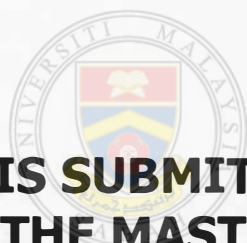


**DEVELOPMENT OF ELECTROSPINNING
PROCESS FOR NANOFIBRES
FABRICATION**

TANG ZI SHENG



UMS

**THIS IS SUBMITTED IN FULFILLMENT FOR
THE MASTER OF ENGINEERING
IN CIVIL ENGINEERING**

**FACULTY OF ENGINEERING
UNIVERSITI MALAYSIA SABAH
2017**

UNIVERSITI MALAYSIA SABAH

BORANG PENGESAHAN STATUS TESIS

JUDUL: **DEVELOPMENT OF ELECTROSPINNING PROCESS FOR NANOFIBRES FABRICATION**

IJAZAH: **SARJANA KEJURUTERAAN (KEJURUTERAAN AWAM)**

Saya **TANG ZI SHENG**, Sesi Pengajian **2012-2016**, mengaku membenarkan tesis Sarjana Kejuruteraan ini disimpan di Perpustakaan Universiti Malaysia Sabah dengan syarat-syarat kegunaan seperti berikut:-

1. Tesis ini adalah hak milik Universiti Malaysia Sabah.
2. Perpustakaan Universiti Malaysia Sabah dibenarkan membuat salinan tesis ini untuk tujuan pengajian sahaja.
3. Perpustakaan dibenarkan membuat salinan tesis ini sebagai bahan pertukaran antara institusi pengajian tinggi.
4. Sila tandakan (/)

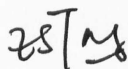
SULIT

(Mengandungi maklumat yang berdarjah keselamatan atau kepentingan Malaysia seperti yang termaktub di dalam AKTA RAHSIA 1972)

TERHAD

(Mengandungi maklumat TERHAD yang telah ditentukan oleh organisasi/badan di mana penyelidikan dijalankan)

TIDAK TERHAD



TANG ZI SHENG

Disahkan oleh,
NURULAIN BINTI ISMAIL

LIBRARIAN
UNIVERSITI MALAYSIA SABAH



(Tandatangan Pustakawan)

Tarikh: 06 Januari 2017

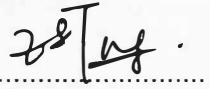


(Prof. Madya Dr. Nurmin Bolong)
Penyelia

DECLARATION

I hereby declare that the materials in this thesis are my own except for quotations, excerpts, equations, summaries and references, which have been duly acknowledged.

16 June 2016



Tang Zi Sheng

MK1211004T



UMS
UNIVERSITI MALAYSIA SABAH

CERTIFICATION

NAME : **TANG ZI SHENG**
MATRIC NO : **MK1211004T**
TITLE : **DEVELOPMENT OF ELECTROSPINNING PROCESS FOR NANOFIBRES FABRICATION**
DEGREE : **MASTER OF ENGINEERING (CIVIL ENGINEERING)**
VIVA DATE : 14 November 2016

DECLARED BY;

1. **SUPERVISOR**
Associate Professor Dr Nurmin Bolong

Signature



UMS
UNIVERSITI MALAYSIA SABAH

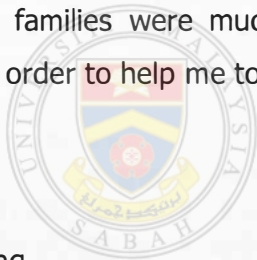
A handwritten signature in black ink, appearing to be "Nurmin", is written over a horizontal line.

ACKNOWLEDGEMENT

I wish to express my deepest gratitude and appreciation to my supervisor, Associate Professor Dr Nurmin Bolong who has been patient enough to advise, guide and supervise me throughout the study. Without her valuable knowledge, suggestion and advises, it would be a tough task for me to complete the research works.

My special sense of gratitude to Dr Md Mizanur Rahman, Dr Nancy Julius Siambun and Dr Melvin Gan Jet Hong for the technical advice. Also, not to forget the civil engineering lecturers who have been provided me the information and gave me advice in completing the project. They are Prof. NSVK Rao, Prof. Abdul Karim Mirasa, Dr Azizul Ladin, Madame Janice Lynn Ayog, Mr Jodin Makinda, Madame Lillian Gungat, Madame Hidayati Asrah and Ms Salinah Dullah.

Last but not least, continuous encouragement and supports from my beloved parents and families were much appreciated. They supported me mentally and financially in order to help me to complete the study.



UMS
UNIVERSITI MALAYSIA SABAH

Tang Zi Sheng

16 June 2016

ABSTRACT

Titanium oxide (TiO_2) is a promising semiconductor material with wide energy bandgap and it is extensively applied in dye-sensitised solar cells and photocatalytic devices. TiO_2 nanofibre offers better electron transfer and hence it is vital to apply nanofibres in the solar cell to improve its efficiency. The study aims to produce electrospun TiO_2 nanofibres using custom-made electrospinning system. The study focuses on the investigation of the operational parameters of the developed electrospinning system on the fibres' diameter experimentally and using response surface methodology. A horizontal-oriented electrospinning system was developed to produce TiO_2 nanofibres. Electrospun TiO_2 nanofibres were produced from the ethanolic solution contains polymer carrier, polyvinylpyrrolidone (PVP), alkoxide precursor, titanium tetraisopropoxide (TTIP) and acetic acid as the stabiliser. TiO_2 nanofibres with mean diameter range from 110 ± 51 nm to 263 ± 78 nm were produced based on the measurement using JMicroVision from scanning electron microscope (SEM) micrographs. Crystalline TiO_2 nanofibres with anatase-rutile phases were established after the calcination process in the furnace for 3 hours at 450°C and the TiO_2 phases were confirmed with X-ray diffractometer (XRD). The relationship between fibre diameters and various parameters were investigated, such as supplied voltage, feeding rate, tip-to-collector distance, the rotation speed of custom-made drum collector and solution concentration. The PVP concentration was added from 4 to 9 wt. % and caused the average fibre size increased as much as 124%. It is also observed that increase in feeding rate resulted in elevating the fibres diameter. On the other hand, a reduction of 27% in fibres diameter occurred with an increment of tip-to-collector distance from 6 to 14 cm. Shrinkage of the fibre diameter occurred when the applied voltage increased. However, the rotation speed of drum collector had no significant effect on the fibres size. At the same time, a response surface model was developed by considering the variables of applied voltage, flow rate and tip-to-collector distance to estimate the fibres diameter. Based on the response surface plots, tip-to-collector distance is the most significant factor which contributed up to 66% influence in determining the fibres diameter. Whereas applied voltage plays a less weighty role at approximately 8% of influence in fibres diameter prediction.

ABSTRAK

PENGHASILAN MEMBRAN GENTIAN NANO DENGAN PROSES ELECTROSPINNING DALAM APLIKASI TENAGA DIPERBAHARUI

Titanium Oksida (TiO_2) merupakan sejenis bahan semikonduktor yang mempunyai jurang tenaga yang tinggi. Oleh itu, TiO_2 digunakan dalam sel suria sensitif pewarna dan peranti pemangkin cahaya. Gentian nano TiO_2 mempunyai aliran elektron yang baik dan meningkatkan efisiensi sel suria sensitif pewarna dan peranti pemangkin cahaya. Kajian ini bertujuan untuk menghasilkan gentian nano TiO_2 dengan kaedah electrospinning. Kajian ini juga bertujuan untuk menyelidik implikasi factor operasi electrospinning terhadap saiz gentian secara uji kaji dan permodelan "response surface". Oleh yang demikian, sistem electrospinning berorientasi mendatar diguna untuk menghasilkan gentian nano TiO_2 hablur satu dimensi. Gentian nano TiO_2 boleh dihasilkan daripada larutan etanol yang mengandungi alkoksida titanium tetraisopropoxide, pembawa polimer polyvinylpyrrolidone dan penstabil asid asetik. Saiz gentian nano diukur dengan perisian JMicroVision daripada gambar mikroskop imbasan elektron (SEM). Purata gentian nano yang dihasilkan adalah antara 110 ± 51 nm dan 263 ± 78 nm. Hablur gentian nano TiO_2 dengan campuran fasa anatase-rutile menunjukkan kecekapan penukaran tenaga yang lebih tinggi. Hablur ini dihasilkan melalui proses pemanasan, dengan memanaskan gentian nano TiO_2 dalam relau selama 3 jam dengan suhu $450^\circ C$. Penukaran fasa TiO_2 disahkan dengan analisa X-ray diffraction (XRD). Perhubungan antara pemboleh ubah seperti kuasa elektrik, kelajuan aliran, jarak antara jarum dengan pemungut, kelajuan putaran pemungut dan kepekatan larutan ke atas saiz gentian nano telah dikaji. Penambahan kepekatan PVP daripada 4 wt.% kepada 9 wt.% menyebabkan purata saiz gentian bertambah sebanyak 124%. Peningkatan kelajuan aliran juga memperbesarkan saiz gentian TiO_2 . Manakala, penambahan jarak antara jarum dengan pemungut dari 6 cm ke 14 cm menyebabkan pengurangan diameter gentian sebanyak 27%. Pada masa yang sama, saiz kecutan gentian berlaku dengan peningkatan kuasa elektrik. Namun demikian, kelajuan putaran pemungut tidak membawa sebarang kesan terhadap saiz gentian. Permodelan "response surface" telah disampaikan dengan mempertimbangkan kuasa elektrik, kelajuan aliran dan jarak antara jarum dengan pemungut sahaja untuk menjangka diameter gentian nano TiO_2 . Dalam permodelan tersebut, jarak antara jarum dengan pemungut merupakan faktor utama dalam penentuan diameter saiz gentian manakala kuasa elektrik memberi pengaruh yang terendah. Jarak antara jarum dengan pemungut menyumbang sebanyak 66% terhadap saiz gentian manakala kuasa elektrik menyumbang hanya 8% dalam penentuan diameter gentian.

LIST OF CONTENT

	Page
TITLE	i
DECLARATION	ii
CERTIFICATION	iii
ACKNOWLEDGEMENT	iv
ABSTRACT	v
<i>ABSTRAK</i>	vi
LIST OF CONTENTS	vii
LIST OF TABLES	xi
LIST OF FIGURES	xii
LIST OF ABBREVIATIONS	xvi
LIST OF SYMBOLS	xvii
LIST OF APPENDIX	xviii
CHAPTER 1: INTRODUCTION	1
1.1 Research Overview	1
1.2 Problem Statement	3
1.3 Project Objectives	4

1.4	Scope of Study	5
1.4.1	Development of Electrospinning System	5
1.4.2	Fabrication of Fibres Samples and the Characteristics	5
1.4.3	Modelling of the Fibre's Diameter	6
1.5	Report Overview	6
CHAPTER 2: LITERATURE REVIEW		7
2.1	Introduction to Nanotechnology and Nanostructures	7
2.2	Production of Nanofibres	9
2.2.1	Drawing	9
2.2.2	Template Synthesis	11
2.2.3	Phase Separation	11
2.2.4	Self-Assembly	12
2.2.5	Electrospinning	13
2.3	History of Electrospinning	15
2.4	The Physical Mechanism of Electrospinning Process	17
2.5	Parameters Settings towards Fibres Diameter	18
2.5.1	Polymer Concentration	19
2.5.2	Applied Voltage	20
2.5.3	Flow Rate	22
2.5.4	Tip-to-Collector Distance	23
2.5.5	Rotational Speed of the Collector	23
2.6	The Properties of Titanium Oxide	24
2.7	Titanium Oxide Nanofibres and Dye-Sensitised Solar Cell	25
2.7.1	Structures for Different Forms of Titanium Oxide	27
2.7.2	Morphology of TiO ₂ /PVP and TiO ₂ Nanofibres	29
2.7.3	Fibres Structural and XRD Characterisations	29
2.8	Modelling of Electrospun Fibres Using RSM	31

3.1	Introduction	36
3.2	Development of Custom-Made Electrospinning System	37
3.3	Spinning Solution Preparation	38
3.3.1	Alkoxide Precursor-Titanium Tetraisopropoxide (TTiP)	39
3.3.2	Polymer-Polyvinylpyrrolidone (PVP)	40
3.3.3	Solvent-Ethanol	41
3.4	Production of TiO ₂ /PVP Nanofibres	41
3.5	Morphology Characterisations of Nanofibres	42
3.6	Heat Treatment Process on TiO ₂ Nanofibres	43
3.7	Structural Characterisations of Nanofibres	44
3.8	Modelling of Fibres Diameter Using Box-Behnken Design	44
3.8.1	Factors and the Coded Levels Determination	44
3.8.2	Model Development and Coefficient Determination	45

CHAPTER 4: ELECTROSPINNING SYSTEM DEVELOPMENT AND FIBRES CHARACTERISATIONS

4.1	Introduction	47
4.2	Electrospinning System Development	47
4.3	Morphology Characterisation for Different Parameters and Variables	51
4.3.1	Effects of Polyvinylpyrrolidone (PVP) Concentration on the Morphology of Nanofibres	51
4.3.2	Effects of Applied Voltage on the Morphology of Nanofibres	54
4.3.3	Effects of Flow Rate on the Morphology of Nanofibres	57
4.3.4	Effects of Tip-to-Collector Distance on the Morphology of Nanofibres	60
4.3.5	Effects of Rotation Speed of Collector on Fibres' Morpholog	63
4.4	Fibres Structural Characterisation	65
4.5	The Comparison of FeSEM and SEM Images	67
4.6	Conclusion	68

CHAPTER 5: INVESTIGATION OF ELECTROSPINNING SYSTEM PARAMETERS ON THE FIBRES' DIAMETERS: A BOX-BEHNKEN DESIGN	69
5.1 Introduction	69
5.2 The Box-Behnken Design	69
5.3 Analysis of the Mean Fibres Diameter	71
5.4 The Diagnostics of the Response Surface Model	75
5.5 Analysis of the Response Surface and Contour Plots	78
5.6 Validation of Response Surface Model	83
5.7 Conclusion	86
CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS	87
6.1 Introduction	87
6.2 Conclusions	87
6.3 Recommendations	88
REFERENCES	90
LIST OF PUBLICATIONS	103
APPENDIX	104



UMS
UNIVERSITI MALAYSIA SABAH

LIST OF TABLES

	Page
Table 2.1: Comparison of nanofibres fabrication method	10
Table 2.2: Summary of previous studies using RSM for electrospinning	35
Table 3.1: Properties of titanium tetraisopropoxide	40
Table 3.2: Properties of polyvinylpyrrolidone	41
Table 3.3: Factors and the associated levels for response surface study	45
Table 3.4: Box-Behnken design matrix and experimental responses	46
Table 4.1: Operating specifications of the developed electrospinning system	49
Table 5.1: ANOVA for response surface full quadratic model	72
Table 5.2: ANOVA for response surface reduced quadratic model	73
Table 5.3: Statistical summary for the reduced quadratic model	74
Table 5.4: Experimental and model predicted mean diameter for statistical model validation for different factors	84

LIST OF FIGURES

	Page
Figure 2.1: Illustration of the nanofibres production by drawing.	10
Figure 2.2: Generic schematic of template synthesis.	11
Figure 2.3: Generic schematics of phase separation process.	12
Figure 2.4: Simple schematic of self-assembly for obtaining nanofibres.	13
Figure 2.5: Vertical-oriented electrospinning system.	14
Figure 2.6: Horizontal-oriented electrospinning system.	15
Figure 2.7: Typical electrospinning setup.	18
Figure 2.8: Summary of the affecting parameters on fibres' diameter.	19
Figure 2.9: Illustration of electron diffusion between nanoparticles and nanofibres in DSSC.	26
Figure 2.10: Reduction of fibres' diameter to channel the electron flow.	27
Figure 2.11: The fundamental structural unit of crystalline TiO ₂ .	28
Figure 2.12: Example of XRD diffractogram of TiO ₂ nanofibres.	31
Figure 2.13: Example of (a) 3D response surface plot and (b) contour plot of a quadratic model.	34
Figure 3.1: Flow chart of the research activities.	36

Figure 3.2:	An electrospinning system setup [1] acrylic closed chamber, [2] rotating drum collector, [3] syringe pump with silicon tubing and metal needle, [4] high voltage.	38
Figure 3.3:	Complete setup of syringe, metal needle, silicon tube, syringe pump with a loaded solution.	42
Figure 4.1:	A custom-made electrospinning system [1] High voltage power supply, [2] syringe pump, luer lock syringe, silicon tube and metal needle, [3] grounded rotating drum collector.	49
Figure 4.2:	Rotational direction of the operating drum collector.	50
Figure 4.3:	The distance between needle tip and collector.	50
Figure 4.4:	SEM micrographs of electrospun TiO ₂ fibres with various PVP contents [Applied voltage=18 kV, flow rate=1.0 ml/hr, tip-to-collector distance=10 cm and rotation speed=105 rpm].	53
Figure 4.5:	Experimental mean fibres diameter for various PVP contents for electrospun TiO ₂ fibres production [Applied voltage=18 kV, flow rate=1.0 ml/hr, tip-to-collector distance=10 cm and rotation speed=105 rpm].	54
Figure 4.6:	SEM images of electrospun TiO ₂ fibres with various applied voltages [Flow rate=1.0 ml/hr, tip-to-collector distance=10 cm, rotation speed=105 rpm and PVP content= 6.5 wt. %].	56
Figure 4.7:	Experimental mean fibres diameter for varying applied voltages in electrospun TiO ₂ fibres production [Flow rate=1.0 ml/hr, tip-to-collector distance=10 cm, rotation speed=105 rpm and PVP content= 6.5 wt. %].	57

Figure 4.8:	SEM micrographs of electrospun TiO ₂ nanofibres for different flow rates [Applied voltage=15 kV, tip-to-collector distance=10 cm, rotation speed=105 rpm and PVP content=6.5 wt. %].	59
Figure 4.9:	Experimental mean diameter of fibres at different flow rates in electrospun TiO ₂ fibres fabrication [Applied voltage=15 kV, tip-to-collector distance=10 cm, rotation speed=105 rpm and PVP content=6.5 wt. %].	60
Figure 4.10:	SEM images of electrospun TiO ₂ fibres for various distances between tip-to-collector [Applied voltage=15 kV, flow rate=1.0 ml/hr, rotation speed=105 rpm and PVP content=6.5 wt. %].	62
Figure 4.11:	Experimental mean diameter of fibres at different distances tip-to-collector in the electrospun TiO ₂ fibres production [Applied voltage=15 kV, flow rate=1.0 ml/hr, rotation speed=105 rpm and PVP content=6.5 wt. %].	63
Figure 4.12:	SEM micrographs of electrospun TiO ₂ nanofibres for various rotation speeds of collector; a) 105 rpm, b) 180 rpm, c) 255 rpm, d) 321 rpm and e) 386 rpm [Applied voltage=18 kV, flow rate=1.0 ml/hr, tip-to-collector distance=10 cm and PVP content=6.5 wt. %].	64
Figure 4.13:	Experimental mean fibres diameter for various rotation speeds in electrospun TiO ₂ fibres fabrication [Applied voltage=18 kV, flow rate=1.0 ml/hr, tip-to-collector distance=10 cm and PVP content=6.5 wt. %].	65
Figure 4.14:	XRD patterns for as-spun fibres and heat-treated fibres at 450 °C. Formation different forms of TiO ₂ nanofibres at different temperature of the heating.	67

Figure 4.15:	Micrographs from a) SEM and b) FeSEM.	68
Figure 5.1:	The perturbation plot for the factors in coded values [Actual factors of A: Voltage = 17.5 kV, B: Flow Rate = 2.0 ml/hr and C: Distance = 10 cm].	70
Figure 5.2:	Proportionate contribution of each term to R^2 .	74
Figure 5.3:	Normal probability plot of the residuals.	76
Figure 5.4:	Standardised residuals plot for each run number.	77
Figure 5.5:	Residuals versus predicted fibres diameter plot.	77
Figure 5.6:	Model predicted against experimental plot for fibres diameter.	78
Figure 5.7:	(a) 3D surface plot and (b) contour plot between tip-to-collector distance and flow rate at a voltage of 17.5 kV.	80
Figure 5.8:	(a) 3D surface plot and (b) contour plot between applied voltage and tip-to-collector distance at flow rate of 1.0 ml/hr.	81
Figure 5.9:	(a) 3D surface plot and (b) contour plot between flow rate and applied voltage at tip-to-collector distance of 10 cm.	82
Figure 5.10:	Mean fibres diameter against applied voltage with flow rate of 1.0 ml/hr and tip to collector distance of 10 cm.	85
Figure 5.11:	Mean fibre diameter against flow rate with applied voltage of 15 kV and tip to collector distance of 10 cm.	85
Figure 5.12:	Mean fibres diameter against tip to collector distance with the voltage of 15 kV and flow rate of 1 ml/hr.	86

LIST OF ABBREVIATIONS

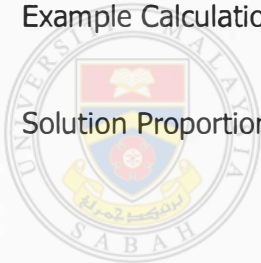
TiO₂	-	Titanium Oxide/ Titania
TTiP	-	Titanium Tetraisopropoxide
PVP	-	Polyvinylpyrrolidone
PEO	-	Polyethylene Oxide
AC	-	Alternating Current
DC	-	Direct Current
TWh	-	Terawatt-hours
DSSC	-	Dye-Sensitised Solar Cell
1D	-	One-Dimensional
UV	-	Ultraviolet
SEM	-	Scanning Electron Microscope
FeSEM	-	Field Emission Scanning Electron Microscope
XRD	-	X-Ray Diffraction
RSM	-	Response Surface Methodology
BBD	-	Box-Behnken Design
FFD	-	Full Factorial Design
CCD	-	Central Composite Design
ANOVA	-	Analysis of Variance
R²	-	Determination Coefficient
LOF	-	Lack of Fit
C.V.	-	Coefficient of Variation
PRESS	-	Predicted Residual Error Sum of Squares

LIST OF SYMBOLS

<i>D</i>	-	Crystalline size, nm
<i>K</i>	-	Shape factor, usually taken as 0.9
<i>λ</i>	-	Wavelength of X-ray, taken as 1.5406 Å
<i>β</i>	-	Full width at half the maximum intensity (FWHM), in radians
<i>θ</i>	-	Bragg angle/ angle of diffraction, in degree
<i>η</i>	-	The response
<i>f</i>	-	The unknown function of response
<i>x₁, x₂, ..., x_k</i>	-	The independent variables
<i>k</i>	-	Number of independent variables
<i>ε</i>	-	Statistical error or sources of variability that not accounted in function <i>f</i>
<i>Y</i>	-	Predicted response (fibres diameter, nm)
<i>A</i>	-	Applied voltage (kV)
<i>B</i>	-	Flow rate (ml/hr)
<i>C</i>	-	Tip to collector distance (cm)
<i>β₀</i>	-	Constant
<i>β₁, β₂, β₃</i>	-	Linear coefficients
<i>β₁₂, β₁₃, β₂₃</i>	-	Interactions coefficients between the factors
<i>β₁₁, β₂₂, β₃₃</i>	-	Quadratic coefficients

LIST OF APPENDIX

	Page
Appendix A: Rotational Speed of Rotating Drum	104
Appendix B: Explode View of Rotating Drum	105
Appendix C: Example Calculations Using Scherrer's Equation	106
Appendix D: Solution Proportion Calculation	107



UMS
UNIVERSITI MALAYSIA SABAH

CHAPTER 1

INTRODUCTION

1.1 Research Overview

The total world electricity generation throughout the year 2013 is 23,322 TWh (terawatt-hours), with an hourly mean of 2.66 terawatts during the year (International Energy Agency, 2015). Of this amount, 67.4% of electricity generation is produced by fossil fuels. Fossil fuels such as coal, oil and natural gas will not replenish in our lifetimes. In addition, electricity generation from fossil fuels is harmful to the environment especially air pollution. Therefore, researchers are looking for a suitable and alternative way to generate electricity. A photovoltaic system is one of the valid and sustainable option for electricity generation if the efficiency of the photovoltaic system can be improved (Gardner, 2008).

In order to fabricate a low-cost photovoltaic system, nanotechnology is introduced to the solar cell. In the year 1991, O'Regan and Gratzel developed a nanostructured solar cell for electricity generation. This nanostructured solar cell is based on dye-sensitised colloidal titanium dioxide films and known as a dye-sensitised solar cell (DSSC) or Gratzel cell (Brinker and Ginger, 2011; O'regan and Grätzel, 1991). Later on, the nanostructured solar cells have been fabricated from different semiconductors by using nanoparticles such as zinc oxide and titanium oxide (Kim *et al.*, 2007). In addition, nanofibres can be applied to the fabrication of DSSC instead of nanoparticles to improve the efficiency of the solar cell.

One-dimensional (1D) nanostructured materials such as nanofibres, nanowires, nanorods and nanotubes have a greater surface-to-volume ratio. This property can improve the rate of absorption, desorption and reaction. In addition, nanofibres are higher in aspect ratio and having better pore interconnectivity which is applicable for energy conversion and storage (Wu *et al.*, 2012; Shi *et al.*, 2015; Behera and Chandra, 2016).

Recently, 1D nanostructures especially titanium oxide (TiO₂) nanofibres are applied in the dye-sensitised solar cell (DSSC) because nanofibres gain the electron transport and enhance the charge collection owing to their properties such as lower transport resistance and larger specific surface area (Elayappan *et al.*, 2015). TiO₂ has wide band gap semiconducting material that possesses high photocatalytic activities and absorbs UV light. In addition, TiO₂ is a non-toxic material with strong oxidising power, exceptional chemical and biological stability as well as low cost and good corrosion resistance in aqueous solution. Therefore, it is a promising material in photocatalysis, solar cell, optical filter and antimicrobial surface coating (Mishra *et al.*, 2012; Elayappan *et al.*, 2015; Tang *et al.*, 2016).

Nanofibres can be produced by using drawing, template synthesis, self-assembly, phase separation and electrospinning (Nayak *et al.*, 2011). Among these process methods, electrospinning is a simple and novel approach with high versatility method to produce nanofibres down to nanometers. Various nanofibres can be produced by using electrospinning such as polymers fibres, metal oxide fibres and composites fibres (Reneker and Chun, 1996; Sigmund *et al.*, 2005, Li and Wang, 2013, Tang *et al.*, 2016). In general, an electrospinning system consists of three main components: a high voltage power supply (in kV range), an electrically conducted spinneret (a syringe pump and a syringe with a metal needle) and a grounded collector. Electrospinning process can be summarised into three stages: jet initiation, jet instability and jet solidification to form fibres (Bhardwaj and Kundu, 2010; Miao *et al.*, 2010; Karimi *et al.*, 2015). Electrospinning process is suitable for fibre fabrication due to the ease of setting up and requirements. Commercially, some of the companies provide industrial level scale electrospinning machines for fibre fabrication.

The focus of the study is based on the experimental investigation on electrospun TiO₂ fibres fabrication and their morphology characteristics from different fabrication parameters. The fibres fabrication is done based on the developed lab-scale electrospinning system. Other than that, the effects of system parameters including applied voltage, flow rate and tip-to-collector distance on fibres' diameter are investigated using response surface methodology.

1.2 Problem Statement

Dye-sensitised solar cell (DSSC) has gained the interest among the researchers owing to cost effective and its notable conversion efficiency. However, nanoparticle-based TiO₂ solar cell has lower efficiencies as compared to the nanofibre-based solar cell (Shi *et al.*, 2015). Nanoparticles have a higher density of grain boundaries between the particles. Thus, the electron diffusion through nanoparticles was in a random electrical pathway and lead to low electron transport rate and poor charge collection efficiency. In contrast, nano-fibrous morphology has lower grain boundaries with improved dye absorption and offer better charge transport rate for the electrons which could improve the efficiency. This is because the electrons were constrained to move directionally (Jose *et al.*, 2009; Cao *et al.*, 2016). Thus, it is vital to introduce TiO₂ nanofibre in the solar cell.

In general, five approaches were employed to fabricate nanofibres. The technique includes drawing, phase separation, self-assembly, template synthesis and electrospinning. However, these approaches possess their limitations such as discontinuous fabrication process, selective solution process, complex process and lack of control on the fibres diameter (Ramakrishna *et al.*, 2005; Vasita and Katti, 2006; Nayak *et al.*, 2011). Thus, in order to rectify the aforementioned disadvantages, electrospinning has been introduced. A custom-made electrospinning system is required in order to fabricate fibres from a polymer solution and polymer melts with controllable fabrication parameters and tunable fibre size. However, jet instability may occur if the fabrication parameters are not controlled properly.

In electrospinning process, jet instability plays an important role in forming continuous fibres. When the jet instability is not regulated properly, the jet from the needle tip tends to break and causing difficulties in electrospinning process, viz forming discontinuous fibres and forming beaded structures. This problem can be solved by offering suitable parameters during the fabrication process. These parameters are solution concentration, solution viscosity, applied voltage, flow rate, tip-to-collector distance, type of collector, ambient temperature and humidity. As the parameters are tuned properly, the continuous fibre is formed with desirable size.

In addition, the interrelationship of the parameters also contributes in adjusting the fibre size. Ray and Lalman (2011) estimated and predicted that the electrospun fibres' diameter using the developed quadratic model from response surface methodology. This quadratic model is merely suitable for their electrospinning system within the parameters boundaries. Thus, a specified model is required to investigate the interrelationship of the fabrication parameters for the custom-made electrospinning system.

1.3 Project Objectives

The objectives of projects are as below.

- i. To investigate the operational parameters of custom-made electrospinning system in nanofibres production.
- ii. To characterise the morphology and structural properties of the produced nanofibers.
- iii. To model and validate the nanofibres diameter for the developed electrospinning system using response surface methodology.

1.4 Scope of Study

Generally, the project consists of three scopes of works. The first part is to develop the custom-made electrospinning system. The second part is to produce nanofibres from the solution containing precursor alkoxide, polymer and solvent with stabiliser. After that, the morphology of nanofibres is characterised and analysed with scanning electron microscope (SEM). The fibres samples are further characterised by X-ray Diffraction (XRD) analysis. Lastly, the parameters are modelled to produce a desirable size of fibres. Each of the parts is briefly explained in the following subsections.

1.4.1 Development of the Electrospinning System

A custom-made electrospinning system was developed which consists of a high voltage power supply, syringe pump, syringe, needle and a grounded collector. In this system, the rotating drum collector was developed to replace the static plate collector.

1.4.2 Fabrication of Fibres Samples and the Characterisations

In this study, the solution prepared was titania based formulation to produce TiO₂ nanofibres. The solution was prepared with the mixture of alkoxide precursor titanium tetraisopropoxide (TTiP) and carrying polymer polyvinylpyrrolidone (PVP) in ethanolic solution with acetic acid as a stabiliser. The parameters were supplied at different ranges: applied voltage (10-25 kV), flow rate (1.0-3.0 ml/hr), tip-to-collector distance (6-14 cm), the rotation speed of collector (105-321 rpm) and PVP content (4-9 wt. %).

The electrospinning system was placed in a closed chamber, the air flow in the system was considered as none. The humidity and ambient temperature were assumed to have no effect on the diameter and morphology of the fabricated fibres. The samples preparation was done in an air-conditioning lab with constant temperature and humidity. The temperature was measured with the thermometer in the lab. For this study, amorphous and mixture anatase/rutile crystalline TiO₂ were produced. Anatase/rutile TiO₂ is well known for its photocatalytic activities.