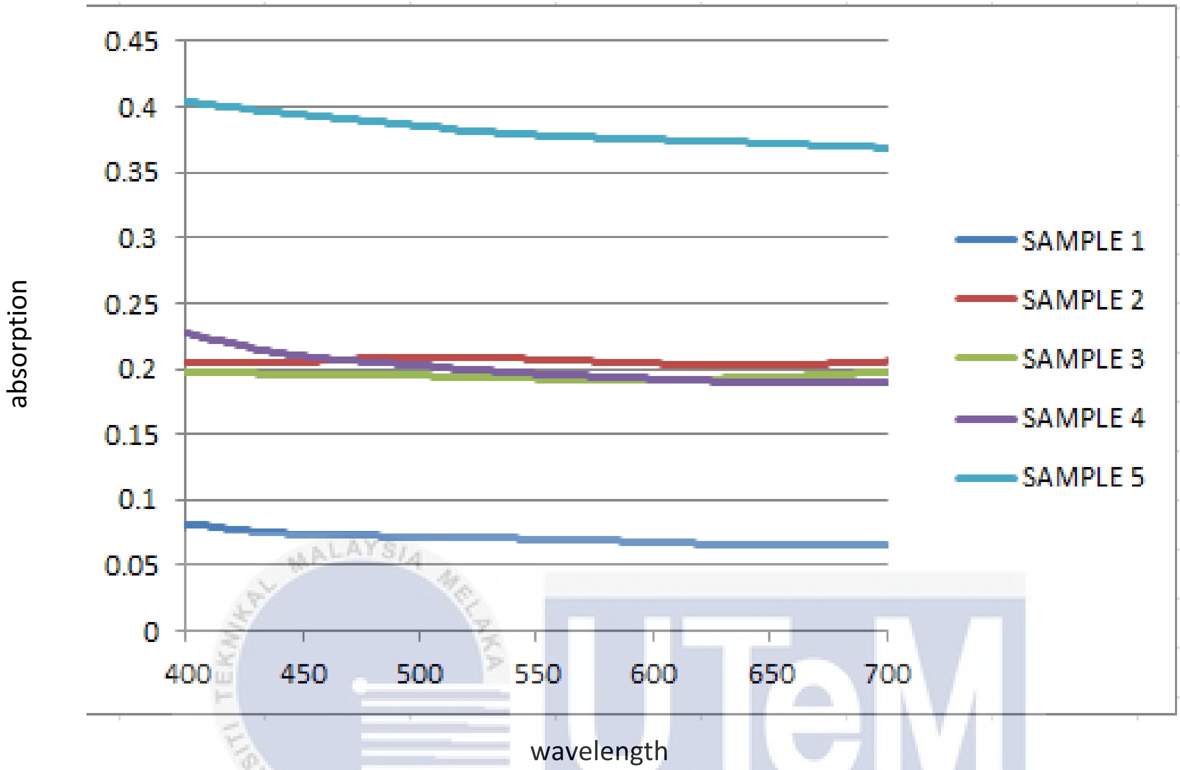


Figure 34 UV-Vis facing up method

4.3 Characterization summary

In summary, all characterization results show that facing down methods during the growth process is the best ideal to get the best quality zinc oxide nanorods. Based on SEM results, the image shows that nanorod that grows more vertical, uniformly, and crystalline. In addition, the XRD result of that peak of diffraction shows that the presence of zinc oxide and high peaks that match with the wurtzite structure. Furthermore, the UV-Vis graph plot the higher absorption of light during the initial wavelength.

4.4 Scattering section and light propagation of cylinder (Nanorod)

4.4.1 Simulation 2D cylinder

Simulation for the 2D cylinder that represents a shape of nanorod to simulate the propagation of light Gaussian beam across the nanorod. Ten nanorods arranged on arrays and the Gaussian beam set up to propagate into the center of arrays. The result of the simulation produced the electric field (ewfd) characterization and graph between the electric field and wavelength.

a) Design a model

The model of nanorod on a flat surface is designed to test the gaussian electromagnetic wave on a dense array between the rods. The distance between 10 rods propagated the electromagnetic wave. Rod array behaves as a continuous metal sheet for light polarized along the rods. For the first model simulation, zinc oxide material added to all nanorods.

Figure 35 Model of array with ten nanorods'

b) Electric field (ewfd)

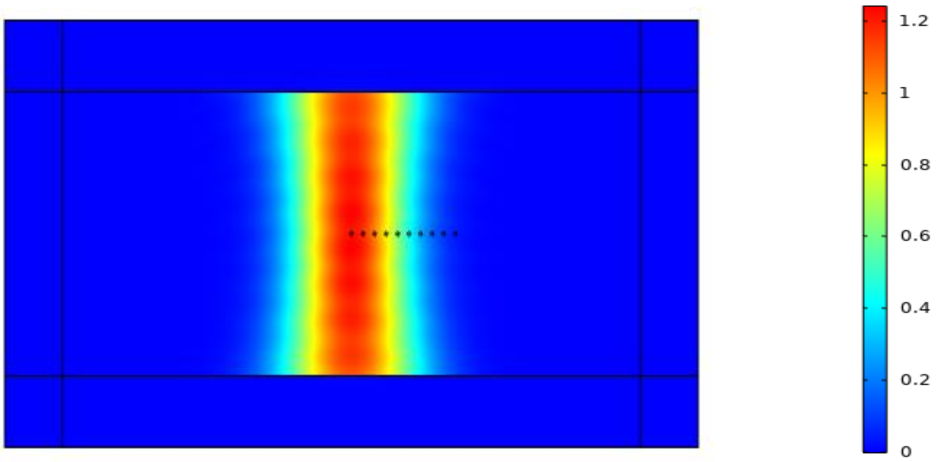


Figure 36 ZnO added to material, 750nm radius gaussian beam

The electric field level is based on color as shown in the right bar. The more likely to read, the higher the electric field. As Zinc oxide semiconductor material added to nanorod, the electrical field of the Gaussian beam higher.

c) Line plot between the beam

For line plot shown below, showing the relationship between electric field and wavelength. The green line indicator as to the Gaussian beam light and the blue line represents the electric field. As Gaussian beam light propagates to center, so the most left of nanorod produced more electric field. It becomes lower to the right nanorod because Gaussian beam light doesn't propagate through right side nanorods.

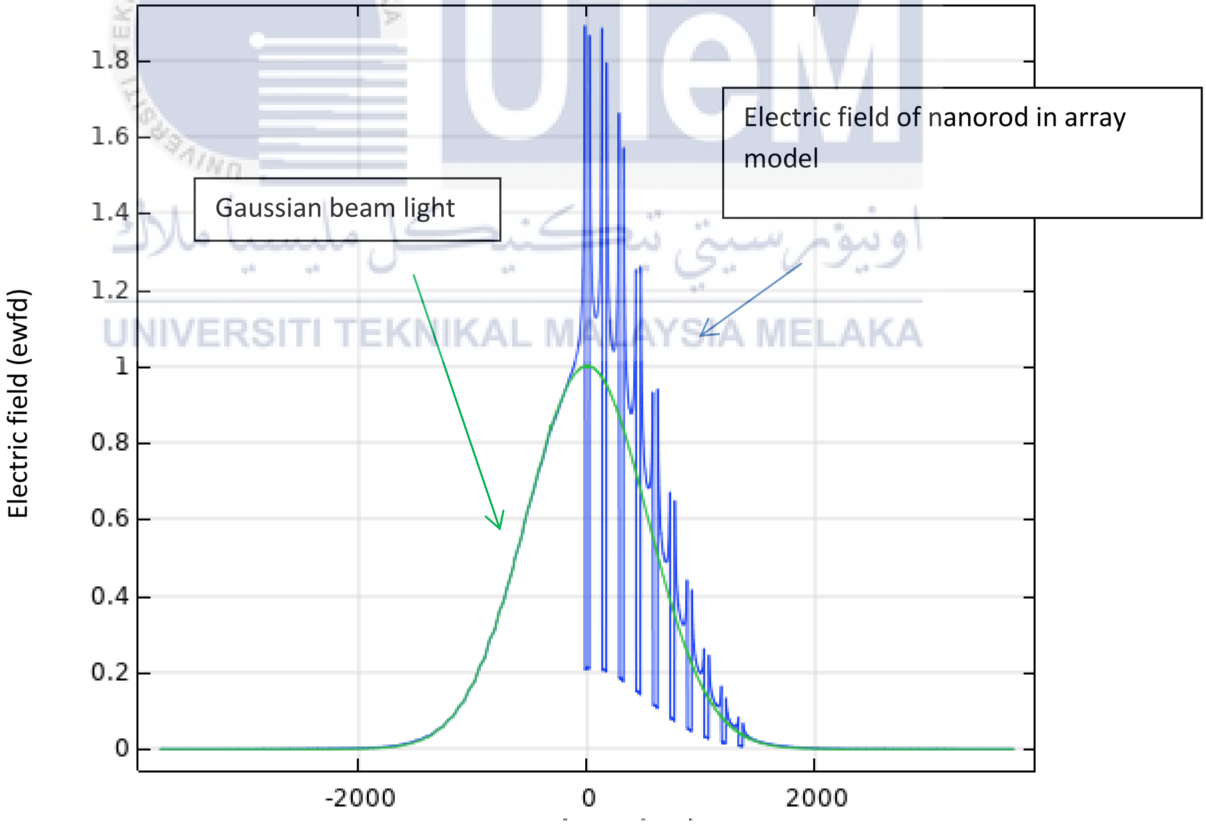


Figure 37 Graph radius 750nm material zinc oxide

4.4.2 Simulation experiment

For the simulation experiment, there is a test for the different radius of Gaussian beam light that propagates through the array is 750nm as shown above, 900nm, 1500 radius, and nanorod without zinc oxide material. The result of the simulation is to analyze the effect radius of Gaussian beam light with an electric field that can be produced.

a) Ten nanorods with normal material (air)

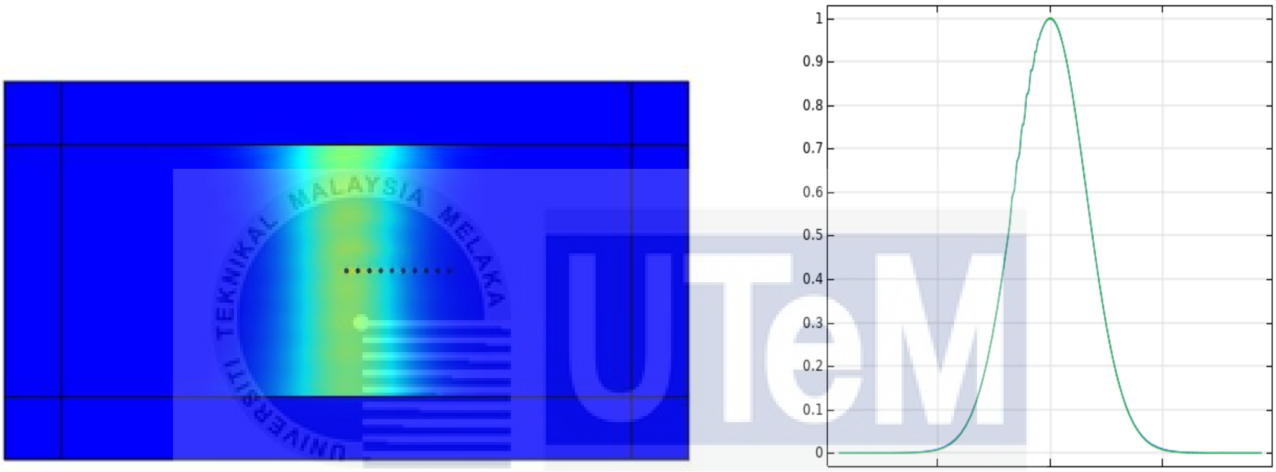


Figure 38 Ten nanorod normal material

b) Gaussian beam with radius 900nm (zinc oxide material)

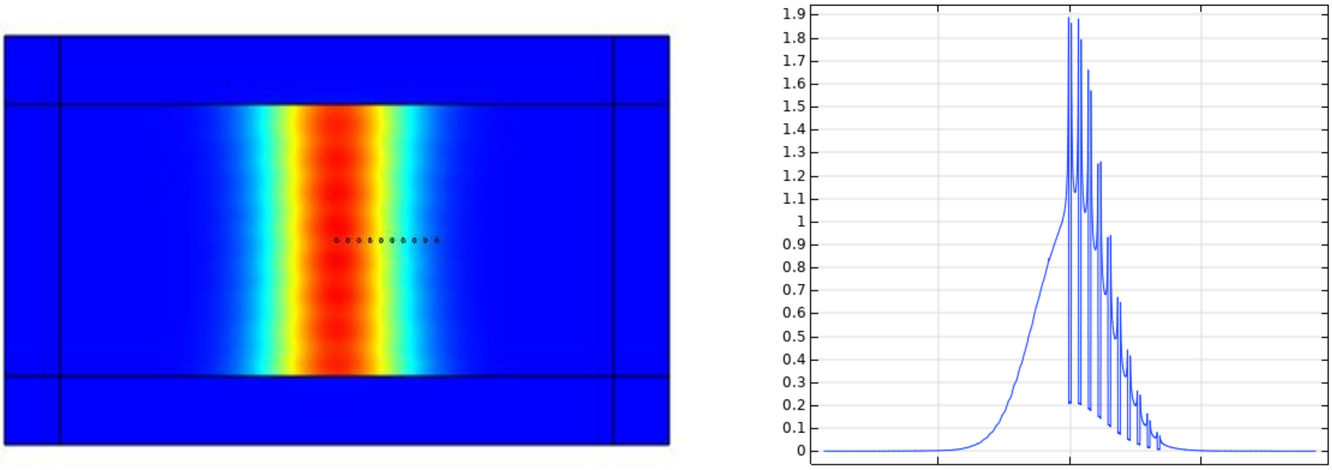
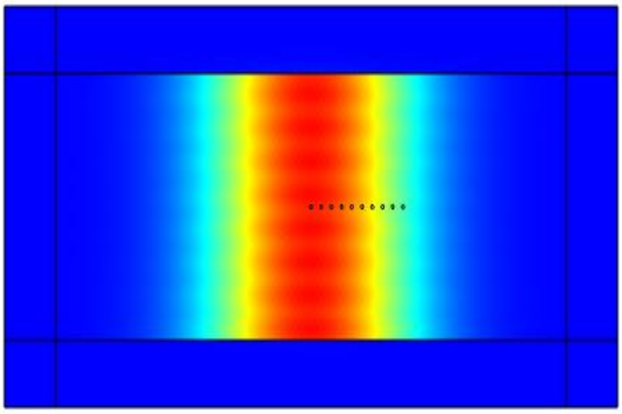


Figure 39 900nm Zinc oxide material

c) Gaussian beam with radius 1500nm (zinc oxide material)



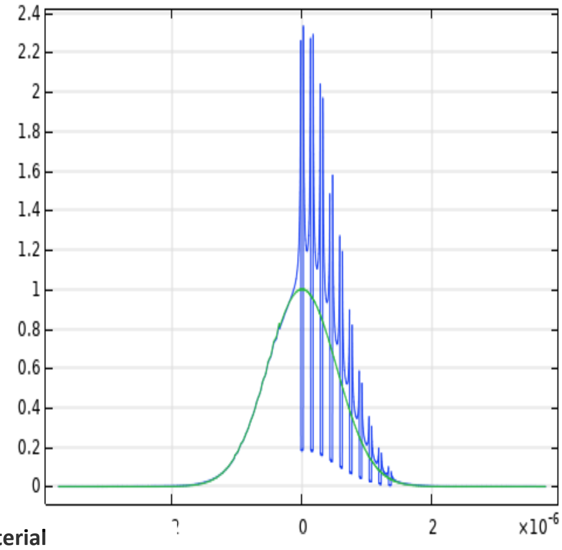


Figure 40 1500nm zinc oxide material

4.4.3 Simulation analysis

Analysis that can be made from the simulation experiment, the larger the radius Gaussian beam light, the higher the electric field. It is because the number of nanorods that exposed to Gaussian beam also increases when the radius increase.

Gaussian beam radius (nm)	Material of nanorod	No of nanorod exposed to light	Max Electric field (ewfd)
750	Air	0	1
750	Zinc oxide	3	1.8
900	Zinc oxide	4	1.9
1500	Zinc oxide	7	2.4

Table 4 Simulation analysis of the result

From the table result, nanorod with normal material which is air produces the blue color of the electric field, the low electric field produces. For nanorod with zinc oxide material, it produced high electric which is red color. In a nutshell, zinc oxide material can help and obtains more electric field when added to the nanoparticle. It shows that zinc oxide is one of the materials that high possibilities to optimize the solar cell.

4.5 Design 3D cylinder scattering cross-section

a) Design a 3D model cylinder

The model of cylinder 3D space dimension been designed as a reference to one nanorod. This model consists of three-layer which is the outer surface is Perfectly Matched Layer(PML), the physical domain the main domain and nanoparticle inside it. Nanoparticle consists of a zinc oxide semiconductor that reacted as a scattering section to get the result of the region.

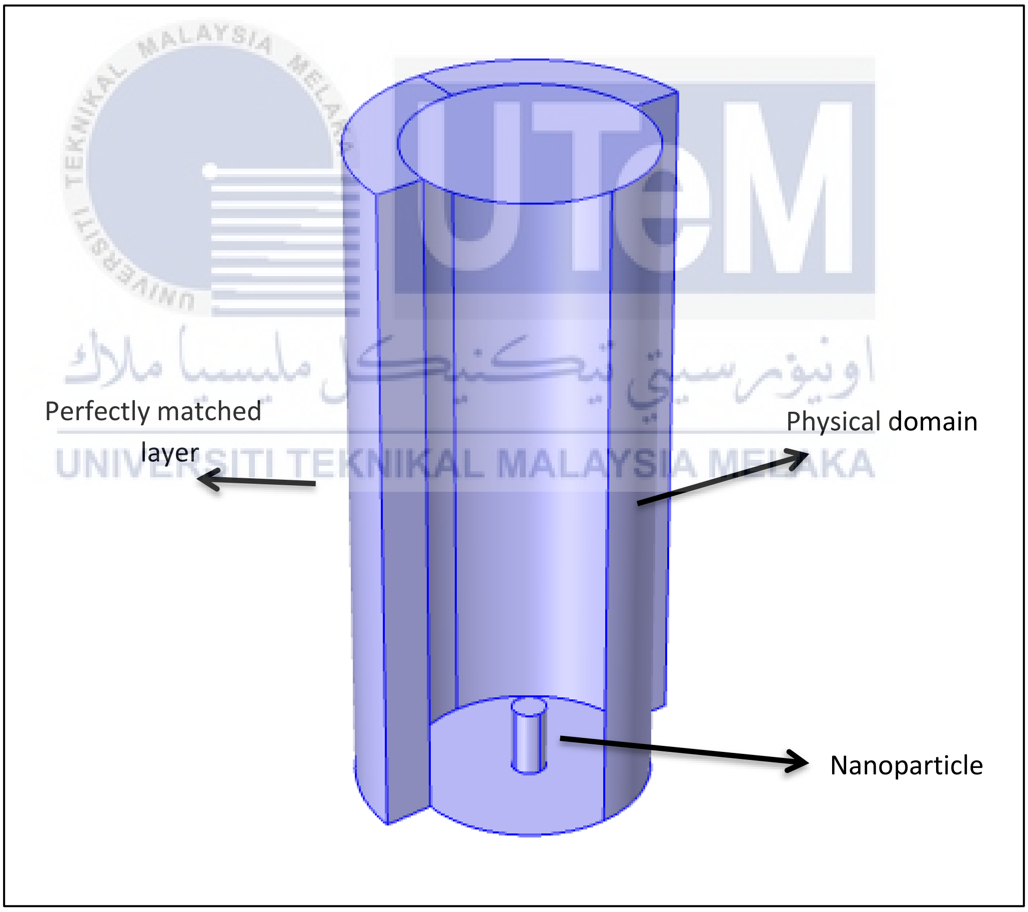


Figure 41 3D nanorod model

CHAPTER 5

CONCLUSION AND FUTURE WORKS

5.1 Conclusion

Dye-Sensitized Solar Cells (DSSCs) is the third generation of photovoltaic cells attributed to the low cost of the fabrication process, high stability, environmental friendliness, and easy fabrication. ZnO has high electron mobility. The main objective of this project is to control the synthesis process of zinc oxide nanorods and study the analysis of zinc oxide nanorods in DSSC. Analysis has been performed by characterization based on the result of SEM, X-ray Diffraction, and UV-VIS spectroscopy. During the synthesis process, the design of the experiment divided into five samples to control the crystalline of zinc oxide nanorod. During the growth process also variables between samples are facing up the surface and facing down the surface. In conclusion, the best sample was facing down surface during the growth process and sample 4 that performed 10 number of cycles and no filtered.

5.2 Recommendation for future works

In the future, DSSC of ZnO nanorod can be fabricated by control the growth process as the growth process makes very impact on to DSSC sample. From the result and discussion also stated that facing down method is the best method. So, the data been taken can be using for future works to obtain the best result of the fabrication of DSSC.

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