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TOPICAL REVIEW

A review on electrospinning design and nanofibre assemblies

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Abstract
Although there are many methods of fabricating nanofibres, electrospinning is perhaps the most versatile process. Materials such as polymer, composites, ceramic and metal nanofibres have been fabricated using electrospinning directly or through post-spinning processes. However, what makes electrospinning different from other nanofibre fabrication processes is its ability to form various fibre assemblies. This will certainly enhance the performance of products made from nanofibres and allow application specific modifications. It is therefore vital for us to understand the various parameters and processes that allow us to fabricate the desired fibre assemblies. Fibre assemblies that can be fabricated include nonwoven fibre mesh, aligned fibre mesh, patterned fibre mesh, random three-dimensional structures and sub-micron spring and convoluted fibres. Nevertheless, more studies are required to understand and precisely control the actual mechanics in the formation of various electrospun fibrous assemblies.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Since the beginning of this century, researchers all over the world have been re-looking at a century old process (Cooley 1902, Morton 1902) currently known as electrospinning. Probably unknown to most researchers for most of the last century, electrospinning is able to produce continuous fibres from the submicron diameter down to the nanometre diameter. It was not until the mid-1990s with interest in the field of nanoscience and nanotechnology that researchers started to realize the huge potential of the process in nanofibre production (Doshi and Reneker 1995). Nanofibres and nanowires with their huge surface area to volume ratio, about a thousand times higher than that of a human hair, have the potential to significantly improve current technology and find application in new areas. Applications for nanofibres include nanocatalysis, tissue scaffolds (Wang *et al* 2005b, Li *et al* 2002), protective clothing, filtration and nano-electronics (Ramakrishna *et al* 2005). Although there are other methods of fabricating nanofibres such as phase separation (Witte *et al* 1996) and template synthesis (Chakarvarti and Vetter 1998), few, if any, can match electrospinning in terms of its versatility, flexibility and ease of fibre production. At a laboratory level, a typical electrospinning set-up only requires a high voltage power supply (up to 30 kV), a syringe, a flat tip needle and a conducting collector.

In terms of the flexibility of the process, electrospinning is able to fabricate continuous nanofibres from a huge range of materials. Of the major classes of materials, electrospinning is able to produce nanofibres of polymers, composites,

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semiconductors and ceramics (Ramakrishna *et al* 2005, Huang *et al* 2003, Chronakis 2005). Although the most commonly electrospun material is polymer, ceramic precursors have also been electrospun without the addition of polymers (Son *et al* 2006, Wang and Santiago-Aviles 2004, Larsen *et al* 2003). Thus, it is not surprising that over 500 research papers on electrospinning were published in the last decade on various issues such as the fundamentals of electrospinning (Hohman *et al* 2001, Feng 2002, Yarin *et al* 2001), electrospinning conditions (Krishnappa *et al* 2003, Tan *et al* 2005, Deitzel *et al* 2001b, Mit-uppatham *et al* 2004) and characterization of fibre for various applications (Shawon and Sung 2002, Desai *et al* 2004, Royen *et al* 2006). A good summary of the various studies on electrospinning, its nanofibres and their references can be found in the book by Ramakrishna *et al* (2005).

Recent research on electrospun fibres has been on exploring various materials that are electrospinnable, characterization of the fibres and finding new applications for it. However, for the potential of electrospun fibres to be fully realized, it is important to fabricate various fibrous assemblies, as the fibre arrangement will have a significant affect on the performance of a device. Ordered nano-grooves and assemblies have been shown to influence cell proliferation and morphology (Xu *et al* 2004). For use as nanowire, it is vital that the single nanowire can be grown or positioned across specific electrodes. In application as filtration membrane, a nonwoven mesh may be desirable. The ability to form yarn made of nanofibre may pave the way for higher performance clothing or woven scaffolds. Due to the size of nanofibres, it is difficult to form various assemblies through physical manipulation. Nevertheless, electrospinning is able to fabricate various nanofibre assemblies *in situ*. This gives electrospinning an important edge over other larger-scale nanofibre production methods. This allows customization of nanofibre assemblies to meet the requirement of specific applications such that its performance is enhanced. In this review, we will concentrate on the different electrospinning designs to obtain various nanofibre assemblies and other modifications in the set-up. This will allow researchers on various domains to know the array of nanofibre assemblies that can be fabricated and their corresponding set-ups. Various concepts, which researchers used to create the nanofibre assemblies, will be described to facilitate understanding of the process such that new designs may be created to construct nanofibre assemblies to meet specific needs.

2. Electrospinning fundamentals

The formation of nanofibres through electrospinning is based on the uniaxial stretching of a viscoelastic solution. To understand and appreciate the process that enables the formation of various nanofibre assemblies, the principles of electrospinning and the different parameters that affect the process have to be considered. Unlike conventional fibre spinning methods like dry-spinning and melt-spinning, electrospinning makes use of electrostatic forces to stretch the solution as it solidifies. Similar to conventional fibre spinning methods, the drawing of the solution to form the fibre will continue as long as there is enough solution to feed the electrospinning jet. Thus without any disruption to the electrospinning jet the formation of the fibre will be continuous.

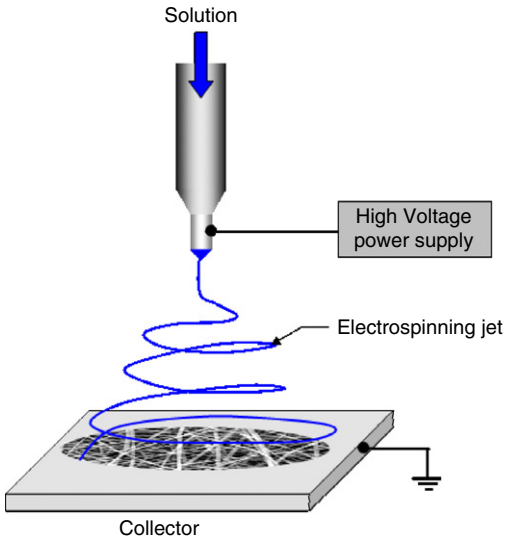


Figure 1. A typical electrospinning set-up using a grounded static collector.

For a typical electrospinning set-up as shown in figure 1, a solution is first fed through a spinneret. A high voltage is applied to the solution such that at a critical voltage, typically more than 5 kV, the repulsive force within the charged solution is larger than its surface tension and a jet would erupt from the tip of the spinneret. Although the jet is stable near to the tip of the spinneret, it soon enters a bending instability stage with further stretching of the solution jet under the electrostatic forces in the solution as the solvent evaporates. Electrospinning devices without the use of spinnerets have also been explored by various researchers (Yarin and Zussman 2004, Kameoka *et al* 2003). Generally, a grounded target is used to collect the resultant fibres which are deposited in the form of a nonwoven mesh. The parameters to control the diameter have been discussed in several good references (Ramakrishna *et al* 2005, Theron *et al* 2004, Mit-uppatham *et al* 2004, Supaphol *et al* 2005, Tan *et al* 2005). A few widely studied parameters include solution viscosity, conductivity, applied voltage, spinneret tip-to-collector distance and humidity. For example, by reducing the spinneret tip-to-collector distance mesh with inter-connected fibres can be collected (Buchko *et al* 1999), while reducing the solution concentration will reduce the electrospun fibre diameter. Although polymer chain entanglement is an important criterion for fibre formation in polymers (Shenoy *et al* 2005), the viscosity of a solution is a more general parameter since ceramic precursors can also be electrospun despite their low molecular weight (Son *et al* 2006, Wang and Santiago-Aviles 2004). To achieve various fibre assemblies, there are generally two main methods, one is to control the flight of the electrospinning jet through the manipulation of the electric field and the other is to use a dynamic collection device. Nevertheless, by using different static collection devices, it is possible to achieve some form of fibre assemblies. To overcome various limitations of the typical electrospinning set-up and to further the performance of the electrospun fibrous mesh, researchers have come out with other modifications to the set-up.

Table 1. List of US patents issued before 1976.

Patent issued date	Inventor	Patent number
04 February 1902	J F Cooley	692,631
29 July 1902	W J Morton	705,691
22 Jan 1929	K Hagiwara	1,699,615
02 October 1934	A Formhals	1,975,504
21 July 1936	C L Norton	2,048,651
13 April 1937	A Formhals	2,077,373
22 February 1938	A Formhals	2,109,333
10 May 1938	A Formhals	2,116,942
19 July 1938	A Formhals	2,123,992
16 May 1939	A Formhals	2,158,415
16 May 1939	A Formhals	2,158,416
06 June 1939	A Formhals	2,160,962
01 August 1939	E K Gladding	2,168,027
16 January 1940	A Formhals	2,187,306
29 June 1943	A Formhals	2,323,025
14 December 1943	F W Manning	2,336,745
30 May 1944	A Formhals	2,349,950
18 October 1966	H L Simons	3,280,229

3. History of electrospinning

For the first inventor of the electrospinning process, it is necessary to understand the effect of electrostatics on liquid. Observation of water behaviour under the influence of electrostatics was made as early as the 1700s (Gray 1731–1732). In the late 1800s, electrodynamics was used to explain the excitation of dielectric liquid under the influence of an electric charge (Larmor 1898). This probably led to the invention of electrospinning to produce fibres in the early 1900s by Cooley and Morton (Cooley 1902, Morton 1902). Early researchers on electrospinning showed in-depth knowledge of the process based on the designs that were invented. In one of the earliest electrospinning inventions, Cooley patented a set-up that used auxiliary electrodes to direct the electrospinning jet onto a rotating collector.

In the 1930s, Formhals came out with several innovative set-ups to produce yarns made out of electrospun fibres including designs that do not require the use of a spinneret (Formhals 1934). In fact, many recent electrospinning set-ups can be traced back to the patents more than half a century ago such as using multiple spinnerets and using parallel electrodes to produce aligned fibres (Formhals 1938a, 1938b, 1938c, 1939a, 1939b). The list of US patents filed before 1976 is given in table 1.

For the fibre industries, one important consideration is the level of fibre production. Electrospinning, compared to the popular industrial fibre spinning process, is very slow. Industrial dry spinning has a yarn take-up rate of 200–1500 m min^{-1} (Gupta and Kothari 1997) while yarn fabricated from electrospinning has a take-up speed of 30 m min^{-1} (Khil *et al* 2005). Thus, before 1990, there was very little research and publications on electrospinning (Baumgarten 1971). Nevertheless, there was some research on the behaviour of thin liquid jets in an electric field (Zeleny 1917, Taylor 1964, 1966, 1969). With melt spinning as the preferred method to produce fibres, efforts were made to electrospin fibres using polymer melts (Larrondo and Manley 1981a, 1981b, 1981c), but there is currently less research in this, probably due to its difficulty in fabricating fibres with nanometre diameter (Lyons *et al* 2004, Sanders *et al* 2005). Nevertheless, Dalton *et al* used electrospun polymer melts to deposit fibres directly on cells to form layered tissue constructs for tissue engineering. This eliminates any chance of introducing cytotoxic solvents into the cell culture when the fibres are deposited (Dalton *et al* 2006). While there have been patents filed for various electrospinning set-ups since the 1900s, it is only in the last decade that academia has been looking into using electrospinning to fabricate various nanofibrous assemblies. Schematic diagrams of the various electrospinning set-ups are shown in table 2. Various principles behind the fabrication of the nanofibrous assemblies will be covered in the following sections.

4. Dynamic mechanical device

The ability to create ordered structures has many implications in the performance of a fibre assembly. Cells cultured on aligned nanofibre scaffolds have been shown to proliferate in the direction of the fibre orientation (Xu *et al* 2004). Several researchers have shown that it is possible to obtain aligned fibres by using a rotating collector (Matthews *et al* 2002, Kameoka *et al* 2003, Subramanian *et al* 2005). A schematic diagram of the set-up is shown in table 2(A). Matthews *et al* demonstrated the effect of the rotating speed of a mandrel on the degree of electrospun collagen fibre alignment. At a speed of less than 500 rpm, a random mix of collagen fibres was collected. However, when the rotating speed of the mandrel was increased to 4500 rpm (approximately 1.4 m s^{-1} at the surface of the mandrel), the collagen fibres showed significant alignment along the axis of rotation. Mechanical testing of the aligned scaffold showed that the peak stress along the principal fibre alignment was 1.5 ± 0.2 MPa and the average modulus was 52.3 ± 5.2 MPa, while the peak stress across the principal fibre alignment was 0.7 ± 0.1 MPa and the modulus was 26.1 ± 4.0 MPa (Matthews *et al* 2002).

Kim *et al* (2004) examined the effect of the linear velocity of the rotating mandrel on the crystallinity, mechanical properties and alignment of electrospun poly(ethylene terephthalate) (PET). Using wide-angle x-ray diffraction, PET electrospun fibres were found to be more amorphous with increasing mandrel rotation. This is probably due to the rapid solidification and collection of the fibres. However, the increased linear velocity of the mandrel induced greater alignment of the PET crystals in the fibres. Although the Young's modulus, yield stress and tensile stress of the mesh along the PET fibre alignment increased with higher mandrel rotation speed and fibre alignment, the same properties tend to decrease above a linear velocity of 30 m min^{-1}. At a linear velocity of 45 m min^{-1}, many fibres were dispersed into the air instead of being deposited on the mandrel (Kim *et al* 2004). At such a high rotation speed, the velocity of the electrospinning jet may be slower than the linear velocity of the rotating mandrel. Reported average velocity of the electrospinning jet ranged from 2 m s^{-1} (Kowalewski *et al* 2005, Sundaray *et al* 2004) to 186 m s^{-1} (Smit *et al* 2005). A separate study by Zussman *et al* using a rotating disc collector demonstrated that at high enough rotation speed, necking of the electrospun fibres was observed (Zussman *et al* 2003). This may account for the reduced mechanical properties of the PET mesh collected at high speed

Table 2. Schematic diagram of various electrospinning set-ups for multiple spinnerets and to obtain various fibrous assemblies. (Assuming spinneret is given a positive charge unless otherwise stated.)

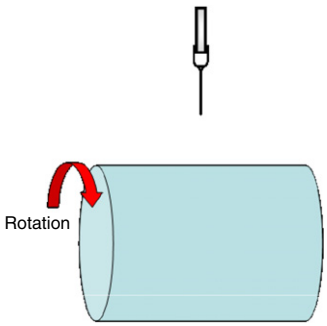
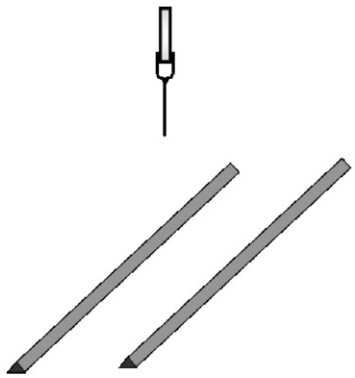
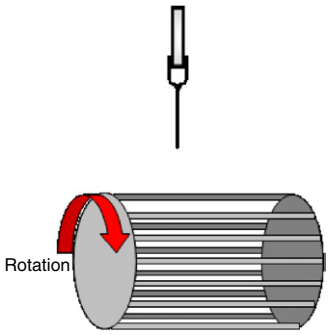
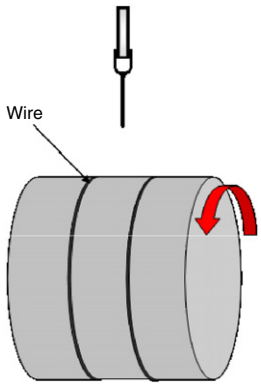
Assembly-aligned fibrous mesh	
A. Rotating drum 	Advantage Simple set-up Large area of aligned fibres can be fabricated Disadvantage Highly aligned fibrous assemblies are difficult to fabricate Fibre breakage may occur if rotating speed is too high (Matthews *et al* 2002, Kim *et al* 2004, Chew *et al* 2005, Wannatong *et al* 2004)
B. Parallel electrodes 	Advantage Simple set-up Highly aligned fibres are easy to obtain Aligned fibres are easily transferable to another substrate Disadvantage Thicker layer of aligned fibres are not possible There is a limit in the length of the aligned fibres (Li *et al* 2003)
C. Rotating wire drum collector 	Advantage Simple set-up Highly aligned fibres are possible Disadvantage Thicker layer of aligned fibres are not possible Fibres may not be aligned throughout the whole assembly (Katta *et al* 2004)
D. Drum collector with wire wound on it 	Advantage Simple set-up Highly aligned fibres are possible Area of aligned fibres on the wire is adjustable by varying wire thickness Disadvantage Aligned fibres are concentrated on the wire instead of the whole drum (Bhattarai *et al* 2005)

Table 2. (Continued.)

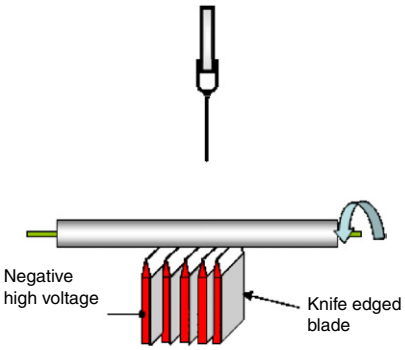
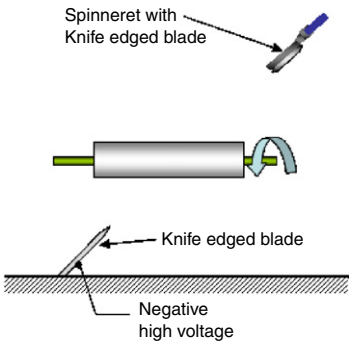
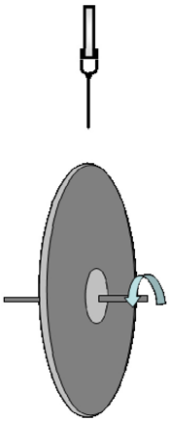
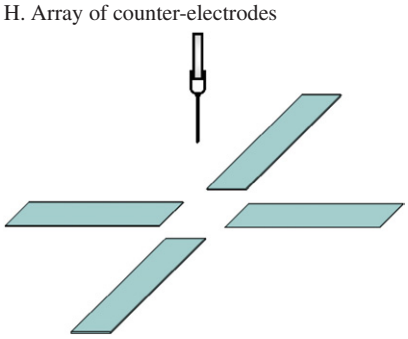
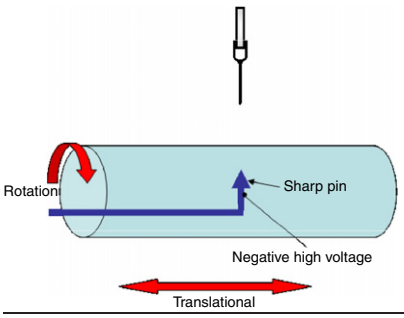
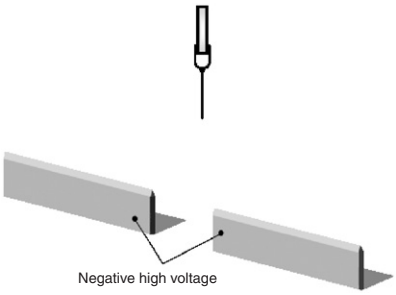
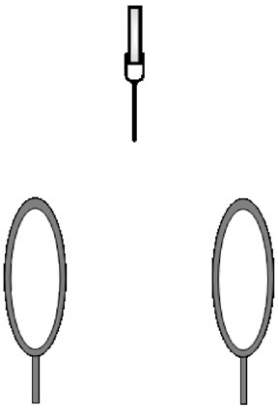
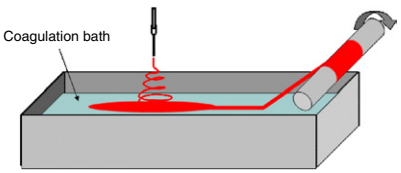
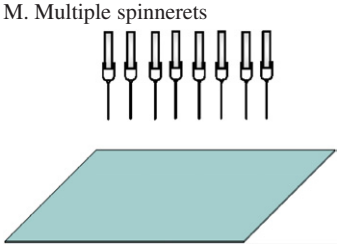
E. Rotating tube collector with knife-edge electrodes below 	Advantage Highly aligned fibres possible Aligned fibres covered the whole tube Thicker layer of aligned fibre deposition is possible Disadvantage Set-up requires a negative electrode to be effective Only possible for small diameter tube (Teo *et al* 2005)
F. Controlling electrospinning jet using knife-edge electrodes 	Advantage Highly aligned fibres possible Able to control the direction of fibre alignment on the tube Thicker layer of aligned fibre deposition is possible Disadvantage Set-up requires a negative electrode to be effective Only possible for small diameter tube (Teo *et al* 2005)
G. Disc collector 	Advantage Simple set-up Highly aligned fibres are possible Able to fabricate arrayed fibres by attaching a rotatable table on the edge of the disc Disadvantage Unable to retain high fibre alignment at the same rotating speed when the deposited fibres are thicker Small area of fibre alignment (Theron *et al* 2001, Inai *et al* 2005, Xu *et al* 2004)
Assembly—fibre arrays	
H. Array of counter-electrodes 	Advantage Simple set-up Disadvantage Fibre patterning is not consistent throughout the assembly Area of the assembly is limited Thicker fibrous assembly is not possible (Li *et al* 2004)

Table 2. (Continued.)

I. Rotating drum with sharp pin inside 	Advantage Large area of arrayed fibres can be fabricated Disadvantage Set-up is complicated Thicker area of arrayed fibre assembly may not be possible (Sundaray *et al* 2004)
Assembly—yarn	
J. Blade placed in line 	Advantage Simple set-up Yarn can be easily removed from the collector Collected yarn is highly aligned Disadvantage Fabricated yarn is of limited length Deposited fibres have to be dipped in water first before yarn is formed (Teo and Ramakrishna 2005)
K. Ring collector placed in parallel 	Advantage Simple set-up Twisted yarn can be fabricated Disadvantage Fabricated yarn is of limited length One of the rings has to be rotated to twist the fibres that are deposited into yarn (Dalton *et al* 2005)
L. Yarn collection using water bath 	Advantage Simple set-up Long continuous yarn can be fabricated Fibres in the yarn are generally well aligned Disadvantage Yarn collection speed is relatively slow (Smit *et al* 2005, Khil *et al* 2005)
Mass production	
M. Multiple spinnerets 	Advantage Relatively simple set-up Able to mix fibres of different materials of desired ratio Disadvantage Interference between the electrospinning jets (Ding *et al* 2004, Kidoaki *et al* 2005, Theron *et al* 2005, Madhugiri *et al* 2003, Kim *et al* 2006)

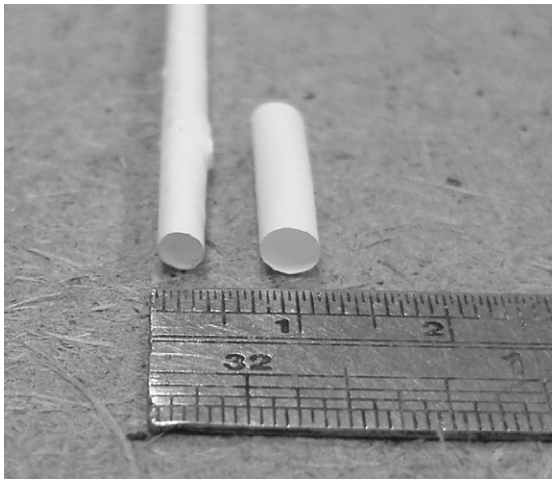


Figure 2. Small diameter electrospun nanofibrous conduit.

by Kim *et al*. Therefore the mandrel rotation speed and fibre orientation have a direct influence on the material properties of the engineered matrix.

The presence of the disoriented fibres collected on the rotating mandrel may be the result of residual charge accumulation on the deposited fibres, which interferes with the alignment of incoming fibres. To achieve greater fibre alignment, a possible way is to reduce the chaotic path of the electrospinning jet and to reduce the residual charge accumulation on the rotating mandrel. Kessick *et al* used an alternating-current (AC) high voltage supply instead of a typically used direct-current (DC) high voltage supply to charge the solution for electrospinning. Polyethylene oxide (PEO) collected on a rotating mandrel showed greater degree of fibre alignment using an AC potential than a DC potential. Using an AC potential to charge the solution may have a dual function. The electrospinning jet from an AC potential may consist of short segments of alternating polarity and this may significantly reduce the chaotic path of the electrospinning jet. This allows the fibres to be wound onto the rotating mandrel with greater ease and alignment. Given the presence of both positive and negative charges on the surface of the rotating mandrel, there will be a neutralizing effect over the area of the mesh, thus minimizing charge accumulation (Kessick *et al* 2004).

4.1. Small diameter electrospun tube

So far, the use of a rotating device has been shown to be able to form aligned two-dimensional fibre mesh. Through the use of a small diameter rod (<5 mm) as a collector, a three-dimensional structure in the form of a small diameter conduit as shown in figure 2 can be fabricated by depositing fibres over a rotating rod. Electrospun fibres have been shown to provide an excellent environment for cell growth. However, many tissue engineering applications require specific assemblies. For the construction of vascular grafts, Stitzel *et al* fabricated a conduit 12 cm long and 1 mm thick by electrospinning a polymer solution containing a mixture of collagen type I, elastin, and poly(D, L-lactide-coglycolide) on a circular mandrel of diameter 4.75 mm. Compliance tests showed that the electrospun fibre conduit had a diameter change of 12–14% within the physiologic pressure range, which is close to the native vessels, with a diameter change of 9%. The rotation speed was deliberately kept low at 500 rpm such that the fibre orientation was random. Longitudinal and circumferential mechanical testing showed no significant difference between the two directions (Stitzel *et al* 2006). Matsuda *et al* fabricated a conduit by depositing electrospun segmented polyurethane (SPU) fibres on a 3 mm diameter rod rotating at two different speeds, 150 and 3400 rpm. The thickness of the mesh that formed the conduit was maintained at 250 μm. When the conduit was fabricated by deposition on the rod at a low rotating speed of 150 rpm, the tensile strength in the longitudinal direction was larger than that in the circumferential direction, which differs from the results obtained from Stitzel *et al*. However, at a higher rotation speed of 3400 rpm, both the tensile tests at the longitudinal axis and the circumferential axis showed no significant differences. No reasons were proposed for the differences in the mechanical properties of the conduits that were constructed from the different rotating speeds. At a rotation speed of 3400 rpm, fibres on the interior circumference of the conduit showed distinct alignment along the circumferential axis while fibres on the external circumference were random. When the rotation speed was 150 rpm, fibres on both surfaces were randomly oriented (Matsuda *et al* 2005). Another advantage of electrospinning nanofibres to form a small diameter conduit for a vascular graft is the ease of spinning different materials to form a layered composite (Vaz *et al* 2005, Kidoaki *et al* 2005). This way, materials such as collagen, which encourages cell proliferation and attachment but is mechanically weak, can be spun as the inner layer, while mechanically stronger man-made polymers can be used as the outer layer.

4.2. Liquid deposition method

In most cases, the deposition of the electrospun fibres is on a solid collector. However, common liquid such as water can be used to collect electrospun fibres (Srinivasan and Reneker 1995). Although more commonly used as a coagulation bath, Smit *et al* and Khil *et al* demonstrated an easy method of collecting continuous yarn composed of electrospun fibres by first depositing them on a liquid medium (Smit *et al* 2005, Khil *et al* 2005) as shown in table 2(L). The ability to form continuous yarn made out of nanofibres is a significant breakthrough in the assemblies that can be formed by electrospinning as it can be woven into textiles. This in turn can be used in areas like protective clothing, high performance fabrics, tissue engineering and composites. In the late 1930s, Formhals patented various electrospinning set-ups for the fabrication of continuous fibre yarn (Formhals 1938a, 1938b, 1938c). However, there are no further studies to show that the patented set-ups are able to fabricate acceptable continuous yarn. In the method proposed by Smit *et al*, the electrospinning was carried out over a water bath. A mesh consisting of electrospun fibres was first deposited on the surface of the water bath and subsequently drawn to the edge of the water bath and collected on a rotating mandrel above it. Visual analysis of the yarn showed that the electrospun fibres were aligned in the direction of the length of the yarn.

Although the electrospun fibres were randomly deposited on the water surface, the fibre mesh would elongate and the fibres would align as the mesh was drawn over the surface of the water. Surface tension caused the fibre mesh to collapse into a yarn when it was lifted off the water surface to the rotating collector. As the resultant yarn was rolled onto the mandrel at a rate of 3 m min^{-1}, more fibres were deposited on the water surface to feed the drawing process. Yarn made out of electrospun poly(vinyl acetate), poly(vinylidene fluoride) and polyacrylonitrile nanofibres were fabricated using this method (Smit *et al* 2005). Khil *et al* used a similar set-up and fabricated yarn using a similar concept but at a rate of 30 m min^{-1}. Although his group used both water and a mixture of water and methanol to collect the fibres, they did not show any evidence or comment on any differences in the yarn collected using water and water/methanol mixture. Nevertheless, the use of water with its high surface tension may be preferred to other liquid with lower surface tension. Electrospun fibres that are deposited on a liquid with lower surface tension may be submerged. This may create a higher drag force on the electrospun fibres as they are drawn to the side of the collector and wound into yarn. More studies have to be carried out to determine the influence of the properties of the liquid bath on the yarn.

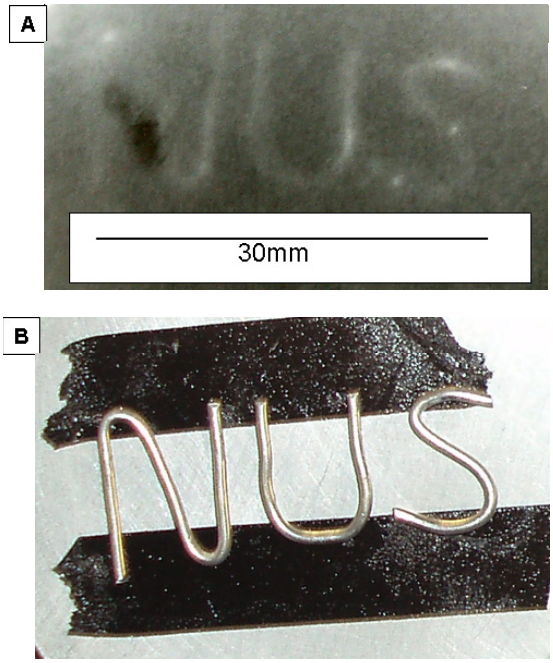


Figure 3. Influence of conducting wire placed below a glass slide on the deposition of the electrospun fibres. (A) Electrospun fibres deposited on glass cover slip. (B) Grounded electrode placed under the glass cover slip.

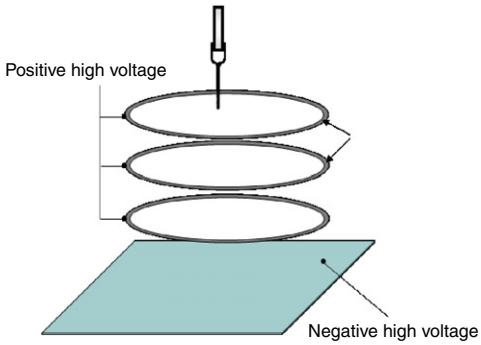
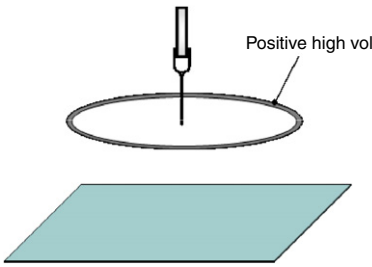
5. Manipulation of electric field

The force that stretches the solution into a fine strand is the electrostatic charge applied to it using a high voltage power supply. Since the electrostatic charges are distributed along the electrospinning jet, an external electric field can be used to control the jet. As early as 1902 (Cooley 1902), researchers manipulated the electric field to control the electrospinning jet. Even with a slight variation in the electric field profile, its effect on the deposition of the electrospun fibres can be seen. When a grounded wire was placed below a non-conducting substrate such as a glass slide, it induced the electrospun fibres to deposit preferentially on the areas on the glass slide just above the grounded wire as shown in figure 3. Slight alteration of the electric field profile due to the presence of other nearby electrospinning jets will also affect the electrospinning process and must be considered when using multiple spinnerets (Theron *et al* 2005). Although a grounded structure is able to exert some control over the deposition location of the electrospun fibres, it is more common to use one or more auxiliary electrodes with charges of either the same polarity as the electrospinning jet or with opposite polarity as they have a greater effect on the electrospinning jet (Teo and Ramakrishna 2005).

To manipulate the external electric field so as to exert some control on the electrospinning jet, the shape, position and polarity of the charges applied to the auxiliary electrode(s) have to be considered. Schematic diagrams of set-ups using ring(s) as auxiliary electrodes to control the electrospinning jet are given in table 3. Deitzel *et al* used rings, placed below the tip of the spinneret, as auxiliary electrodes and gave it the same positive charge as that of the solution. The positively charged rings that were evenly spaced out between the tip of the spinneret and the collector created a cylindrical 'electrical wall' that discouraged the charged electrospinning jet from travelling out of it. To create a pulling force on the electrospinning jet through the charged rings, a negative charge was applied to the collector. As shown in figure 4(A), the electric field lines converged to a centreline above the collecting plate as given in figure 4(B). Control of the electrospinning jet was shown by significantly reduced deposition area to 1 cm diameter as compared to electrospinning without the charged rings with a deposition area of 7 cm diameter (Deitzel *et al* 2001a). Although a deposition area of 1 cm diameter is not good enough for precise patterning, this method still offer advantages such as controlled fibre deposition area and location since the chaotic flight of the electrospinning jet and the residual charge accumulation on the deposited fibres may otherwise cause the electrospun fibres to deposit on areas outside the designated collector. Stankus *et al* used a single positively charged cylindrical steel mesh near the tip of the positive spinneret to control the deposition area of a negatively charged collector (Stankus *et al* 2004). Buttafoco *et al* used a single charged ring to designate and reduce the deposition area such that most of the fibres would be directed on a rotating 3.1 mm diameter tube (Buttafoco *et al* 2006).

Since the electric field profile between the tip of the spinneret and the collector has an influence on the electrospinning jet, this can also be used to create aligned or patterned fibres. As early as 1938, Formhals patented an electrospinning set-up where bars were placed in parallel with gaps between them as collectors to collect aligned fibres. Later, Li *et al* demonstrated that two electrodes placed in parallel were able to collect aligned fibres in the gap as shown in figure 4(C). From the electric field profile, the electric-field lines in the gap near to the electrodes are drawn towards their edge as given in the electric field profile in figure 4(D). This

Table 3. Schematic diagrams of electrospinning set-up for controlling fibre deposition (assuming spinneret is given a positive charge unless otherwise stated).

	Controlled deposition
A. Controlled deposition using ring electrodes 	Advantage Area where fibres are deposited can be minimized Disadvantage Complicated set-up Rings have to be given a positive charge (Deitzel *et al* 2001a)
B. Controlled deposition using single ring 	Advantage Relatively simple set-up Deposition of the fibres can be controlled over an area Disadvantage Ring have to be given a positive charge Deposition area of the fibres is quite large although confined within the ring (Stankus *et al* 2004, Buttafoco *et al* 2006, Kim 2006, Kim *et al* 2006)

exerts a pulling force on the electrospinning jet across the gap towards the parallel electrodes (Li *et al* 2003).

Using a similar concept, Li *et al* arranged an array of counter-electrodes in parallel to create some form of patterning of the electrospun fibres (Li *et al* 2003). However, the arrangement and the pattern formed by the fibres were different throughout the fibre mesh and it depended on their location in the gap as shown in figure 5. This greatly reduces the usefulness of the electrospun mesh. Another drawback of using parallel auxiliary electrodes as collectors is that the alignment of the fibres would become more random as more fibres are deposited (Katta *et al* 2004). This is probably due to the accumulation of residual charges on the deposited fibres distorting the desired electric field profile. The length of the aligned electrospun fibres across a gap is also limited by the gap, which is typically less than 100 mm. At a greater distance, the electrospinning jet may not deposit across the gap or the electrospun fibres may break under its own weight, especially if the fibre is of smaller diameter (Li *et al* 2003). Although patents in the 1930s and 1940s using parallel electrodes claim that this can be used to form continuous fibre yarn, it seems highly improbable that this is possible, based on current knowledge of this method.

Nevertheless, several advances in the assemblies of electrospun fibres are based on electrospinning jet behaviour when placed in the electric field profile of a pair parallel electrode. Teo and Ramakrishna made use of the deposition behaviour of the electrospinning jet over a gap to create a highly aligned fibre bundle. Their set-up consisted of placing two blades in line with one another with a gap between them as shown in table 2(J). A negative charge was applied to the blades such that there was a greater attractive force on the positively charged electrospinning jet. This way, the electrospun fibres would consistently deposit across the gap from the tip of one blade to the other. However, above a certain negative voltage applied to the blades, no electrospun fibres were deposited on the blades. A possible reason could be the ionization of the air due to the high voltage applied to the knife edge. The negatively charged ions may be attracted to the positively charged electrospinning jet, which will result in a net negative charge on the electrospinning jet, and subsequently repelled by the negatively charged blades. Therefore, the negative charge applied to the blade must be low such that the electrospinning jet will retain its positive charge so as to be attracted by the blades. Due to the repulsive forces caused by residual charges on the deposited fibres, all the fibres were spread apart across the gap. Teo and Ramakrishna demonstrated that by dipping the fibres in water while the fibres were still attached to the blades they were able to make use of water surface tension to compress the fibres together to form a tight and highly aligned electrospun fibre bundle. An important advantage of the set-up is that the two ends connecting the fibre bundle to the electrodes are precise and consistent. Controlled positioning of the fibre bundle can then be achieved (Teo and Ramakrishna 2005). One potential application for the highly aligned nanofibre bundle is in gas sensors where the fibres are required to be placed across conducting electrodes (Kessick and Tepper 2006). The alignment and orientation of the fibres may facilitate the transfer of electrical signals across the electrodes.

Dalton *et al* used two rings placed in parallel to collect highly aligned fibres that were deposited at the perimeters of the rings, across the gap as shown in table 2(K). By rotating one of the rings after the fibres were deposited, he was able

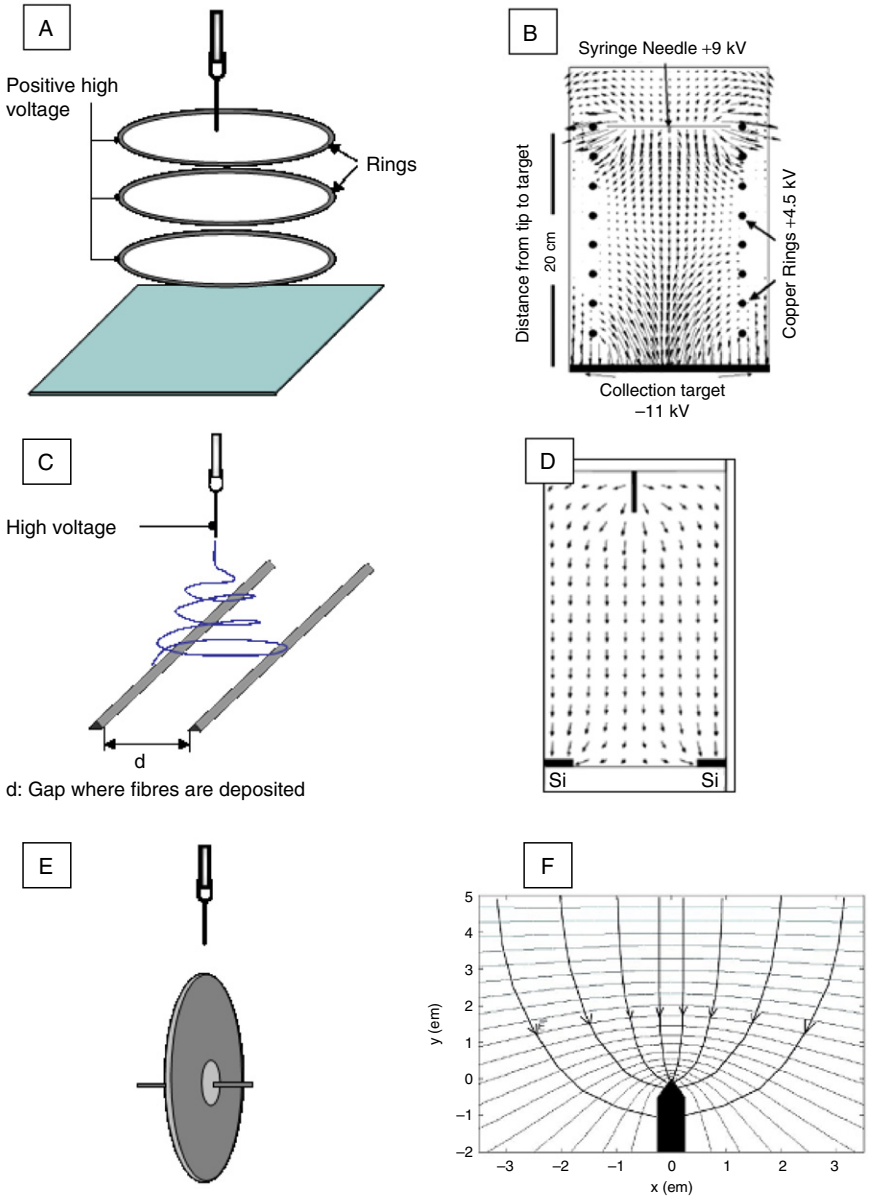


Figure 4. (A) Set-up for controlling fibre deposition area using rings as auxiliary electrodes. (B) Electric field profile of the region between the syringe needle and the collection plate with the ring as auxiliary electrodes (reprinted from Deitzel *et al* 2001b *Polymer* **42** 8163, © 2001 with permission from Elsevier). (C) Schematic diagram of parallel auxiliary electrode arrangement. (D) Electric field profile from the spinneret to the parallel auxiliary electrodes (reprinted with permission from Li *et al* 2003, © American Chemical Society). (E) Schematic diagram of a knife-edge rotating disc as a collector. (F) Electric field profile from the tip of the spinneret to the knife edge (reprinted with permission from Theron *et al* 2001).

to obtain twisted, multi-filament yarn. Such twisted yarn is expected to exhibit greater strength than yarn consisting of just aligned fibres (Dalton *et al* 2005). Suitable applications include sutures for medical applications. However, the limited length of the yarn will reduce its versatility.

5.1. Combining electric field manipulation with dynamic collector

Since both the manipulation of electric field and the use of a dynamic collector are the most common methods of getting ordered fibre assemblies, the two methods have been combined to achieve greater order in the fibre assembly. Theron *et al* used a rotating disc collector to take advantage of the rotating motion and the convergence of electric field lines toward the knife edge of the disc to collect highly aligned fibres as shown in figure 4(E). For a typical electrospinning process, the electrospinning jet undergoes bending instability which spreads over a larger area, resulting in a large deposition area on a static collector. However, when a knife-edge disc was used, the electrospinning jet converged towards the knife-edge of the disc as shown in figure 4(F), which was subsequently aligned along the edge as it rotates (Theron *et al* 2001). Glass coverslips or any non-conducting substrates can be attached along the edges of the disc to get highly aligned fibres which can be used in tissue engineering studies (Xu *et al* 2004).

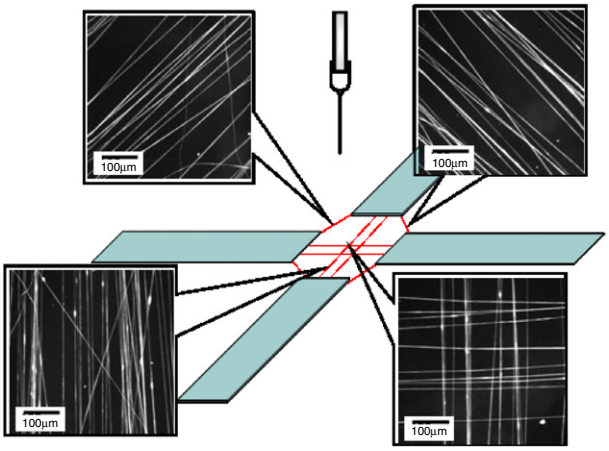


Figure 5. Different fibre arrangements at different locations on the gap.

Crossed arrays of electrospun fibres can also be obtained by attaching a rotating table. Using a similar concept as the disc collector, Bhattarai *et al* wound a copper wire as an electrode on an insulating cylinder as shown in table 2(D) to collect a highly aligned fibre bundle by rotating the cylinder at an optimum speed of ∼2000 rpm. The size of the fibre bundle was said to be controllable by varying the wire diameter (Bhattarai *et al* 2005).

Instead of using static electrodes placed in parallel, Katta *et al* used a rotating wire drum collector to collect aligned fibres as shown in table 2(C). With just a rotating speed of 1 rpm, the aligning of the fibre is more likely due to the influence of the wire arranged in parallel than the rotation of the drum. However, after 15 min of electrospinning, the fibre alignment was reduced, probably due to increased residual charged accumulation on the collected fibres (Katta *et al* 2004).

Teo *et al* demonstrated the effect of a knife-edged auxiliary electrode on the deposition of electrospun fibres using a set-up shown in table 2(E). When parallel knife-edged auxiliary electrodes were used instead of parallel conducting stripes as auxiliary electrodes placed under a rotating rod, fibres collected on the rod showed greater degree of alignment (Teo *et al* 2005). The influence on the deposition of electrospun fibres in the presence of a knife-edge had also been demonstrated by Theron *et al* using a disc collector. Sundaray *et al* used a sharp pin as an electrode instead to direct the path of the electrospinning jet. The sharp pin was placed in a rotating collector which had the effect of focusing the deposition point of the electrospinning jet. By introducing a lateral movement to the rotating cylinder collector, cross-bar patterned fibres were obtained (Sundaray *et al* 2004). However, since increased deposition of fibres will often result in an accumulation of charges, it remains to be seen whether this method is able to obtain thick, patterned fibre mesh.

Rather than just having the electrode directly below the spinneret to focus the deposition of the electrospinning jet, Teo *et al* used a knife-edged electrode to direct the flight of the electrospinning jet as shown in table 2(F). The polymer solution was given a positive charge while the knife-edged electrode was given a negative charge such that it exerts an attractive force on the electrospinning jet. The negatively charged knife-edge electrode was placed at a distance from the spinneret such that there was an angle between the tip of the spinneret and the knife edge of the electrode. The electrospinning jet was found to travel at the same angle as that of the diagonal electric field lines from the tip of the spinneret to the knife edge. Placing a rotating tube in the path of the electrospinning jet, diagonally aligned fibres were collected on it (Teo *et al* 2005). With this, laminate composite consisting of aligned fibres in different orientations can be fabricated and may have applications in vascular grafts or coating over stents.

With the vast interest in electrospinning and the desire to control the electrospinning process and to fabricate different assemblies, various set-ups have been constructed. The use of both rotating devices and the manipulation of electric field profile has proven to be successful in the fabrication of various fibrous assemblies.

6. Static collector without the use of auxiliary electrodes

The use of a mechanical rotating device is not the only way to obtain ordered fibre assemblies. It is also possible to obtain two-dimensional patterned structures or even three-dimensional structures using a static collector. Formation of honeycomb (Deitzel *et al* 2001b) and dimpled (Ramakrishna *et al* 2005) structures as shown in figure 6(A) has been reported. This is attributed to the build-up of electrostatic charges on the deposited collector, which prevents in-coming electrospun fibres from depositing directly on the collector. These fibres would form honeycomb or dimpled structures as they accumulate and dry just above the collector before they are laid down on it. Although electrospinning was not known to form three-dimensional structure, figure 6(B) shows a three-dimensional structure formed from electrospun polysulfone fibres. The conditions required to form such three-dimensional structures are still unclear and more studies have to be carried out to determine their formation. However, as the fibres that formed this structure are very loosely packed, it can be easily compressed. Thus, it is not suitable in applications where mechanical strength is required to maintain the integrity of the three-dimensional shape.

At the sub-micron level, electrospun polysulfone fibres were found to fold into intricate shapes as shown in figure 7. The main reason behind this is yet to be studied. However, the fluffy texture of the resultant electrospun fibre mesh may shed some light in the formation of this micro-structure. As the electrospun fibres are not held down tightly by other fibres when they are deposited, this may allow the fibres to 'recoil' when they lose its charge or when the fibre loses its initial acceleration due to the repulsive forces caused by residual charges on the already deposited fibres. Further experiments must be performed to determine the cause for such fibre assemblies. The assembly as shown in figure 7(A) may have the potential for use as a nano-spring if it can be fabricated consistently at a nano-scale.

To form a patterned two-dimensional mesh, a collector with either patterns in the form of ridges and indentations or a grid with pores in between can be used. The resultant fibre mesh formed would take the shape of the patterned collector. Ramakrishna *et al* used a collector that was made of ridges and indentations without any pores. The electrospun fibres were

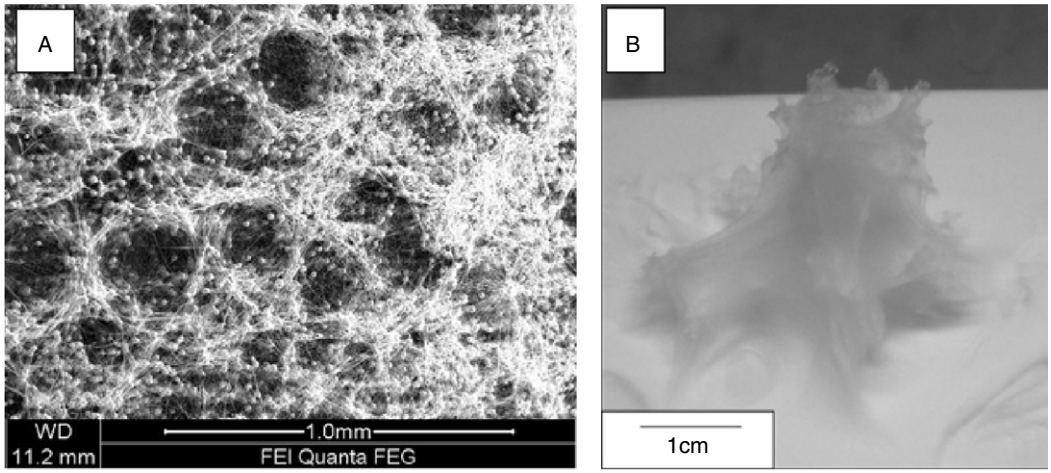


Figure 6. (A) Electrospun fibre mesh with 'dimples' formed by the self-arrangement of the fibres. (B) A three-dimensional structure formed from polysulfone fibres during electrospinning.

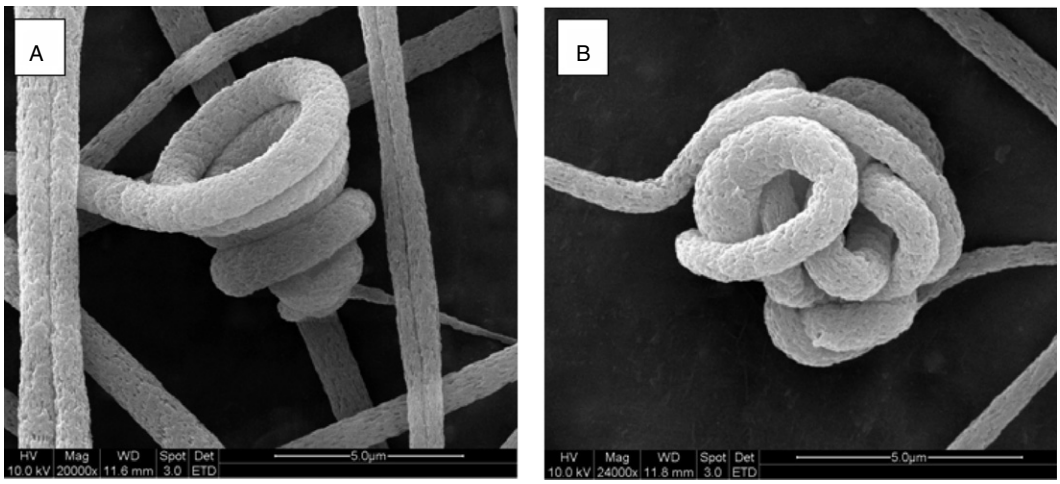


Figure 7. Intricate electrospun fibre structures. [A] Polysulfone 'submicron-spring'; [B] polysulfone convoluted fibres.

randomly deposited, although they still take the pattern of the collector (Ramakrishna *et al* 2005). Gibson and Schreuder-Gibson used a collector that was made out of a conducting grid with pores. They found that fibres deposited on the conducting ridges of the grid were aligned while fibres deposited in the pores of the grid, which was non-conducting, were randomly oriented. Grids with different spacings were used to collect the electrospun fibres. By using porometry, the patterning of the electrospun fibres showed no obvious difference in the mean pore size and the airflow resistance from that of the nonwoven mesh collected on a smooth substrate. Burst testing on the patterned mesh showed that grid patterns tend to inhibit further tearing of the ruptured membrane. Since fibres tend to deposit preferentially on the conductive region, the regions with thicker fibre deposition would therefore inhibit the tears (Gibson and Schreuder-Gibson 2004).

7. Electrospinning solution delivery system

So far, various methods of achieving fibrous assemblies have been described. However, modification of the electrospinning set-ups is not restricted to just attempting to achieve different assemblies; some designs sought to address various limitations in the typical electrospinning set-up while others are meant to improve the spinning process and the performance of the resultant fibrous mesh. Table 4 is a summary of various solution delivery constructions to address different electrospinning issues and to incorporate greater versatility in the nanofibres.

A well known limitation of the electrospinning process is the level of fibre production, which is very much lower than that of current fibre spinning technology. A straightforward method of increasing the productivity of the electrospinning is by increasing the number of spinnerets used in the process (Ding *et al* 2004, Kidoaki *et al* 2005, Theron *et al* 2005, Madhugiri *et al* 2003). This design has the additional advantage of spinning a composite mesh consisting of fibres of different materials. Other materials such as chitin nanoparticles (Min *et al* 2004) and even cells (Stankus *et al* 2006) have been sprayed onto the electrospun mesh during the electrospinning process to form a composite. However, as mentioned earlier, the presence of nearby spinnerets has an undesirable influence on the electrospinning jets (Theron *et al* 2005). The distribution of the fibre diameter may be

Table 4. Schematic diagrams of electrospinning set-up using various solution delivery constructions (assuming the spinneret is given a positive charge unless otherwise stated).

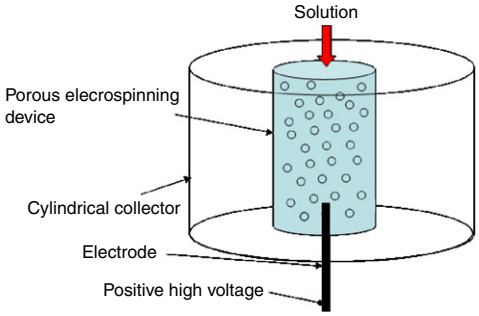
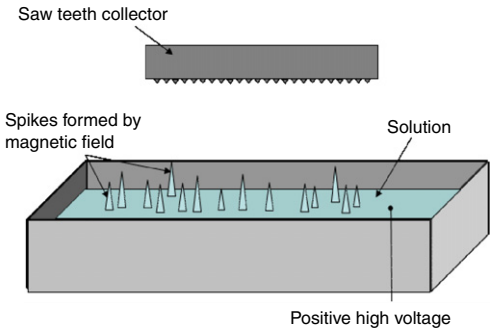
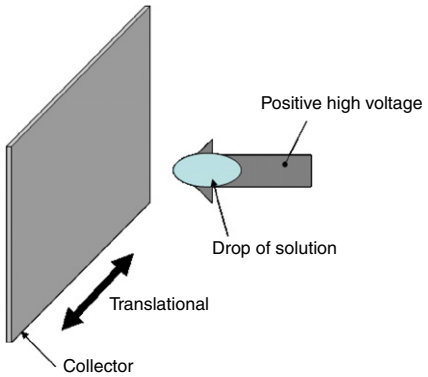
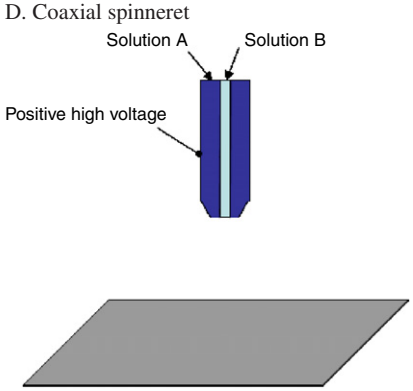
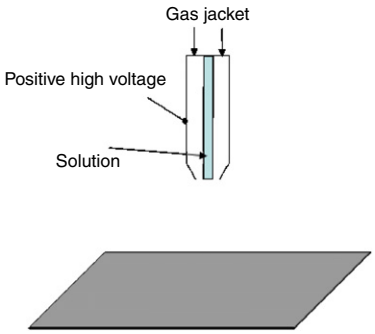
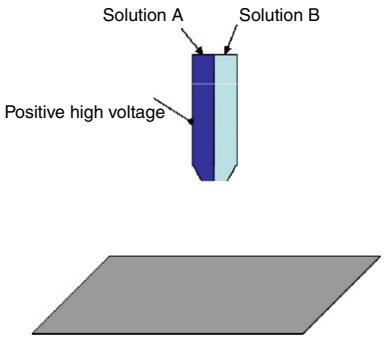
Needleless electrospinning	
A. Porous electrospinning source  	Advantage High production of fibres Disadvantage Larger variation in fibre diameters (Dosunmu *et al* 2006)
B. Multiple spikes electrospinning source  	Advantage No clogging of solution at the source High production rate of fibres Disadvantage Complicated set-up Variation of fibre diameter may be large (Yarin and Zussman 2004)
C. Pointed tip electrospinning source  	Advantage No clogging of solution at the source Solution can be spun at close distance to collector Patterning by fibre deposition is possible if collector is moving at high enough speed Disadvantage Small amount of solution can be used at a time (Kameoka *et al* 2003, Sun *et al* 2006)
Spinneret modification	
D. Coaxial spinneret  	Advantage Single fibres made out of two different materials can be electrospun Hollow fibres can be fabricated by removing the core material Materials normally not electrospinnable can be made into nanofibre by using an electrospinnable outer material Disadvantage Materials to be electrospun must be chosen carefully to reduce mixing of the materials (Sun *et al* 2003, Zhang *et al* 2004, Li and Xia 2004, Loscertales *et al* 2004, Wang *et al* 2006a, Wang *et al* 2006b)

Table 4. (Continued.)

E. Gas jacket electrospinning 	Advantage Gas jacket will assist in the formation of smooth fibres Disadvantage The speed of the injected gas must be controlled properly (Larsen *et al* 2004, Wang *et al* 2005a, Um *et al* 2004)
F. Bicomponent spinneret 	Advantage Single fibres made out of two different materials can be electrospun Disadvantage Materials to be electrospun must be chosen carefully to reduce mixing of the materials (Schreuder-Gibson *et al* 2004, Gupta and Wilkes 2003, Lin *et al* 2005)

large as a result in the fluctuation of the electric field between the spinnerets and the collector. Dosunmu *et al* demonstrated an innovative method of using a porous tube to significantly increase the electrospinning rate. The polymer solution was first injected into the porous cylindrical tube where an electrode was inserted into it as shown in table 4(A). By applying air pressure, the solution was forced through the numerous pores on the tube. An electrode was used to charge the solution such that as the solution approached the outer surface of the tube spinning of numerous jets commenced and the fibres were deposited on the inner surface cylindrical collector that enclosed the porous cylindrical tube (Dosunmu *et al* 2006).

7.1. Needleless electrospinning

To eliminate the problem with clogging of the pores during multiple jet electrospinning, Yarin and Zussman devised a set-up that used spikes to facilitate the spinning process rather than the extrusion of the solution through a needle. Magnetic fluids were prepared using magnetite powder in silicone oil. Under the influence of a magnetic field, numerous spikes were formed on the free surface of the magnetic fluid. A schematic diagram of the set-up is presented in table 4(B). A polymer solution was carefully added such that it forms a layer on the surface of the magnetic fluid. An electrode was submerged in the polymer solution and a high voltage was applied. When a grounded piece of metal saw was used as a counter-electrode, thousands of jets erupted from the surface of the magnetic fluid and the fibres were deposited on the metal saw (Yarin and Zussman 2004).

Using a pointed tip instead of a needle, Sun *et al* reported a breakthrough in the electrospinning process. The group is able to form fine patterns using electrospinning by depositing fibres at the stable region of the electrospinning jet. The distance between the tip and the collector in this set-up was less than 3 mm. To allow for the solidification of the fibres and the stretching of the jet to the nanometre diameter level, the solution source has to be sufficiently small. A tungsten tip of 25 μm tip diameter was used and the polymer solution was transferred to the tip by immersing and pulling the tungsten electrode in and out of the polymer solution. At a distance of 1 mm from the tip to the collector, a 1 kV voltage was sufficient to initiate the electrospinning process. Using a movable collector at a speed of 20 cm s^{-1}, straight line nanofibres were constructed with resolution of up to 25 μm (Sun *et al* 2006). However, this method is not without its disadvantages. The small amount of polymer solution that can be spun at one time means that there is a limitation in the length and the production rate of the nanofibre that can be fabricated. Nevertheless, this method may still be useful in applications such as sensors or as one-dimensional polymer transistors where the fibres can be deposited over specific conducting electrodes (Liu *et al* 2004, 2005, Gonzalez and Pinto 2005).

7.2. Coaxial and dual-capillary spinneret

By modifying the spinneret design, different properties can be introduced to the nanofibre. Coaxial spinneret design has been utilized by various researchers for various aims in electrospinning. Although many different solutions can be electrospun, there are some polymer solutions which cannot be electrospun perhaps due to high surface tension or low conductivity of the solvent (Jarusuwannapoom *et al* 2005, Supaphol *et al* 2005). In this case, this polymer

solution can be extruded through the inner capillary while the spinnable solution is extruded through the outer capillary during electrospinning. During electrospinning, the solution at the outer capillary would carry the inner solution in its core. Thus, when the outer polymer is removed, the desired inner polymer nanofibre is retained (Wang *et al* 2006b). Using a similar concept, the inner solution can be removed instead of the outer polymer after electrospinning can give rise to hollow nanofibres. This has been adopted by Wang *et al* to fabricate hollow silica nanochannels (Wang *et al* 2006a) and Li and Xia to fabricate hollow titania nanofibres (Li and Xia 2004). To impart different properties to the resultant nanofibres, a nanofibre consisting of two different types of polymer has been fabricated. In the core–shell nanofibre, the electrospinning is carried out using the same spinneret design as described above. This has the potential for use in applications such as drug delivery systems where drug loaded solution can be introduced into the core of the nanofibre (Sun *et al* 2003, Zhang *et al* 2004). A schematic diagram of the coaxial set-up is shown in table 4(D).

Although the use of needless spinneret can be used to eliminate clogging of the spinneret during electrospinning, there is another method of reducing this problem. Larsen *et al* used a coaxial gas jacket to reduce the clogging of the spinneret tip when volatile solution was used in electrospinning. By making use of the coaxial design, the solution is injected into the inner capillary while the outer capillary tube is used to blow a jacket of gas saturated with the corresponding solvent of the solution to be electrospun. This set-up has the added advantage of controlling the morphology from smooth fibres to beaded fibres or particles without the need to vary the applied voltage (Larsen *et al* 2004). In another group, led by Benjamin S Hsiao, they used the same method of blowing air to fabricate hyaluronic acid (HA) nanofibres. By increasing the blow rate of the air, the diameter of the nanofibres can be reduced until an optimum rate, where further increase in the blow rate would increase the fibre diameter instead. With increasing blow rate, the increased evaporation rate of the solvent and subsequent increased in the concentration mean that the polymer jet can be stretched further. However, if the concentration increase is too rapid, stretching of the polymer jet is not possible, resulting in an increased in the fibre diameter. With the assistance of the blowing air to stretch the highly viscous HA solution, a lower voltage is required to initiate the spinning process (Wang *et al* 2005a, Um *et al* 2004).

Using a concept similar to the coaxial spinneret design, the spinneret can be fabricated with two capillaries side by side as shown in table 4(F). Bi-component fibres can be produced by electrospinning using this design (Lin *et al* 2005, Schreuder-Gibson *et al* 2004, Gupta and Wilkes 2003). A possible application for the bi-component fibre is that one of the sides is able to absorb chemicals while the other side is electrically conducting. Absorption of the chemicals on one side will result in swelling on that side, causing the nanofibre to bend. This bending may then be used to switch an electrical circuit (Lin *et al* 2005).

8. Challenges in electrospinning process

There has been much research and progress in the development of various designs and modification to the electrospinning process over the last century. Nevertheless, there are still many areas where further refinement of the process will be welcomed. To begin with, although there are several set-ups designed to achieve fibre alignment, there is still a serious shortcoming in getting highly aligned nanofibres over a large area of substantial thickness. Generally, a drum collector is not able to get highly aligned fibres even though it is able to get a larger area of fibrous mesh. Aligned nanofibres have been shown to induce cell elongation and proliferation in the direction of the fibre alignment. The ability to fabricate highly aligned fibres in large quantity over a large area will allow more investigation in cellular response to the fibre alignment in terms of gene expression and cell interaction.

Typically, electrospun assemblies are in a two-dimensional form, and in the case of yarn a one-dimensional form. The only three-dimensional electrospun structure with significant length, width and height is a fibrous tube. However, researchers have yet found a way to consistently fabricate a solid three-dimensional structure through electrospinning. With the ability to fabricate three-dimensional structure, other applications such as bone replacement scaffold can be considered. Recently, Smit *et al* and Khil *et al* demonstrated the fabrication of continuous yarn made out of purely nanofibres. However, the spinning speed of 30 m min^{-1} is still much slower than that of the industrial fibre spinning process, which runs from 200 to 1500 m min^{-1} for dry spinning (Gupta and Kothari 1997). Yarn made out of electrospun fibres has many applications, especially when fabricated into textiles. However, for electrospun yarn to be adopted by the textile industry, its yarn spinning speed has to be improved significantly.

Although Sun *et al* made a breakthrough in the electrospinning process by creating controlled patterning using electrospun nanofibres, the small volume of solution that can be spun at one time significantly reduced the practicality of the process. An advantage of electrospinning is its ability to spin long continuous fibres at high speed. However, it is still not possible to form highly ordered structures rapidly. Arrayed nanofibre assemblies created thus far are based on arranging aligned nanofibres with very little control on the distance between each fibre.

9. Conclusion

Through this review, various concepts behind obtaining ordered nanofibre assemblies are described. The use of a rotating device and auxiliary electrodes to control the electrospinning jet and the deposition has been studied for more than a century. Progress and research into various electrospinning set-ups to obtain different fibrous assemblies has resulted in several innovative designs and greater understanding of the current limits of the process. With the development of the electrospinning set-ups and the ability to fabricate various fibrous assemblies, more applications may find nanofibres attractive in improving current technology. New techniques such as using a liquid bath to control the deposited fibres and the behaviour of fibre deposition on a static collector may be the way to achieve more ordered fibre assemblies at a high production rate and open up new possibilities.

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