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EFFECT OF POLYVINYLPYRROLIDONE AND FABRICATION PARAMETERS ON ELECTROSPUN TITANIUM OXIDE NANOFIBRES' DIAMETER

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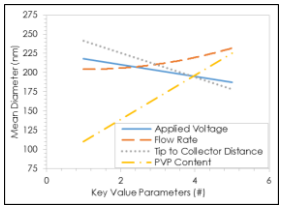
Graphical abstract



-EFFECT OF DIFFERENT PARAMETERS ON ELECTROSPUN NANOFIBRES-

Abstract

Electrospinning is the most versatile and cost effective technique to produce titanium oxide (TiO_2) nanofibres. An ethanolic solution containing titanium tetraisopropoxide, polyvinylpyrrolidone and acetic acid was loaded in the syringe to produce TiO_2 nanofibres. In the present work, a custom-made electrospinning system was developed to investigate the fabrication and solution effects to the diameter of electrospun TiO_2 fibres. The fabrication parameters were applied voltage (kV), flow rate (ml/hr) and tip to collector distance (cm). In addition, the effect of varying the weightage of polymer carrier on electrospun TiO_2 nanofibres was investigated. The surface morphology of the fibres was examined with scanning electron microscope (SEM) and further analysed with the aid of JMicroVision. The significance of the influencing parameters was observed from high to low order as PVP content > tip to collector distance > applied voltage > flow rate. In conclusion, the parameters of applied voltage (15 kV), flow rate (1 ml/hr), tip to collector distance (10 cm) and PVP content (6 wt. %) are able to produce uniform TiO_2 nanofibres.

Keywords: Electrospinning, titanium oxide, nanofibres, parameters

Abstrak

'Electrospinning' merupakan teknik yang versatil dan murah dalam penghasilan gentian nano titanium oksida (TiO_2). Larutan yang mengandungi titanium tetraisopropoxide, polyvinylpyrrolidone dan asid asetik diisi dalam picagari untuk menghasilkan gentian nano TiO_2. Tujuan kajian ini adalah untuk mengkaji kesan fabrikasi dan kesan larutan ke atas diameter gentian TiO_2. Dalam kajian ini, sistem 'electrospinning' dibangunkan untuk menghasilkan gentian nano. Parameter fabrikasi adalah seperti kuasa elektrik (kV), kelajuan aliran (ml/hr) dan jarak antara jarum dengan pemungut (cm). Di samping itu, kesan wajaran pembawa polimer terhadap diameter gentian nano juga dikaji. Morfologi permukaan gentian nano diuji dengan mikroskop imbasan electron (SEM) dan saiz gentian nano ditaksir dengan *JMicroVision*. Pengaruh parameter dari tinggi ke rendah adalah; kandungan PVP > jarak antara jarum dengan pemungut > kuasa elektrik > kelajuan aliran. Sebagai kesimpulan, , parameter yang diperlukan bagi penghasilan gentian nano yang seragam dan selanjar seperti dalan kajian ini adalah 15 kV kuasa elektrik, 1 ml/hr kelajuan aliran, 10 cm jarak antara jarum dan pemungut dan 6 wt. % kandungan PVP dalam larutan.

Kata kunci: Electrospinning, Titanium oksida, gentian nano, parameter

1.0 INTRODUCTION

One-dimensional (1D) nanostructured materials such as nanofibres, nanowires and nanotubes have engrossed the interests of the researchers. These nanomaterials are high in porosity and having larger surface area offer faster electron transportation rate which can improve the efficiency of the electronic devices and photovoltaic panels [1-2]. The 1D nanostructures have been produced by sol-gel synthesis, electrochemical fabrication, dip-coating, hydrothermal technique, phase separation, electroless deposition, crystallise growing method and electrospinning [3]. However, these approaches possess their limitations such as discontinuous fabrication process, selective solution process, complex process and lack of control on the fibres diameter [4]. Among the fabrication methods, electrospinning is the most versatile and straightforward technique to produce continuous nanofibres down to few nanometre [5]. Titanium dioxide (TiO_2) nanofibres have gained its popularity recently. This is because TiO_2 is low cost, environmentally friendly and exceptional chemical stability with amazing optical and electronic properties which can be applied in photocatalysis, solar cell, optical filter and antimicrobial surface coating [6]. Furthermore, TiO_2 can be produced by electrospinning with an ethanolic solution containing alkoxide precursor and a polymer carrier [7].

The goal of the study focuses on producing titanium oxide (TiO_2) nanofibres using custom-made electrospinning system. The effects of the fabrication parameters and PVP content on TiO_2 nanofibres diameter are investigated in order to produce continuous fibres with uniform size.

2.0 METHODOLOGY

2.1 Preparation of Spinning Solution

The alkoxide precursor, carrying polymer, solvent and stabiliser are essential to prepare the as spun solution. The alkoxide precursor used was titanium tetraisopropoxide (TTiP, Sigma-Aldrich, 205273). For carrying polymer, polyvinylpyrrolidone (PVP, 437190) with a molecular weight of 1,300,000 was purchased from Sigma-Aldrich, Malaysia. The solvent ethanol (ACROS, 99.5%, Anhydrous) has been used to mix the solution. Acetic acid (Fisher, Glacial) was added to act as a stabiliser to retard the hydrolysis reaction of the sol-gel precursor [8]. These chemicals were used without further purification.

Typically, solution S1 was prepared (as suggested by [11]) by dissolving PVP in 15 ml ethanol and magnetic-stirred for 2 hours. The transparent and homogeneous solution was formed. Then, 2 ml of TTiP was added into a mixture containing 4 ml glacial acetic acid and 6 ml ethanol with a 10 minutes magnetic stirring to form yellowish homogeneous solution as S2. Lastly, solution S2 mixed with S1 followed by 2 hours stirring and formed a pale yellow solution. The pale yellowish solution was used as the spinning solution in fabricating fibres. In order to study the effect of PVP concentration on the fibres' diameter, the solutions with PVP content of 4, 6, 7, and 8 wt. % were prepared.

2.2 Electrospinning System Development

A custom-made electrospinning system was developed to produce nanofibres. The developed system was illustrated in Figure 1. This system consisted a high voltage power supply, a syringe pump with metal needle, Teflon tube and a grounded rotating drum collector. The high voltage power supply (Gamma High Voltage, ES30P-5W) was used to supply electrical potential to the 18G syringe needle which connected to Teflon tube and 50 ml luer lock syringe. A syringe pump (Terumo Terufusion TE-331) was employed to regulate the flow rate of the jet solution. A custom-made rotating drum collector was employed to collect fibres. For safety purposes, the developed electrospinning system was kept in a closed acrylic chamber and to control the ambient effects such as air flow and humidity.

The positive terminal of power supply was connected to metal needle whereas negative terminal was attached to the grounded collector. The electrical potential was applied on the needle tip to charge the solution. When sufficient electrical potential was supplied, the solution at needle tip elongated and formed Taylor cone [9]. As electrical potential was increased to the threshold value, the surface tension of the solution was overcome by the repulsive electrostatic force. Subsequently, the charged jet was ejected from Taylor cone. Then, the charged jet undergone instability, whipping and elongation process to form thin and long fibres [10]. Before reaching the collector, the charged jet experienced solvent evaporation process throughout the needle tip and collector distance. This process could reduce the fibres diameter depending on the needle tip to collector distance. Lastly, the fibre was collected on the grounded collector. The collected fibre was left in the air for 24 hours for complete drying and hydrolysis.

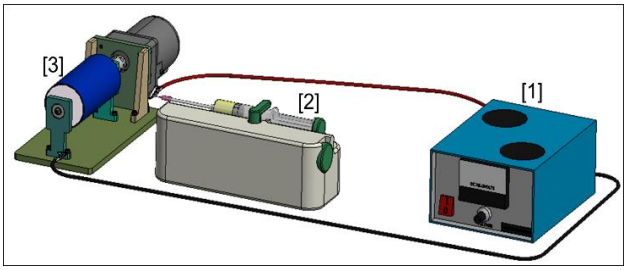


Figure 1 Custom-made electrospinning setup: [1] High voltage power supply, [2] syringe pump with syringe, silicon tube and metal needle, [3] grounded rotating drum collector

2.3 Samples Preparation

In the present study, the concentration of PVP, applied voltage, flow rate and tip to collector distance were experimentally manipulated in determining fibres diameter. Thus, samples with different key factors were prepared as presented in Table 1. The rotation speed of the rotating drum collector was tuned at 105 rpm. Total of 19 samples were prepared.

2.4 Fibres Morphology Characterisation

The morphology of the fibres was revealed with scanning electron microscope (SEM). All the fibres samples were sputter-gold coated before scanning. Next, all SEM images were furthered analysed with JMicroVision v1.2.7 to determine the fibres diameter [11]. The mean diameter of fibres was determined from 15 random fibres and summarised in Figure 6. In addition, the standard deviation for each sample was calculated and recorded in Table 1.

Table 1 The samples for each parameter with their standard deviation

Sample ID	Parameters				Standard deviation of fibre size, σ (nm)
	Voltage (kV)	Flow Rate (ml/hr)	Distance (cm)	PVP Content (wt. %)	
V10	10	1.0	10	6.5	94
V15	15	1.0	10	6.5	**36**
V20	20	1.0	10	6.5	130
V25	25	1.0	10	6.5	102
V30	30	1.0	10	6.5	128
F0.5	15	0.5	10	6.5	120
F1.0	15	1.0	10	6.5	**55**
F1.5	15	1.5	10	6.5	78
F2.0	15	2.0	10	6.5	66
F2.5	15	2.5	10	6.5	78
D6	15	1.0	6	6.5	98
D8	15	1.0	8	6.5	98
D10	15	1.0	10	6.5	**60**
D12	15	1.0	12	6.5	106
D14	15	1.0	14	6.5	79
P4	18	1.0	10	4.0	51
P6	18	1.0	10	6.0	**45**
P7	18	1.0	10	7.0	73
P8	18	1.0	10	8.0	76

3.0 RESULTS AND DISCUSSION

Table 2 shows the parameters studied and its range at different levels. Effects of different parameters on fibres diameters were summarised and illustrated in Figure 2.

Table 2 The fabrication and PVP content parameters and its respective experimental values

Parameters	Parameter Key Level (#)				
	1	2	3	4	5
Applied Voltage (kV)	10	15	20	25	30
Flow Rate (ml/hr)	0.5	1	1.5	2	2.5
Tip to Collector Distance (cm)	6	8	10	12	14
PVP Content (weight %)	4	N. A.	6	7	8

Revealed from Figure 2, the weightage of PVP content in the solution found to be the most significant factor in determining the fibres size, followed by the tip to collector distance, applied voltage and flow rate. Respective parameters were discussed in the following subsections.

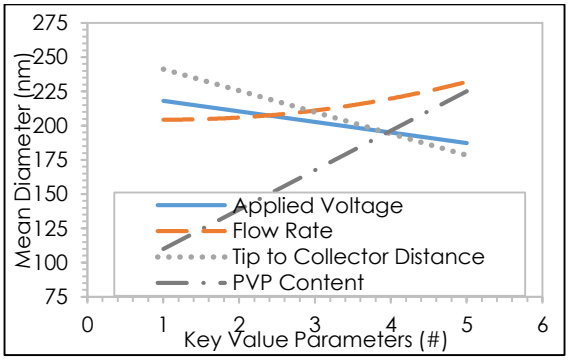


Figure 2 Relationship of different parameters on mean diameter of fibres at different levels

3.1 Effect of Polymer Content

Varying weightage PVP from 4 to 8 wt. % in the as-spun solution has the most significance effect on fibres diameter. When the PVP content increased from 4 to 8 wt. %, the diameter of the fibres increased from 110±51 to 225±76 nm. In other words, there was a twofold increase in the electrospun fibres diameter when the PVP content was doubled. SEM images of the fibres were illustrated in Figure 3 a-d.

Increase in PVP content in the spinning solution causing elevation to the viscosity of the solution which could induce the formation of wider fibres diameter [12]. When the viscosity of the solution increased, jet initiation was harder to take place. This is because higher PVP content required higher electrical force to stretch the jet. Consequently, the jet experienced inadequate stretching and thinning process and resulted in bigger diameter [13].

However, low PVP content was likely to form beaded structures as similarly observed by a previous study [7]. This could be observed from Figure 3. Deitzel *et al.* (2001) claimed that mixture of fibres and droplets were observed at low solution viscosity [14]. The formation of droplets led to the undesired beaded structures under the inspection of SEM images. Based on the calculated standard deviation of fibres in Table 1, the fibres diameter variation was greater than 70 nm when the PVP content is at 7-8 wt. %. This undulating morphology is undesirable. It showed that the produced fibres were non-uniform with high standard deviation value. Thus, by considering the diameter, formation of beaded structures and calculated standard deviation of fibres diameter, the preferable PVP content in producing uniform TiO_2 fibres is 6 wt. % due to the low standard deviation of fibres size and formation of smaller fibres. This study used a 6.5 wt. % of PVP content solution for the investigation of fabrication parameters as suggested by [11]. However, we found that 6.0 wt. % PVP content is the optimised parameter in this study.

3.2 Effect of Tip to Collector Distance

Tip to collector distance is an essential parameter in affecting electrospun fibres diameter [15]. As tabulated in Table 1, when the tip to collector distance increased from 6 to 14 cm, the fibres size decreased from 242±98 to 175±79 nm. Tip to collector distance had an inversely proportional effect on the fibres diameter. Figure 4 a-e showed the SEM images of fabricated fibres using the different tip to collector distance.

By offering a longer tip to collector distance, the fibres jet could have longer travel duration before being collected on the collector. Thus, it offered longer time for the fibres for thinning process and the fibre jet had sufficient time for solvent evaporation [16]. Eventually, broader tip to collector distance resulted in reducing fibres diameter.

Based on Figure 4a, flattened structures fibres were formed with beaded structures, when the tip to collector distance was too short. This is because the fibre experienced inadequate drying before reaching on the grounded collector [12]. In addition, the size variation of the fibres was the highest (98 nm) when 4 cm tip to collector distance was implied. As a comparison on the standard deviation, when 10 cm of the tip to collector distance was offered, the standard deviation appeared to be the lowest, which is 60 nm. Furthermore, less beaded structures were a presence at 10 cm of the tip to collector distance. Thus, it is suggested that uniform fibres could be obtained at 10 cm of the tip to collector distance.

3.3 Effect of Applied Voltage

Applied voltage is vital in offering electrical force to initiate the jet formation. The diameter of electrospun fibres could be reduced by increasing the applied voltage, as shown in Figure 2. The morphology of fibres was shown in Figure 5. As the applied voltage was raised from 10 to 30 kV, the fibres size decreased slightly from 220±94 to 189±73 nm.

When higher electrical force was applied on the needle tip, it created a greater electrostatic repulsive force on the jet solution. Subsequently, the jet solution experienced greater stretching and pulling effect which could reduce the fibres diameter [17]. Furthermore, increase in electrical repulsive force could increase the evaporation rate of the solvent and hence reduce the fibre size [18]. Thus, an increase in applied voltage could reflect better thinning effect in fibres size. However, when the applied voltage was too high, the occurrence of over pulling effects and caused breakage and discontinuous in fibres [3, 19]. This could be seen from SEM images shown in Figure 5d (25 kV) and 5e (30 kV).

In terms of size distribution, fibres produced with 15 kV has the lowest standard deviation (i.e. 36 nm) which indicated the fibres were having better uniformity. From Table 1, the fibres produced with lower or higher than 15 kV were having a standard deviation of greater than 94 nm. Thus, based on the result, 15 kV voltages were favourable to produce uniform fibres.

3.4 Effect of Flow Rate

Flow rate of the jet solution should be considered in the characterization of the electrospun fibres diameter. Figure 6 a-e indicated the morphology of fibres that fabricated at a different flow rate. The jet solution flow rate was controlled by the syringe pump in order to maintain stabilised Taylor cone [20]. Figure 1 showed the increase in flow rate led to increasing in fibres diameter. When the flow rate increased from 0.5 to 2.5 ml/hr, the fibres size increased gradually from 208±103 to 229±78 nm. Increasing in flow rate could elevate the transfer rate of the jet solution. When the transfer rate was higher, more volume of the solution was dragged out and formed an unstable jet. Thus, the fibres were collected without sufficient solvent evaporation with bigger in size under constant applied

voltage. Furthermore, insufficient solvent evaporation could form flattened structures in the fibres. Figure 6d and 6e indicated the flattened web-like fibres at a flow rate of >2.0 ml/hr. In producing TiO_2 nanofibres, the flow rate of 1.0 ml/hr is preferable because uniform and continuous fibres can be obtained without flattened structures.

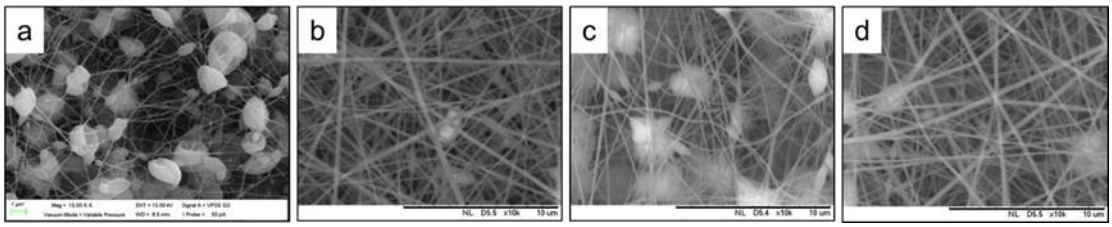


Figure 3 SEM images for varying weightage of PVP: a) 4 wt. %, b) 6 wt. %, c) 7 wt. % and d) 8 wt. %

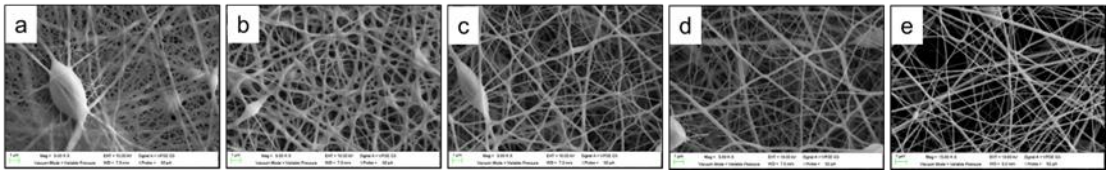


Figure 4 SEM micrographs at varying tip to collector distance: a) 6 cm, b) 8 cm, c) 10 cm, d) 12 cm and e) 14 cm

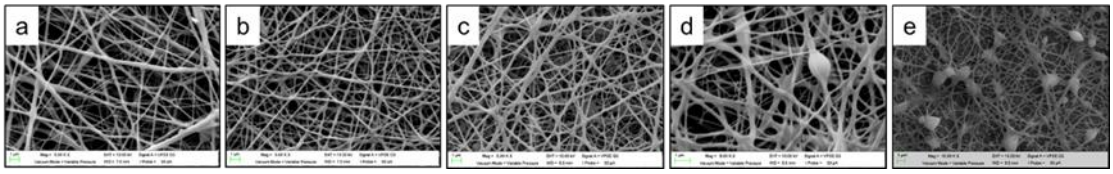


Figure 5 SEM images for different applied voltage: a) 10 kV, b) 15 kV, c) 20 kV, d) 25 kV and e) 30 kV

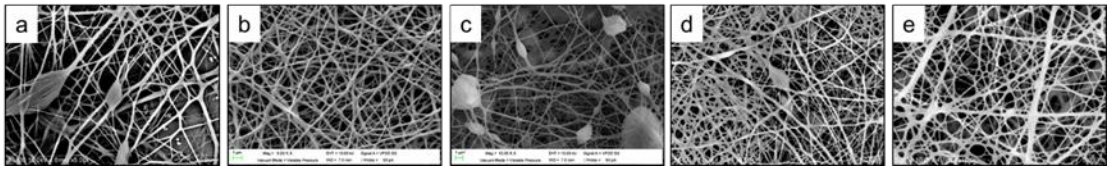


Figure 6 SEM micrographs for different flow rate: a) 0.5ml/hr, b) 1.0ml/hr, c) 1.5ml/hr, d) 2.0ml/hr and e) 2.5ml/hr

4.0 CONCLUSION

A custom-made electrospinning system was developed in order to fabricate nanofibres. An ethanolic solution containing TTiP, PVP and acetic acid was prepared to produce TiO_2 nanofibres via the developed electrospinning system. The effect of PVP weightage and fabrication parameters such as applied voltage, flow rate and tip to collector distance were investigated on the diameter of electrospun TiO_2 fibres. The diameter of the fibres was examined by SEM and further analysed with JMicroVision. In this study, the significance of each factor was investigated based on the fibres diameter. Among the parameters, PVP content was the most influencing factor on the fibre diameter, followed by the tip to collector distance and applied voltage. Flow rate of the solution jet indicated the least significance in tuning the diameter of electrospun fibres.

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