DEVELOPMENT OF ELECTROSPINNING PROCESS FOR NANOFIBRES FABRICATION

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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.

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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 pemanasanan, dengan memanaskan gentian nano TiO_2 dalam relau selama 3 jam dengan suhu 450°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.

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LIST OF ABBREVIATIONS

TiO_2	-	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
R^2	-	Determination Coefficient
LOF	-	Lack of Fit
C.V.	-	Coefficient of Variation
PRESS	-	Predicted Residual Error Sum of Squares

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LIST OF SYMBOLS

D	-	Crystalline size, nm
K	-	Shape factor, usually taken as 0.9
λ	-	Wavelength of X-ray, taken as 1.5406 Å
β	-	Full width at half the maximum intensity (FWHM), in radians
θ	-	Bragg angle/ angle of diffraction, in degree
η	-	The response
f	-	The unknown function of response
$x_1, x_2, \ldots, x_k$	-	The independent variables
k	-	Number of independent variables
ε	-	Statistical error or sources of variability that not accounted in function f
Y	-	Predicted response (fibres diameter, nm)
A	-	Applied voltage (kV)
B	-	Flow rate (ml/hr)
C	-	Tip to collector distance (cm)
β_0	-	Constant
$\beta_1, \beta_2, \beta_3$	-	Linear coefficients
$\beta_{12}, \beta_{13}, \beta_{23}$	-	Interactions coefficients between the factors
$\beta_{11}, \beta_{22}, \beta_{33}$	-	Quadratic coefficients

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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).

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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 (TiO_2) 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). TiO_2 has wide band gap semiconducting material that possesses high photocatalytic activities and absorbs UV light. In addition, TiO_2 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.

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The focus of the study is based on the experimental investigation on electrospun TiO_2 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 TiO_2 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 TiO_2 nanofibre in the solar cell.

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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.

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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 TiO_2 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 TiO_2 were produced. Anatase/rutile TiO_2 is well known for its photocatalytic activities.

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