High throughput electrospinning of high-quality nanofibers via an aluminum disk spinneret

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Guokuo Zheng

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Guokuo Zheng

We, the thesis committee for the above candidate for the

Master of Science degree, hereby recommend

acceptance of this thesis.

Perena Gouma - Advisor
Professor Department of Materials Science and Engineering

Jonathan C Sokolov
Professor Department of Materials Science and Engineering

Dilip Gersappe
Professor Department of Materials Science and Engineering

This thesis is accepted by the Graduate School

Charles Taber
Dean of the Graduate School

Abstract of the Thesis

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In this work, a simple and efficient needleless high throughput electrospinning process using an aluminum disk spinneret with 24 holes is described. Electrospun mats produced by this setup consisted of fine fibers (nano-sized) of the highest quality while the productivity (yield) was many times that obtained from conventional single-needle electrospinning. The goal was to produce scaled-up amounts of the same or better quality nanofibers under variable concentration, voltage, and the working distance than those produced with the single needle lab setting. The fiber mats produced were either polymer or ceramic (such as molybdenum trioxide nanofibers). Through experimentation the optimum process conditions were defined to be: 24 kilovolt, a distance to collector of 15cm. More diluted solutions resulted in smaller diameter fibers. Comparing the morphologies of the nanofibers of MoO_3 produced by both the traditional and the high throughput set up it was found that they were very similar. Moreover, the nanofibers production rate is nearly 10 times than that of traditional needle electrospinning. Thus, the high throughput process has the potential to become an industrial nanomanufacturing process and the materials processed by it may be used as filtration devices, in tissue engineering, and as sensors.

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Chapter 1

Introduction

Nano materials means at least one dimension in the nanometer scale in the three dimensional space scale [1]. It is a new generation of materials. Due to the small size of component unit, and the interface is a considerable part of the materal. So nanometer material has many characteristics, and results many special properties in the system. Nanometer system can be used to contact atoms, molecules and the macroscopic system [2], it is a new areas that people had never been explored.

Nano materials are divided into the different dimension of the material according to the spatial dimension [3]. Mainly includes the zero dimension, one and two dimensional nano materials. Nanoparticles are zero dimension nano material. Nanowire, nanorods, nanotubes are one dimensional nano materials. Ultrathin membrane, multilayer film, superlattice are two dimensional nano materials.

1.1 Nanofiber

1.1.1 Fiber

Fiber is familiar with everybody, such as the clothing material with wool, silk, linen, cotton. They are all natural fiber in daily life. The chemical fiber industry which emerged in the 20th century [2], provides all kinds of synthetic fiber and artificial fiber, metal fiber, mineral fiber, ceramic fiber for human beings [4]. Fiber has two apparent geometrical characteristics. The first one is that the proportion of length and diameter is large. The second is the diameter of the fiber must be very thin, it is necessary to appear a certain flexibility. The diameter of traditional material in the range of 5~50 microns [5]. Silk is the thinnest fiber, the diameter in the range of 4 ~ 5 microns [5].

Based on the research of the fiber, researchers found that compared with the corresponding materials, polymer fiber will show several remarkable characteristics after the diameter decrease from microns to submicrometer or nanometer. Such as very large specific surface area, flexibility and strong mechanical behavior, these excellent features make nanofibers suitable for many important application [6]. Lots of methods were proposed for produce nanofibers fiber in recent years, such as tensile, template polymerization, phase separation, Self-assembly and electrospinning, etc [7]. Tensile is similar to the dry spinning fiber in industry, this method can produce a long single nanometer fiber filament. However, only those viscoelastic material are able to withstand great stress drawing deformation and stretch into nanofibers. Template polymerization use the nano porous membrane as the template to produce nanofibers or hollow nanofibers. The main characteristic of this method is that can use it to spinning different raw materials, such as conductive polymer, metal, semiconductor, carbon nanotubes and fibril. On the other hand, can't continuous produce the long fiber. Phase separation process is including dissolution, gelation, using different solvents extraction, condensation and drying, get the nano porous foam at last. This method takes a long time to make the solid polymer into nano porous foam. The Self-assembly is a kind of process, this method is similar to the phase separation method. The existing components spontaneously assembled into a kind of thought pattern and function. Self-assembly process is very time-consuming. The electrospinning is currently the only way can directly, continuous to produce polymer nanofibers.

1.1.2 The Fabrication of Nanofibers

Electrospinning is an easy route and straightforward method to produce nanofibers, this method has gained a lot of attention in the last few years [8-9], but it operates in a lab setting. It is a simple technique to produce continuous nanofibers with many outstanding characteristics, such as high porosity, high ratio of surface area to mass and superior mechanical properties [10]. So, with these unique properties, electrospun nanofibers are finding applications in various field such as in filtration.

The ideal destination for polymer made by electrospinning is that the diameter of the fiber is stable and can be controlled, the fiber surface without defects or defects can be controlled, the consecutive single fiber can be controlled. The most important parameters for the electrospinning is the diameter of the fiber [11]. Fiber diameter mainly depends on the size of the jet, and the solid content of polymer solution. Already know, maybe the original jet could split into multiple root jet or not, and get a different fiber diameter in the process of the jet come out from the spinneret to the collector, as long as it doesn't involve the division, the viscosity of the solution is one of the most important factors to influence the diameter of nanofibers. The higher the viscosity, the larger the fiber diameter [12]. In addition, the applied voltage has significant effect on the diameter of the fibers. The higher the applied voltage, the more the jet flow out, the larger the fiber diameter [13].

With the development of nanotechnology and the increase of nano textiles requirement, researchers proposed a series of improvement of electrospinning for made a high yield and good quality of nanofibers. There are more than one hundred kinds of synthetic polymers that have been made by electrospinning successfully so far [14]. Conventional single needle electrospinning is widely used to produce nanofibers. However, the traditional single needle electrospinning system has a lower productivity, the production in the range of 0.01-0.1g/h[15],which inhibits the development of nanofibers and industrial production. In order to solve this problem, several new approaches to electrospinning of polymer nanofibers were proposed, for example, forming many spinning sites instead of the single site.

1.2 Electrospinning of Nanofibers

1.2.1 The Fundamental Concepts and Principles of Electrospinning

Electrospinning has the characteristics of electrospray and dry spinning of fibers [7]. The fundamental theory is that the surface of fluid produce a large number of electrostatic charge when applied electric field acting on the top of the capillary [15]. The surface tension of the droplet occurred on the top of the capillary was weakened by electrostatic repulsion, and form charged cone gradually. That was named Taylor cone [16]. When the electric field strength increases to a particular threshold, the charge repulsion on the fluid surface is larger than the surface tension, electrically charged fluid will erupt out from the top tip of Taylor cone. After that electric jet will experience a process of acceleration in the injection zone, at the same time, forming polymer fiber due to the solvent evaporation, condensation, and is highly stretched .It will be deposited on the collector at last.

Taylor cone is thus the critical point occurring when the liquid erupts and it was described by Sir Geoffrey Ingram Taylor [16] in 1964 before electrospray was discovered. His research showed that there is a approximately 49.3° taper half angle that the liquid cone makes in mechanical equilibrium, and the shape of this cone has a whole angle of 98.6[16], its internal surface tension is balanced by the external electrostatic force. The formation of the Taylor cone is very important in the electrospinning process and it is influenced by the concentration of solution, the voltage, the flow rate of solution, and the external environment [17].

The jet instability exists in the process of electrospinning. There are three kinds of instability in electrospinning. The first is viscous instability, it is caused by the effect of capillary force and viscous force. The other two kind of instability is caused by the nature of electricity. One is called axisymmetric varicose instability, another one called nonaxisymmetrical bending instability. The jet of electrospinning may show one or more different instability modes, and that depends on some basic parameters, like jet velocity, the radius, charge density on the surface. Here make a simple analysis for the bending instability. The bending instability exists in the process of electrospinning. The fibers are affected by electric field force, surface tension, gravity, inner viscoelastic force, etc, in the stretched region. Actually, some influence factors such as air resistance, and charge repulsion play a role in the spinning process. As the spinning progresses, solvent evaporation or solidification of molten mass occurs, some of these factors changing constantly, the jet will bend and then become a series of rings, and the closer to the receiving plate, the greater the diameter of the ring is, and the finer the fiber obtained.

In the process of electrospinning, the bending instability of the charged polymer solution occupies an important position. Shin [18] and other researchers thought that fibers form the division and bending instability under the effect of repulsive force in this process, and resulting in finer fibers. Spivak [19] thought this phenomenon was caused by lateral instability or jet division, they also found that this phenomenon appear only after the jet develops to a certain distance. The instability restricts the development of electrospinning, as it makes it difficult to obtain a single fiber.

Currently, the electrospinning method has widely used in the process of produce polymer nanofibers. As long as the polymer can melt or dissolved in a volatile solvent, we can produce nanofibers by electrospinning. But the electrospinning technology still in the stage of laboratory research, has not formed industrialization scale. The main reason is that the designed structure of the electrospinning machine can not produce single nanofibers and the strength of the nanofibers is low.

1.2.2 The setup and Process of Electrospinning

The electrospinning setup is shown in Figure 1, which consists of a syringe pump, a syringe with needle, a metal collector and a power supply. The needle of the syringe is connected to the power supply, the collector is connected to ground.

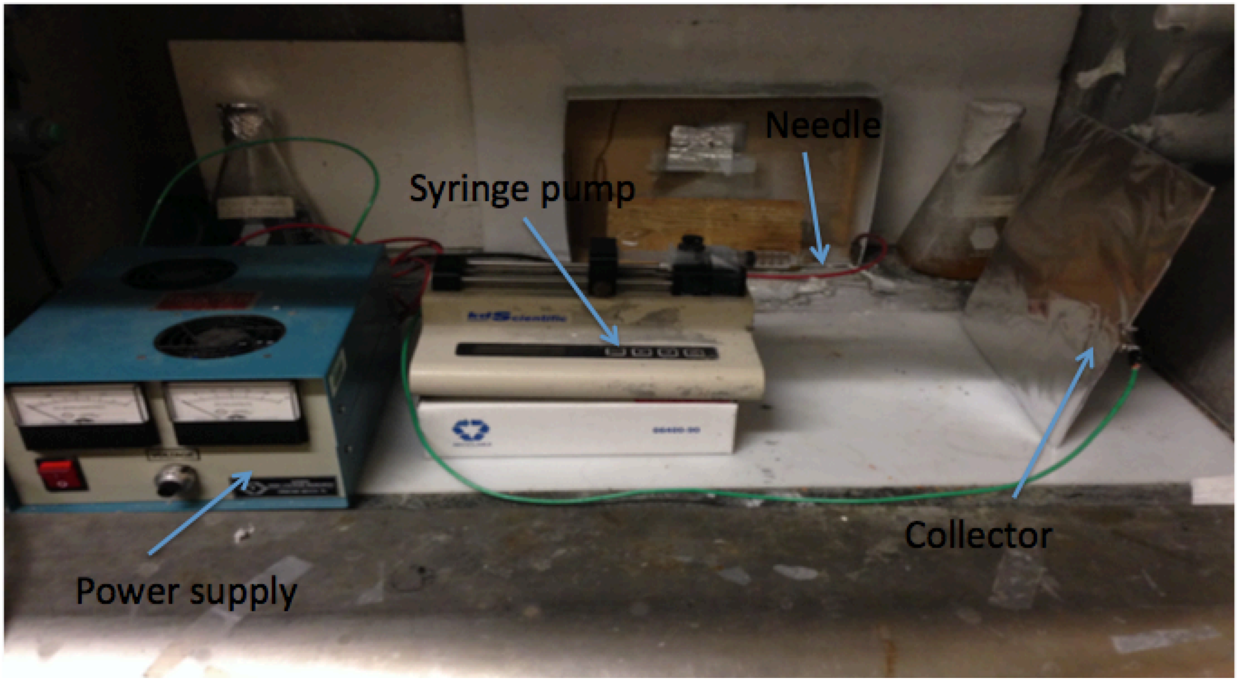


Figure 1 Traditional single needle electrospinning setup

The traditional single electrospinning setup is showed in Figure 1 and the process involved is shown in the schematic of figure 2. The solution is pumped out under a fixed flow rate through a programmable syringe pump. The drop is formed at the tip. This drop has inherent surface tension trying to pull it inside due to the solution viscosity [20]. After a high voltage is applied, the droplet is pulled towards the grounded collector screen. The repulsive force is due to the electric charges. Before the fibers reach the screen, the solution stretches and evaporates and some fibers form on the collector screen at last. In this process, the solution viscosity plays an important role in the formation of the Taylor cone, which is crucial for the fiber formation. In addition, the interplay of surfaces, shapes, rheology, and electrical charge would produce a different result in the process of electrospinning [21]. These phenomena interact in a complicated way to form fibers.

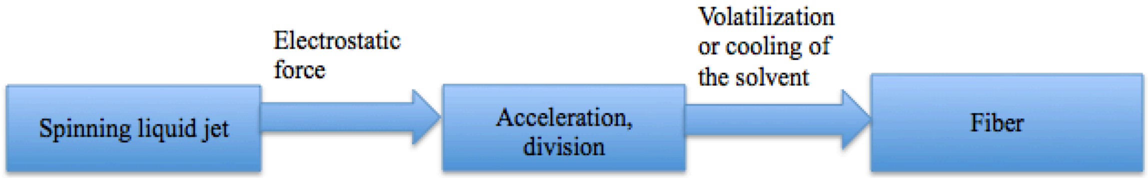


Figure 2 Original mechanism of electrsopinning fibers

The quality of fibers is dependent on four parameters: the concentration of the polymer solution, the working distance between the needle and collector, the flow rate of the solution and the applied voltage. The higher the concentration of polymer solution, the larger surface tension and viscosity, the droplet split ability will decrease after leaving the nozzle with the increase of surface tension. In general, the diameter of fiber also increases with the increase of concentration of polymer solution [22]. Increase the voltage on polymer solution, electrostatic force of the system increase, the droplet split ability enhancement, the diameter of the fibers tend to decrease. The applied voltage directly affects the bead formation [23]. Usually the more the distance between the needle and collector is allowed, the more slender the nanofibers become, and lesser are the chances to form beads [24]. For different material systems, the influence of working distance is different. In order to make fibers with smaller diameter, the flow rate has to be less. Moreover, the size of diameter depends on the flow rate. The flow rate is proportional to the fiber diameter under the condition of the spinneret is fixed. So for make fibers with smaller diameter, the flow rate has to be less. In addition, the different status of collector, the different status of nanofibers. When using a fixed collector, the nanofibers present a random irregular situation. When using a rotary plate collector, the nanofibers present a kind of parallel arrangement. The

Table 1 is a simple summary of other electrospinning setups. All of them have advantages and disadvantages.

Table 1 The different electrospinning setup

Collector	Pros	Cons
A cylinder with a high speed [25]	The aligned fiber was collected	Low success rate It was difficult to collect the continuous fibers when the speed was overfast The production rate is low
A thin wheel with a sharp edge [25]	The uniaxially aligned nanofiber yarns was collected	The production rate is low
A rectangular frame collector [25]	The individual nanofiber was obtained The different frame materials could get the different fiber alignments	The frame was fixed usually The production rate is low

1.2.3 Morphology Analysis of Nanofibers

Scanning electron microscope analysis is widely used in the lab. SEM has a higher spatial resolution, which can be used to observe the morphology of samples. The mechanism is that by receiving the signal which stimulated from the samples and then imaging, does not require the electronic penetrate the sample. So researchers can use the block sample. When do analysis for the polymer nanofibers, because of most of the polymer nanofibers are non-conductive or a poor conductive material, the possibility of electron excitation is very small, the electron beam reach to the surface of fiber samples at the same time, the redundant charge can't run away, and form the phenomenon of local charging, it will be have a significant impact for observe the sample. Therefore, it is necessary to coat a layer of conductive material on the sample before using the scanning electron microscope, gold is good material for coating. The thickness of coating in the range of 0.01~0.1 micron [26]. The process is called metal spraying. As a result of the existence of gold layer, the accumulated charge will flow away, and we get a clear image.

1.3 High Throughput Electrospinning Methods of Nanofibers

1.3.1 Background

Nanofiber has a large specific surface area, ultrafine porosity and excellence mechanical properties. These unique advantages are widely used in tissue engineering scaffolds, drug delivery, filter medium, artificial blood vessels, biochip, nano sensors, optical, composites, and other fields [27]. There are lots of methods to produce nanofibers. The method of electrospinning can produce the continuous fiber from composite material or polymer directly. Its operation is simple, has a broad applicable scope, and relatively higher efficiency.

However, the production efficiency of nanofibers is very low in the world. The kinds of nanofibers is limited, the functionalization modification technology of fiber is not mature yet. Europe and the United States launched the nanofibers on the market were produced by electrospinning[28]. But the electrospinning method mainly aimed at the solution spinning system, and the production efficiency is low, need to solve the problem of mass production. Melt electrospinning, although can not be restricted by the solvent, but due to the high viscosity of molten polymer, the diameter of the fiber obtained is very difficult to less than 500 nm. Also there are some other spinning methods, such as template spinning, melt-blown spinning. The experiment results of template spinning is ultra unstable, production efficiency is lower than electrospinning, only suitable for laboratory study. The short fiber with disordered arrangement and blanket material composed of spherical particles can be produced by melt-blown method, and the polymer materials which suitable for this method are limited. The electrospinning technology research will focus on smaller fiber diameter, higher precision and more reliable homogeneity and the control of microcosmic performance in the future. At the same time, improve the production of fibers.

1.3.2 The Summary of High throughput Electrospinning Methods

Researchers have already created various techniques and proposed diverse mechanisms [17]. Here six methods are described below used to launch multiple electrospun liquid jets. The first method, uses as a source a flat disk, the collector is a cylinder, the initiation voltage 55KV, the working voltage is 16KV, the production rate is up to 0.684g/ h[29]. The second method, which source is a circular cylindrical electrode, the collector is a kind of wire mesh, 70Kv for working voltage, the production rate is 5.2g/h [30]. The third method, which source are multiple needles, the collector is a flat grounded collector, 10KV is used as the working voltage across all nine nozzles, the production rate is 22.5ml/(cm^2 min) to 22.5 l/(cm^2 min) per 1 /cm^2 of the spinneret plate [31]. The forth method, the source is a stepped pyramid shaped spinneret, which has a flat collector, the working voltage in the range of 55Kv to 70Kv, the yield of fibers in the range of 2.3 g/h to 5.7 g/h [32]. The fifth method, whose source is a conical metal wire-coil, which has a flat collector, 60KV for working voltage, the production rate is up to 2.75g/h [33]. The sixth method, which source is a spiral coil spinnerets which has a flat collector, and the working voltage is up to 30KV, the production rate shows a 10 to 12-fold increase [34]. All of methods listed above have shortcomings, like the Table 2. That is why we need a new scaled up setup with an operating mechanism for high throughput electrospinning. In our design described below all of parameters are variable which provides great flexibility for synthesizing a wide range of materials.

Table 2 The pros and cons of high throughput electrospinning methods

Name of set up [*ref*]	**Advantages**	**Shortcomings**	**Parameters used**
- Edge Electrospinning via a bowl [29]	- Achieves high production rates. - High number of jets formed.	- Very high initiating voltage - Materials with only specific viscosity can be spun	- the initiation voltage:55KV, - the working voltage:16KV - the production rate: 0.684g/ h
- Tip-Less Electrospinning via a Circular Cylindrical Electrode [30]	- No clogging on the syringe tip - No need to control the polymer solution flow rate	- Have to clean the polymer solution after experiment finished - It is hard to estimate the number of polymer jets exactly	- Working distance: 15 cm - Working voltage: 70KV - Production rate: 5.2g/h

- electrospinning via multiple needle [31]	- A higher production rate - This setup can be scaled up	- Jet paths was affected by the external applied electric field and Coulombic inter- actions - The repulsion force of the jets results in the distribution of fibers was nonuniform	- Working distance: 40cm - Applied air pressure: 100 mbar - Inter nozzle distance: 1 cm - The production rate: 22.5ml/(cm2 min) to 22.5 l/(cm2 min) per 1 /cm2 of the spinneret plate
- electrospinning via a stepped pyramid shaped spinneret[32]	- The charge distribution is homogeneous at the edge of spinneret - The yield is several hundred times higher than TNE	- A higher viscosity will block the jet hole - Too much solution was wasted each time	- the working voltage: 55Kv -70Kv - working distance: 15 cm
- Needleless electrospinning via a Conical Wire Coil [33]	- The conical wire coil is an open container, so can inject the solution continuously - No corona discharge happened	- Working voltage is too high - The jet is not stable	- Working distance: 15 cm - Working voltage: 60 KV - Production rate is up to 2.75g/h
Our Set Up	- **A wide range of materials can be synthesized** - **All parameters can be individually changed** - **High production rate** - **Scalable technology** - **Relatively low working voltage**		

Other high throughput electrospinning methods like via a multi-nozzle spinneret [35], or multiple jets in electrospinning [36], foam high throughput electrospinning[37], splashing needleless electrospinning[38] and so on. In our experiment, we produced a higher quality nanofibers via an aluminum disk spinneret.

1.3.3 Comparison with Traditional Electrospinning

Traditional single-needle electrospinning is widely used in research. Even through it gives good lab results, the low production rate is unacceptable for industrial scale consideration. What is more, capillary action is involved in the traditional single-needle electrospinning set up [39] that influences the quality of fibers and increase the chance of experiment failure.

For the high throughput setup developed in this thesis, one may produce more fibers at the same time than a single jet process. The result of the experiments outlined below were obtained through adjusting the programmable values, such as applied voltage, working distance, concentration of solution. And there is not capillary action in place in this high throughput setup. The underlying assumption is that the internal pressure generated inside the disk after turning on the syringe pump pushes the liquid out of the holes. The scaled up version presented here can be used to produce to turn electrospinning into an industrial process. In addition, it does not affect the morphology and diameter of fibers too much in high throughput significantly after increase the working distance, but for the TNE, generally speaking, increase the working distance, the diameter of fiber will decrease and the morphology will change obviously. Through compare the method of TNE and high throughput, the concentration of the solution has the same impact on the diameter of the fiber. The smaller the concentration, the smaller the diameter. The voltage of

TNE in the range of 10 to 20Kv, the voltage of high throughput above 20kv,due to it needs a larger excitation voltage. Moreover, the flow rate in TNE is much smaller than high throughput electrospinning setup, it is restrict the yield of fibers. That is why we got a high production in high throughput setup with a higher flow rate.

1.4 The Application of Nanofibers

The nanofibers has unique property, it has become one of the focus on the field of materials science research. Nanofibers can be used in enhance the composite material, filtering, tissue engineering, drug slow-release, sensing and other fields. The research of these fields have achieved fruitful results. It has the function of nano device inherent, can translation and rotation polymer molecules.

1.4.1 Electronic Devices

Nanofibers can be used to produce a variety of nanoscale devices, like nanowires, light-emitting diodes, photocells and sensors. It also can be used to connect a large amount of nano device into a larger system. Nanofibers has special arrangement of polymer molecules, called crystal defect. Nanofibers was produced by electrosinning, not only can increase the specific surface area, but also can obtain the ideal chemical properties. Nanofibers has a potential application value in the optoelectronic field.

1.4.2 Filtering Material

The filtering material plays an important role in separation and purification in raw materials or products, air and water purification, waste things treatment before emissions and other industrial production. In the rapid development of modern biology, medicine, etc, also put forward new requirements to the filter material. Such as the diameter in micro and nanoscale particles has good filtering effect, then insist on channel of filter materials and space structure must be matched with the filter object size. Electrostatic nanofibers is one of the most directly and effective method to produce the high efficient filter medium. The aperture of the electrospinning of nanofibers membrane changes between tens of nanometers to several microns, high porosity, and with a coherent hole structure, good air permeability and intercept, adsorption performance for object.

1.4.3 Tissue Engineering and Sensor

Cell adhesion on the fiber and grow along the fiber when the diameter of fiber is less than or equal to the diameter of animal somatic cell. In recent years, nanofiber membrane is considered to be a good scaffold material in tissue engineering with its huge potential of extracellular matrix bionic [40]. With the development of nanotechnology, which provide excellent nano sensitive materials to sensor. Compared with traditional sensors, the nano sensor has the merit of small size, high sensitivity, application field widely, the sensor was made based on nanotechnology is greatly enrich the basic theory of the sensor. Due to the strong adsorption force, good biological compatibility, high catalytic efficiency, easy separation from reaction system, nanofiber got a widely attention in sensor. The introduction of nanofibers improves the detection sensitivity, shorten the response time significantly, make the instrument to the development of miniaturization be possible [41].

1.4.4 Composite Modified Materials

Using nanofiber as reinforced material can get a better mechanical performance when compared with the conventional fiber reinforced composite materials. When the size of nanomaterials in composite material is smaller than the visible wavelength, material is transparent. Due to the electrospinning superfine fiber has a higher specific surface area, so can be used to improve the interlaminar shear strength of laminated composite materials [42].

Chapter 2

Experimental Methods

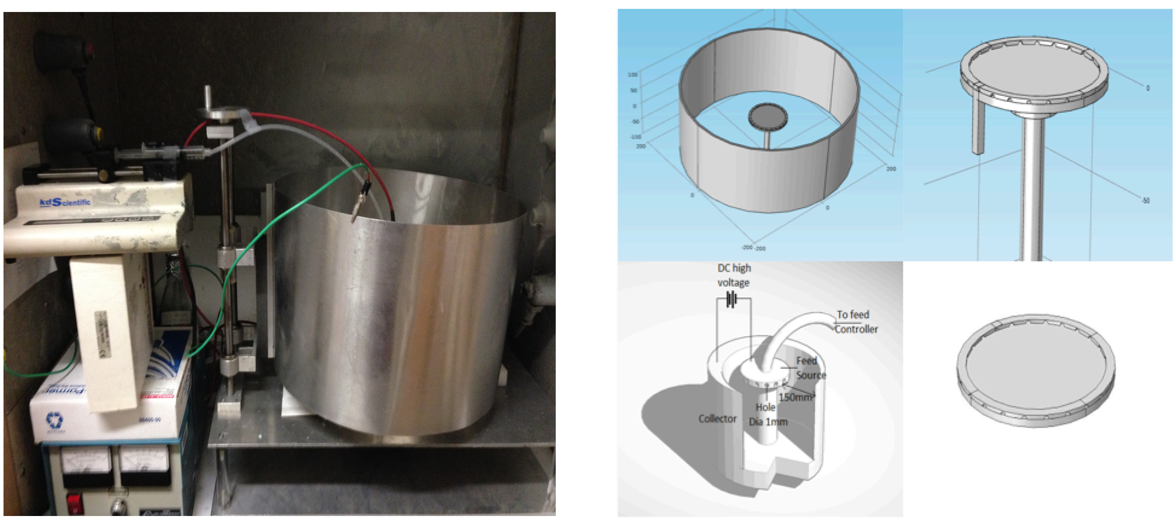
2.1. Materials

The precursor materials were polyvinylpyrrolidone (PVP; $(C_9H_9NO)n$) with an average molecular weight of 1,300,000 g/mol as solute , and ethanol as the solvent. They were mixed together and ultrasonic agitation was performed for 90 minutes. Several solutions with different concentrations were thus prepared. The aims was get high quality nanofibers out of these solutions and thus process maps were obtained to map out the optimum values of concentration, voltage and working distance.

Next, the set up was used to produce ceramic nanofibers of MoO_3. Earlier work by our group has successfully produced nanofibers of MoO_3 using the traditional set up. The precursor solution consisted of 2.5ml Molybdenum isopropoxide with 0.075ml water. Then ultrasonic agitation was performed for 2 hours, and the sol was allowed to settle for 20 hours. Polyvinylpyrrolidone (PVP) with a large molecular weight of 1,300,000 (Sigma-Aldrich) was mixed with ethanol to form solutions of different concentrations. Then, after mixing together the two precursor solutions, ultrasonic agitation was performed for another 30 minutes. After electrospinning, a precise annealing process was necessary through the Lindberg Blue tube furnace. The nanowires of MoO_3 obtained after the following stepwise heat treatment: furnace heated up from 25to 500 °C in 2 hours, then it was held constant for 8hs, then the temperature was decreased from 500-25 °C in another 2 hours.

2.2. High Throughput Electrospinning Setup

The high throughput electrospining setup is shown in Figure 3, which has the same flow control mechanism with the traditional setup. Most known polymer materials' solution may be electrospun by this high throughput setup. And all the parameters that are variables, such as flow rate, working distance, voltage and concentration of the solution.



(a) (b)

Figure 3 (a) Schematic of the high throughput set up (b) Source disk, 24 Equidistant holes were drilled on the disk and the graphic analysis of the equipment

Figure 3(a-b) describes the scalable high throughput setup. We got multiple droplets formed at the surface, The height of the metallic source disk (Figure 3(b)) was 6 mm, the outer diameter was10 cm, the depth was 2mm, the inner diameter was 90 mm. We connected the syringe pump with disk through a kind of plastic tube. The solution was pumped into the disk with the help of syringe pump. The flow rate was kept at a relative higher value, about 10 or more times higher than the traditional needle electrospinning. The value is 0.340 ml/min in our experiment process.

There are 24 holes drilled at the bottom of the disk. Furthermore, the charge accumulation and the charge distribution was homogeneous at the edge of the bottom plate. The working distance was 15cm, but this is changeable. Figure 4 showed the working condition of the high throughput set up. It was perfect as nearly all holes worked.

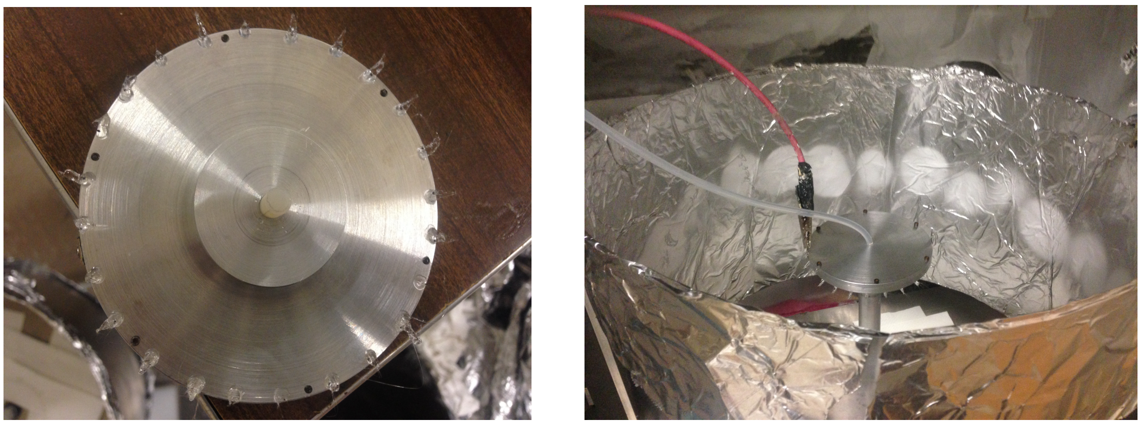


Figure 4 The working condition of the high throughput setup

2.3. Characterization

In order to observe the morphology of the nanofibers after high throughput electrospinning, Scanning Electron Microscopy (SEM) was performed through using a LEO-1550 Field Emission Gun. Gold Particles were spraying to the surface of fibers for ensure conductivity and reduce charging effects of the surface [43]. In order to measure the fiber physical size characteristics, the SEM images were analyzed by Revolution software.

The production rate of nanofibers was calculated after the high throughput electrospinning. Measuring the duration of the run, and finding out the weight of the aluminum foil before electrospinning and after, and calculating their ratio, gave us the fabrication rate in grams per hour (g/h).

Chapter 3

Experiment Process, Results and Discussion

3.1. The Experiment Process of High Throughput Electrospinning

During the process of electrospinning, the solution was continuously pumped into the hollow disk so that every hole of the spinneret was filled with the polymer solution, meanwhile the excessive solution flowed out from the hole after full of disk. The applied voltage was increased until a number of jets were observed and nanofibers occured on the collector.

Initially, the PVP solution was electrospun at the different applied voltages, concentration, and the working distance between the disk and collector. The electrospinning parameters were set as shown in Table 3. It was concluded that the more dilute solutions resulted in a smaller diameter fibers. In addition, see Figure 5, the fibers fabricated under the concentration of 0.08mM and the voltage of 24 KV were the smoothest and slimmest, and the distribution of the fibers was uniform throughout. And the production was higher. Figure 6 and Figure 7 are SEM images of the fibers fabricated under the concentration of 0.10mM and 0.12mM respectively.

Table 3 Effect of electrospinning parameters on PVP fibers under various PVP concentrations and voltage

Concentration/mM	Voltage/kV	Distance/cm	flow rate/ml/min	Production/g/h	Diameter/um
0.08	22	15	0.340	1.357	0.480
0.08	24	15	0.340	1.598	0.825
0.08	26	15	0.340	1.681	0.996
0.08	28	15	0.340	1.423	0.836
0.08	30	15	0.340	0.997	0.611
0.10	22	15	0.340	1.492	0.593
0.10	24	15	0.340	1.828	0.800
0.10	26	15	0.340	2.177	0.917
0.10	28	15	0.340	1.630	0.805
0.10	30	15	0.340	1.046	0.643
0.12	22	15	0.340	1.690	0.629
0.12	24	15	0.340	2.031	0.760
0.12	26	15	0.340	2.556	0.938
0.12	28	15	0.340	2.018	0.820
0.12	30	15	0.340	1.379	0.726

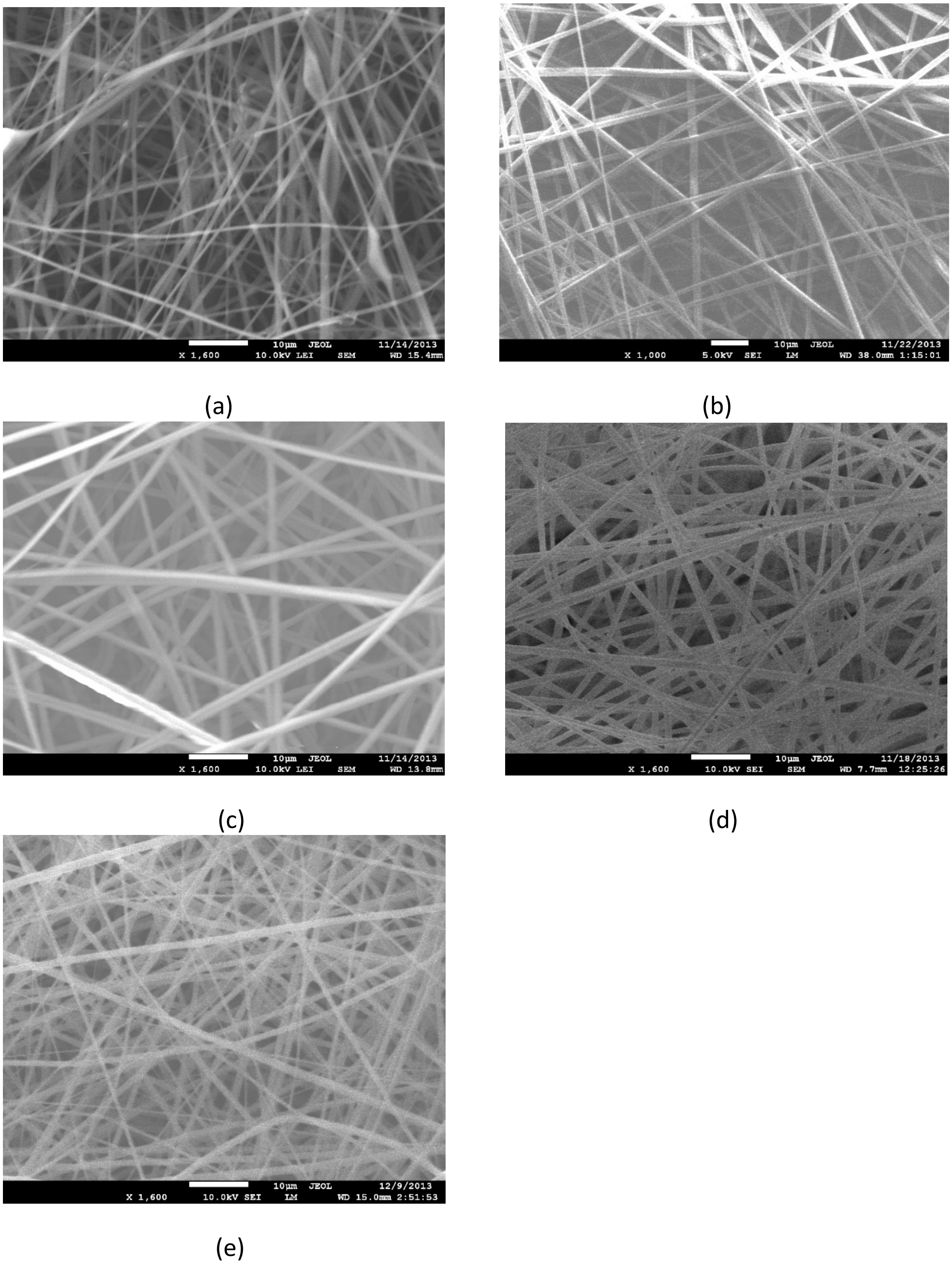
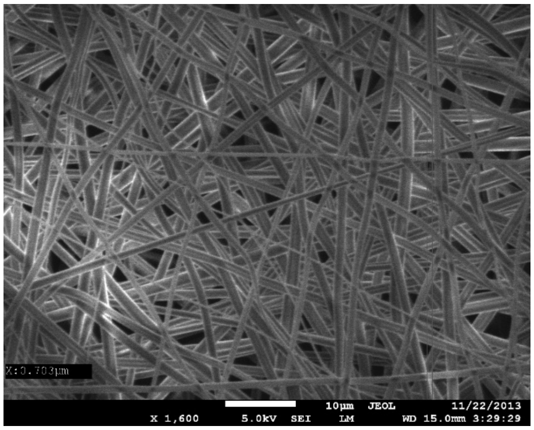
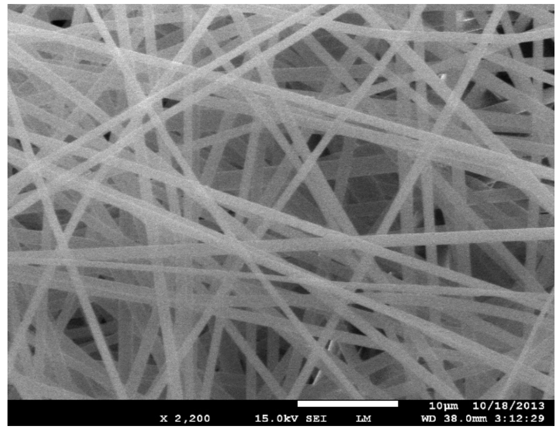


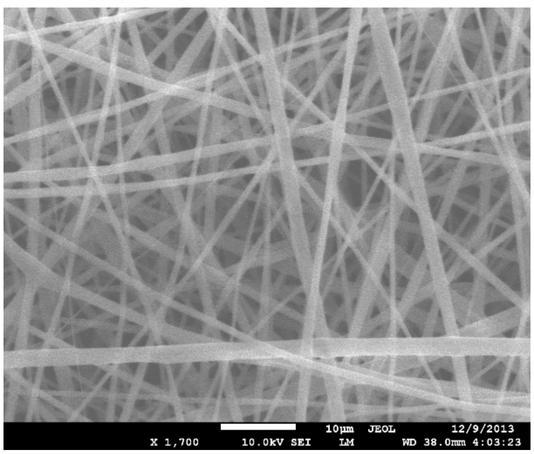
Figure 5 SEM images of PVP fibers under the concentration of 0.08mM, the voltages are (a) 22 kV, (b) 24 kV, (c) 26 kV, (d) 28 kV, (e) 30kV



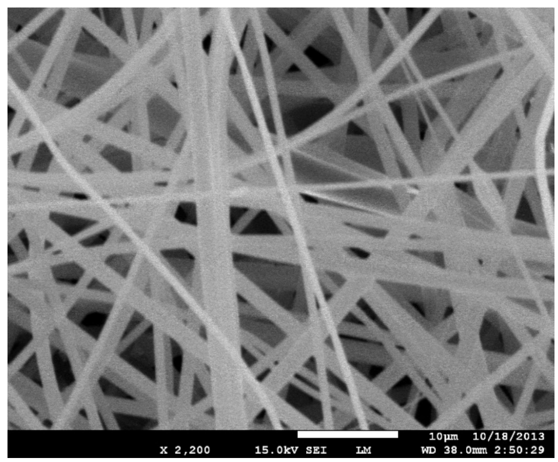
(a)



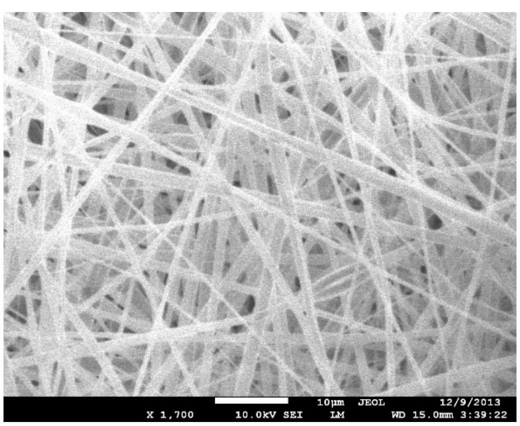
(b)



(c)



(d)



(e)

Figure 6 SEM images of PVP fibers under the concentration of 0.10mM, the voltages are (a) 22 kV, (b) 24 kV, (c) 26 kV, (d) 28 kV, (e) 30kV

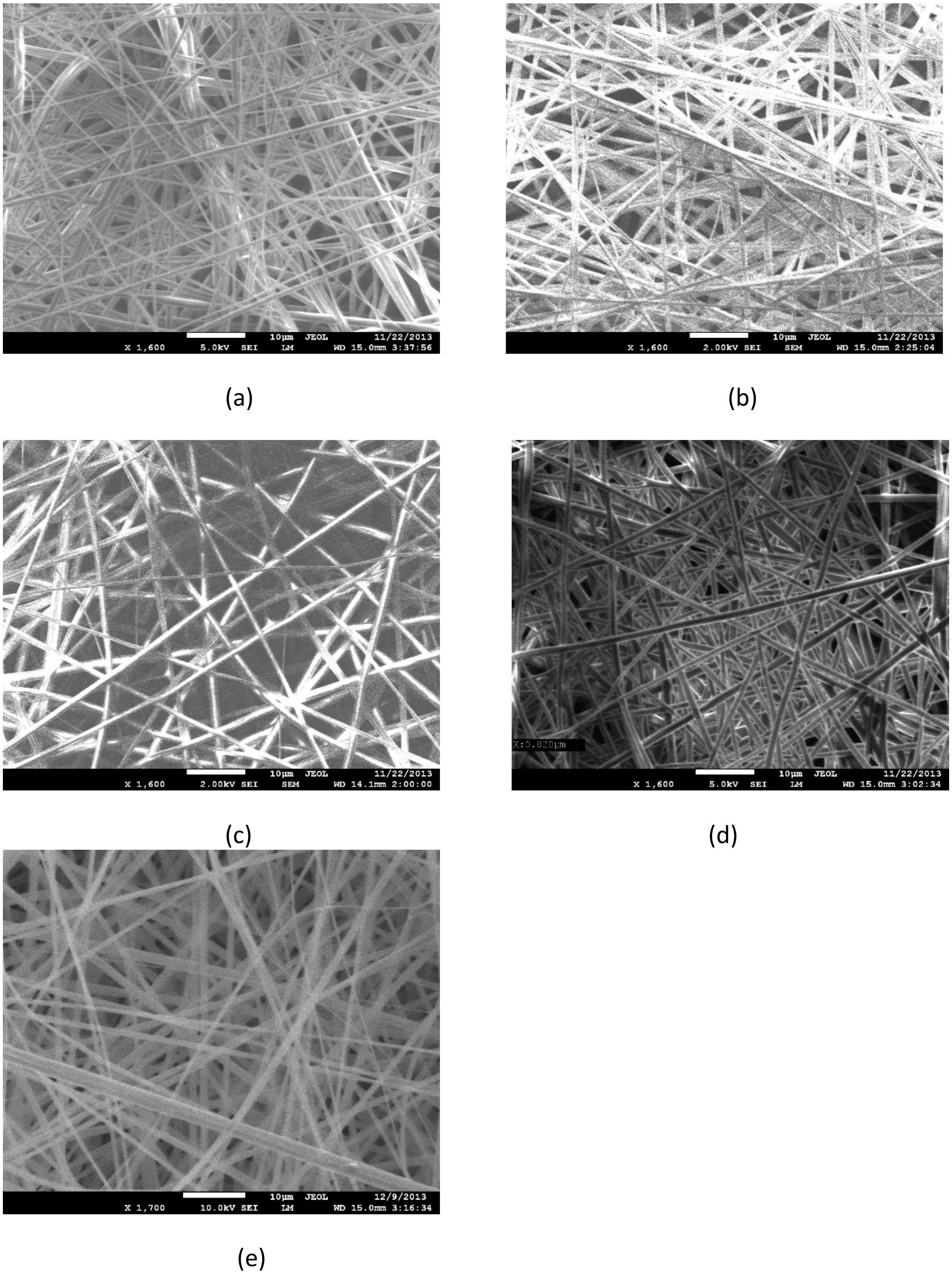


Figure 7 SEM images of PVP fibers under the concentration of 0.12mM, the voltages are (a) 22 kV, (b) 24 kV, (c) 26 kV, (d) 28 kV, (e) 30kV

3.1.1 Analysis of Electrical Field

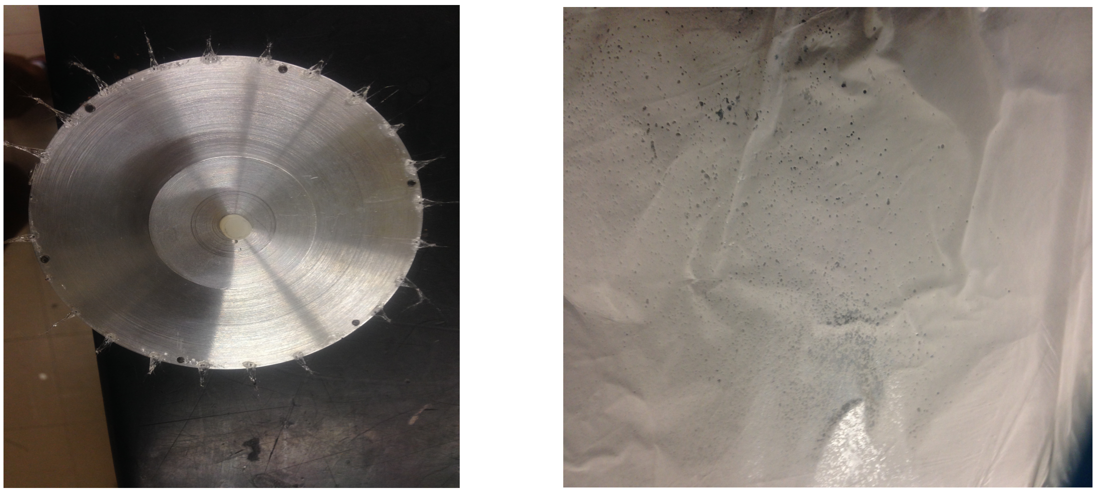
In order to understand the process, the electric field distribution on the collector and aluminum disk surface was calculated. For ensuring effective self-initiated jetting, the electric field gradient is an important parameter. There is a high intensity field on one side where the terminals were connected when voltage is applied, that is why a higher yield of fiber formation was first observed on this side, while the other side has a lower yield. For obtaining an uniform electric field distribution, the collector needs to be stored in a large reservoir and this will be implemented in future designs. In addition, we got a uniform electric field distribution and maximum charge accumulation at the edge of the bottom of the disk, that is why a hole was drilled there.

3.1.2 Analysis of High Throughput Electrospinning Experiment

Base on the results shown in Figure 5, 6 and 7, the fibers appear to have a dynamic variability. In this experiment, no jet was ejected out from the aluminum disk when the applied voltage was lower than 18KV, due to the electric force being lower than the surface tension. Increasing the applied voltage led to a stable jet stream.

Under the voltage of 22KV, even through thinner fibers could be obtained, the production was relatively low. There were also some beading observed, which had a significant influence to the quality of fibers. One can observe the beads in Figure 5(a). After increasing the concentration from 0.08mM to 0.12mM, the beads disappear gradually.

The fibers fabricated at 24KV were the smoothest and slimmest. Observing the fiber distribution and measureing the diameter of fibers, a higher quality of fibers was obtained. The production was increased after increased the concentration. After that, increasing the voltage to 26KV, the plurality of discharge occurs at the droplet, as seen in Figure 8(a), so could not get a stable Taylor cone and jet stream. Figure 8(b) showed that some small droplet appears on the collector. The quality of fibers would decrease at this stage.



(a) (b)

Figure 8 The formation of unstable Taylor cone and jet stream

As voltage increased to 28KV and 30KV respectively, the fibers stuck together gradually, too much droplets seen on the collector. Just a few fibers were seen after electrospinning. With the electric field being too high, poorly dried fibers were seen, as in Figure 9, thus the diameter and the production rate of fibers were decreased. The reason is that, on one hand, driven by the high electrostatic force, a large amount of solution aggregated at the tip. Too much solution was pump out from the syringe at the same time. It then transformed into a jet. On the other hand, the high electrostatic force shortened the flight time [44], it was difficult for fibers to stretch and volatilize. Thus, by the effect of the two reasons, the fibers could not be stretched sufficiently and separated from each other thoroughly before arriving at the collector.

Figure 9 The sample of poorly dried fibers

Initially, the concentration and voltage were varied. Through Figures 6 and 7, it is seem that the fiber diameter increased at first with the voltage, and got the highest point under the voltage of 26 KV, then started to decrease. The production rate followed the same trend, as the concentration increased, the production rate increased too.

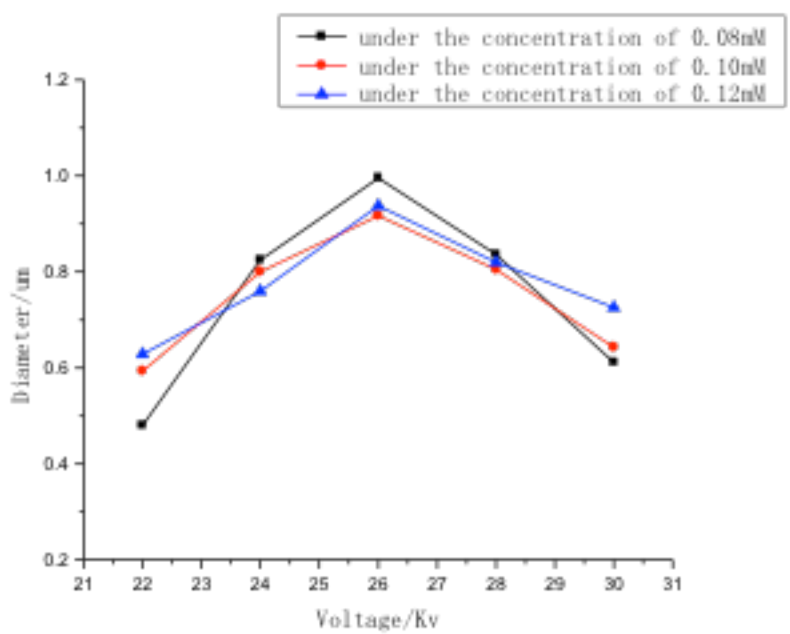


Figure 10 Plot of Voltage vs Nanofiber diameter for different concentrations

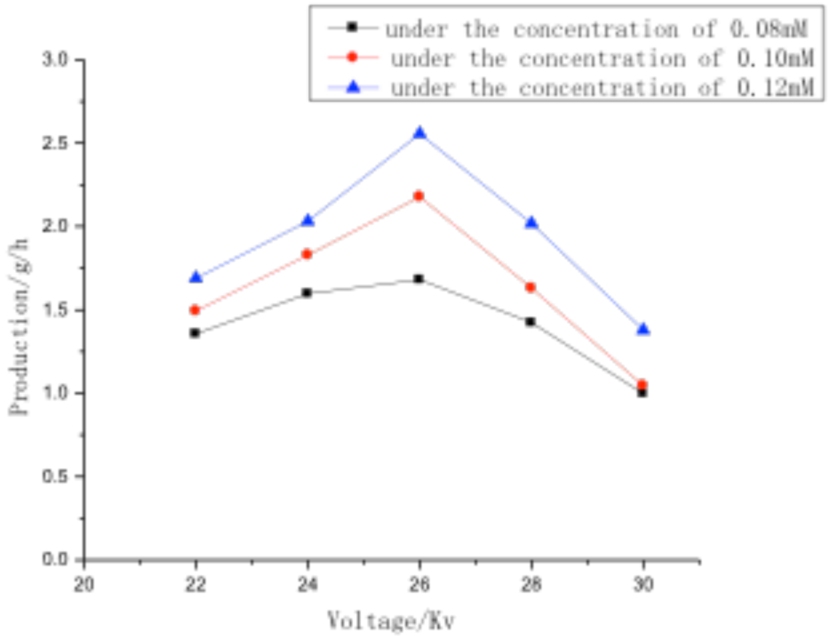


Figure 11 Plot of Voltage vs Production for different concentrations

In this experiment, the optimum voltage was 24KV,and smaller diameter fibers were obtained for concentrations under 0.08 mM. But the size of fibers was not small enough. It has not reached nanometer level. Thus, the goal next was to achieve nanofiber production at high rates.

3.2. The Influence of the Working Distance

In order to decrease the diameter of fibers in the high throughput electrospinning experiment, the working distance between was increased between the disk and the collector. Table 4 shows that the diameter of fibers was not changed significantly after the test. So, the original distance was kept for the subsequent experiments.

Table 4 Effect of electrospinning parameters on PVP fibers under various PVP working distance

Concentration/mM	Voltage/kV	Distance/cm	flow rate/ml/min	Production/g/h	Diameter/um
0.08	24	15	0.340	1.598	0.825
0.08	24	16	0.340	1.315	0.783
0.08	24	17	0.340	1.275	0.731
0.08	24	18	0.340	1.261	0.645
0.08	24	19	0.340	1.228	0.616

3.3. The Influence of the Concentration

Based on the upon experiment, the lower the concentration, the smaller the fiber diameter. Table 5 shows a better quality of nanofibers was obtained after decreasing the concentration to 0.05mM. The production rate was acceptable.

Table 5 Effect of electrospinning parameters on PVP fibers under various PVP concentration

Concentration/mM	Voltage/kV	Distance/cm	flow rate/ml/min	Production/g/h	Diameter/um
0.05	24	15	0.340	1.186	0.180
0.05	26	15	0.340	1.343	0.252
0.20	24	15	0.340	3.528	1.215
0.20	26	15	0.340	3.836	1.306

In summary, the fibers fabricated under the voltage of 24 KV and a lower concentration like 0.5mM, the diameter of nanofibers was 180nm. These were the smoothest and slimmest of nanofibers. And the production rate was higher. The concentration of solution is the most important factor for the diameter of nanofibers in this high throughput experiment.

3.4. Production Process of Molybdenum Trioxide Nanofibers

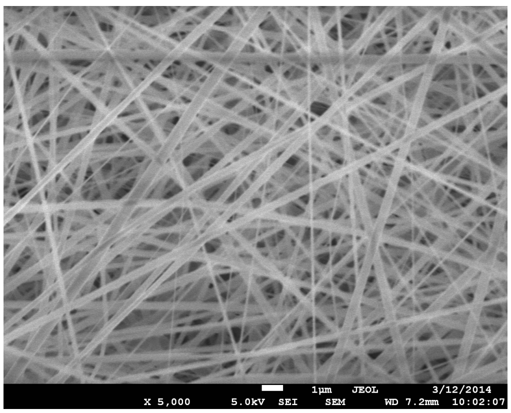
This high throughput set up can be used for various engineering applications [35], such as obtaining high yield of nanofibers of ceramic materials which can be applied in environmental monitoring, gas sensing and so on.

The high throughput set up was used to produce nanofibers of MoO_3. Earlier work in our group[55] has successfully produced nanofibers of MoO_3 using the traditional set up. It was found that after mixing molybdenum trioxide with different concentrations of polymer solution would influence the diameter of nanofibers. Table 6 and Figure 10, show that molybdenum trioxide nanofibers were synthesized by using a mixture solution. The solution was composed of MoO_3 sol-gel and PVP solution. The best quality nanofibers were achieved under the concentration of 0.05mM. Even through the production of MoO_3 nanofibers was a low percentage of the total fibers, but it was markedly higher as a quantitative comparison.

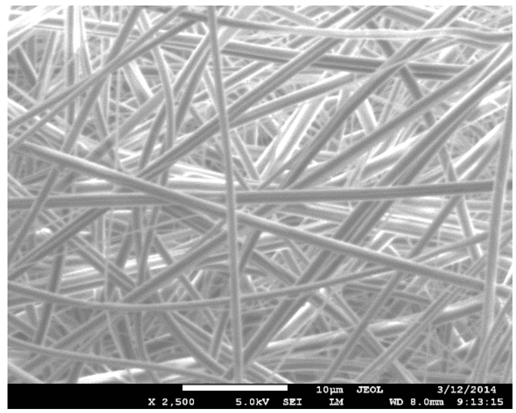
Table 6 Effect of electrospinning parameters on MoO_3/PVP fibers under various PVP concentration

Concentration/mM	Voltage/kV	Distance/cm	flow	Production/	Diameter of nanowires/u

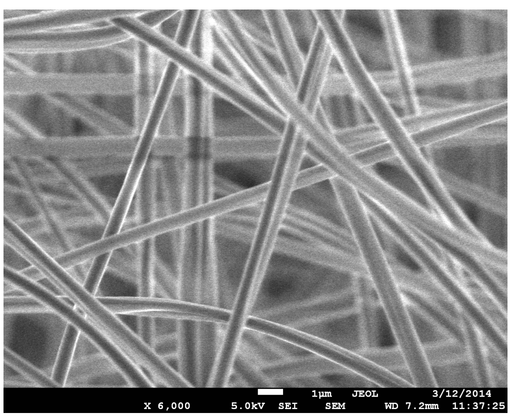
(PVP and ethanol)			rate/ml/min	g/h	m
0.05	24	15	0.340	1.241	0.176
0.08	24	15	0.340	1.496	0.690
0.10	24	15	0.340	1.659	0.540



(a)



(b)

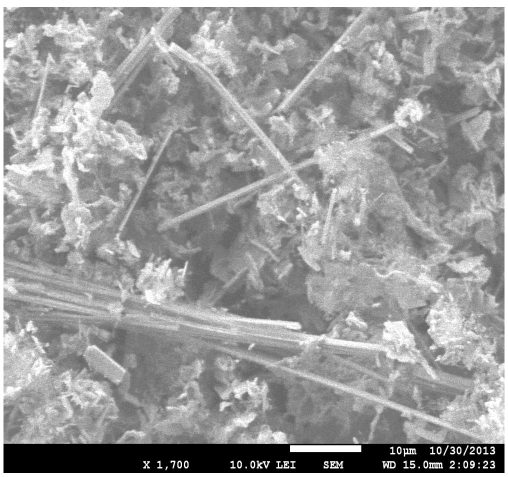


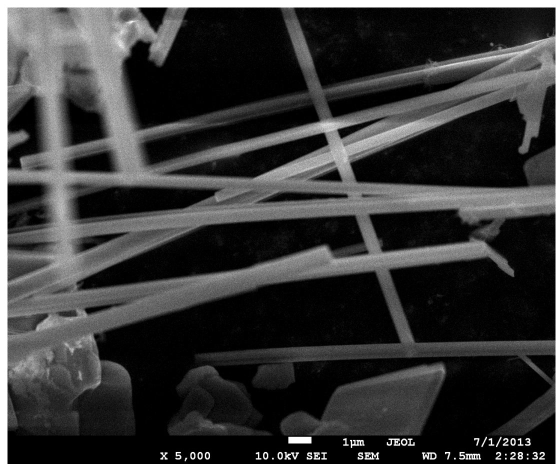
(c)

Figure 12 SEM images of MoO_3/PVP fibers under the different PVP concentration, the concentration are (a) 0.05mM, (b) 0.08mM, (c) 0.10mM

3.4.1 Analysis of MoO_3 Nanowires

The as-spun molybdenum trioxide nanofibers were annealed in air and the nanowires of molybdenum trioxide were obtained after the heat treatment [45]. Figure 11, compares the SEM micrographs of the nanowires of MoO_3 produced by traditional vs the high throughput setup. SEM micrographs show the similarity in the morphology of the nanofibers produced from each technique. The production of nanofibers that were electrospun under the high throughput setup was nearly 10 times than that of the traditional electrospinning method.





(a) (b)

Figure 13 MoO_3 nanowires produced by (a) High throughput electrospinning setup (b) Traditional single needle electrsopinning setup

Chapter 4

Conclusion

We have presented a high throughput electrospinning setup that via an aluminum disk spinneret. And, the quality of nanofibers produced from this high throughput setup are almost identical to those fabricated by TNE, with a demonstrated 10 times production rate increase. In order to decrease the diameter of fibers in the high throughput electrospinning experiment, we try to decrease the working distance between the disk and the collector, but the diameter of fibers was not changed significantly after the test. So, we kept the original distance. And it told us the working distance had a little influence in this high throughput setup. After that we try to decrease the concentration, the quality of fibers was good enough under a lower concentration. In summary, the optimum voltage for the solution we used in this experiment is 24 kilovolt, the distance is 15cm, a lower concentration is important for the diameter of fibers, less concentrated solutions resulted in a smaller diameter fibers. We use this high throughput setup to produce molybdenum trioxide nanofibers, after an annealing process and test, the morphology of the nanowires is similar with nanowires produced by TNE. There are some merits in this high throughput setup. Such as a wide range of materials can be synthesized, all parameters can be individually changed, high production rate, scalable technology, and relatively low working voltage, so this setup can be scale up and application in the field of industry. For the future efforts, improve the flow rate to a higher value, because the maximum value of flow rate is 0.340 ml/min in this experiment. For obtain an uniform electric field distribution, the collector could be stored in a large reservoir in the future design, due to the water conductive uniformity. Or increase the number of coaxial aluminum disk for improve the yield of nanowires, In addition, we could focus on using a rotating disk for produce a continuous fibers.

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