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Niu, Haitao and Lin, Tong 2012, Fiber generators in needleless electrospinning, *Journal of nanomaterials*, vol. 2012, Article ID 725950, pp. 1-13.

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Review Article

Fiber Generators in Needleless Electrospinning

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Received 18 December 2011; Accepted 4 March 2012

Academic Editor: Gajanan S. Bhat

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The conventional electrospinning often uses a needle-like nozzle to produce nanofibers with a very low production rate. Despite the enormous application potential, needle electrospun nanofibers meet difficulties in broad applications in practice, due to the lack of an economic and efficient way to scale up the electrospinning process. Recently, needleless electrospinning has emerged as a new electrospinning mode and shown ability to produce nanofibers on large-scales. It has been established that the fiber generator, also referred to as “spinneret” in this paper, in needleless electrospinning plays a key role in scaling up the nanofiber production. This paper summarizes the recent advances in the development of needleless spinnerets and their influences on electrospinning process, nanofiber quality, and productivity.

1. Introduction

The central image in Figure 1 shows a basic needle electrospinning setup, which comprises a high voltage power supply, a syringe container, a needle nozzle, and a counter-electrode collector. Polymer solutions are often used as spinning materials. During electrospinning, the solution droplet at the needle tip is electrified by the high electric field formed between the needle and the opposite electrode, and this deforms the droplet into a cone shape, that is, “Taylor cone” [1, 2]. When the electric force exceeds a critical value, the solution is ejected from the tip of “Taylor cone” forming a jet. This charged jet is subsequently stretched into a long filament because of the intensive interaction with the electric field and the repulsion of the same type of charges inside. Solvent evaporation leads to the solidification of the filaments into fibers, which are finally deposited on the collector forming a randomly oriented fiber web in most cases. Such a setup has been widely used in hundreds of laboratories around the world for various research and development purposes.

Electrospinning is mainly suitable for processing thermoplastic polymers, and electrospun fibers are typical in the range from several nanometers to a few microns in diameter, but the diameter is controllable. Most of the electrospun nanofibers have a round cross-section with a smooth surface.

However, nanofibers with different morphologies can also be produced depending on the polymer used, polymer solution properties, nozzle structure, and operating conditions. Figure 1 also summarizes nanofibers having various morphologies prepared by needle electrospinning. Beaded fibers or beads-on-string structures can be electrospun from almost all spinnable polymers [3], but they are normally treated as fiber defects. For some polymers or polymer solutions using special solvents, grooved fibers [6], fibers with a porous surface [5, 14], ribbon fibers [7], or helical fibers [11] could also be prepared from a electrospinning process directly. When a special nozzle, which contains two or more channels, is employed for feeding different polymer solutions, depending on the nozzle structure, nanofibers having a bicomponent cross-sectional configuration, such as side-by-side [9], core/sheath [13], hollow [12], or crimped structure [9], can be produced. Islands-in-a-sea nanofibers can also be prepared in a similar way. However, even with a conventional needle nozzle, islands-in-a-sea [15], core-sheath [16], or hollow nanofibers [17] could also be electrospun from a specific solution.

Electrospun nanofibers have many unique characteristics, such as high surface-to-mass (or volume) ratio, ability to form a highly porous fibrous membrane with excellent pore interconnectivity, controllability in fiber diameter, surface

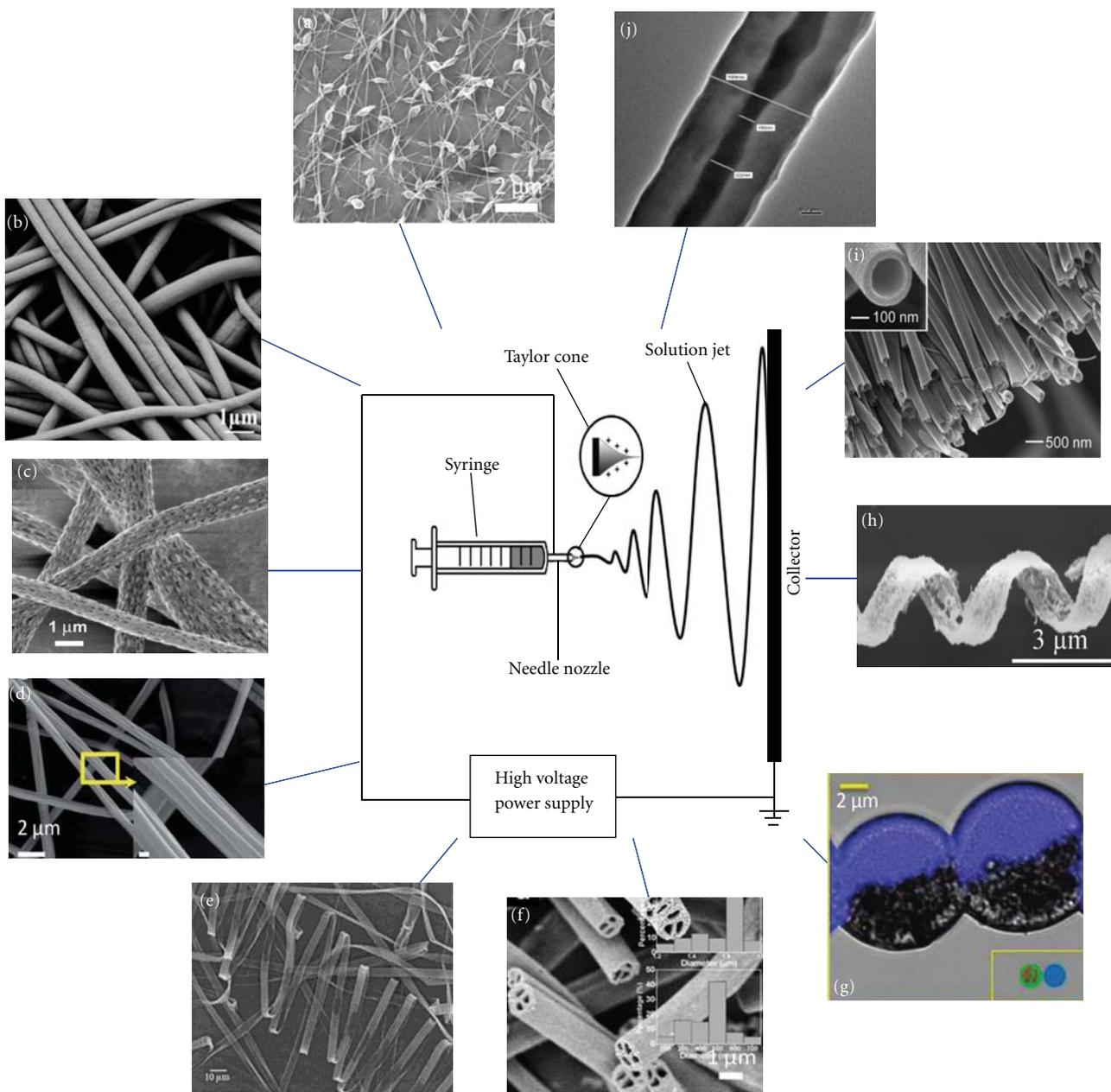


FIGURE 1: (Central) a typical apparatus for needle electrospinning and (outer) images of electrospun nanofibers with various morphologies, (a) beaded fiber [3], (b) round fiber [4], (c) fiber with a porous surface [5], (d) grooved fiber [6], (e) ribbon [7], (f) multichannel fiber [8], (g) side-by-side fiber [9, 10], (h) crimped fiber [9, 11], (i) hollow fiber [12], and (j) core-sheath fiber [13]. (a–f) are prepared by conventional needle electrospinning, and (g–j) are electrospun mainly by a special needle spinneret.

morphology and fibrous structure, and easiness of being functionalized by using functional polymers or adding functional chemicals into polymer solutions for electrospinning. These unique features have provided electrospun nanofibers with enormous opportunities to be used in various fields. Figure 2 presents the important applications of electrospun nanofibers, including tissue engineering scaffolds [18], filtration [19], catalyst and enzyme carriers [20, 21], release control [22], sensors [23], energy storage [24], affinity membranes [25], and recovery of metal ions [26–28].

In spite of the enormous application potential, electrospun nanofibers have not been widely used in practice. The main reason is that needle electrospinning has a very low nanofiber production rate, typically less than 0.3 g/hr. For needle electrospinning, each needle nozzle normally generates one jet each time. As a result, the fiber production rate is far lower than the requirement for commercial usage. A straightforward way to increase the electrospinning productivity is to increase needle number [29, 30], the setup of which is also called “multineedle electrospinning.” However,

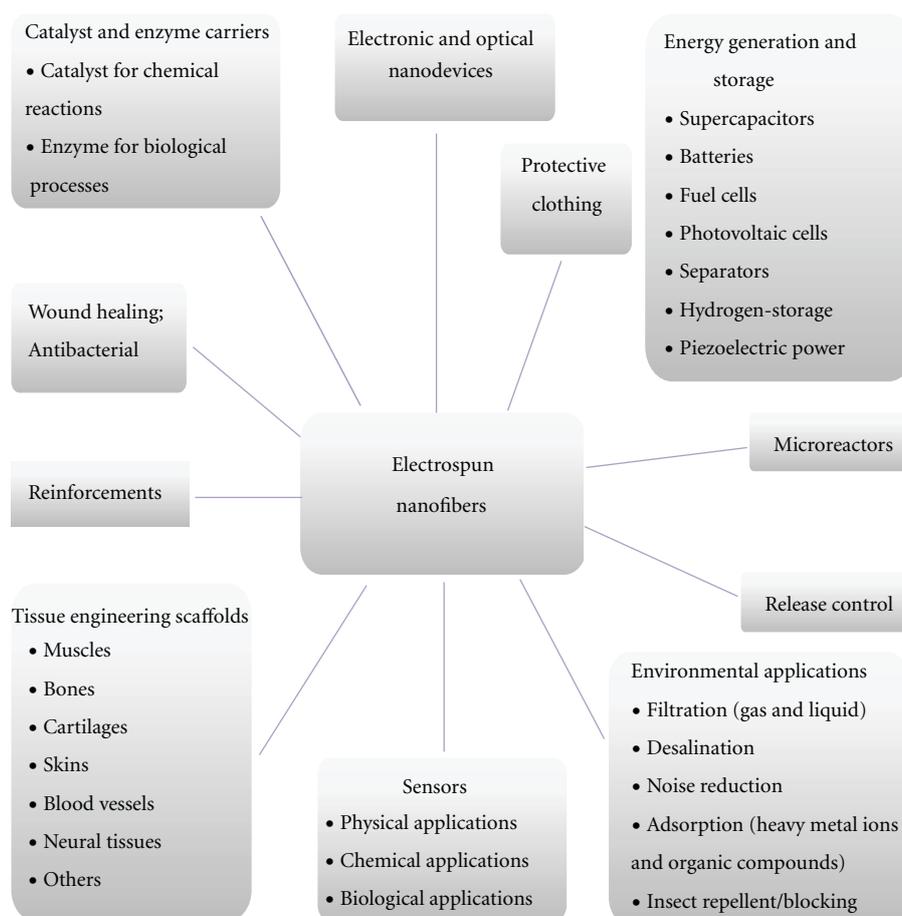


FIGURE 2: Application map of electrospun nanofibers.

the issues related to multi-needle electrospinning are that a large working space has to be used so that the strong interferences between adjacent solution jets can be avoided and a regular cleaning system has to be set for each needle nozzle so that no solution blockage happens during the fiber production. Porous tubes, sometimes with drilled large holes, were reported as alternative fiber generators to improve the electrospinning productivity. The pores/holes conveyed polymer solutions to the tube surface, where the solution drops under the action of a high electric field were drawn into jets and then fine filaments. Compared with the multi-needle electrospinning, the tube electrospinning occupies a smaller space and it is easy to operate. However, it is still difficult to manage the jet interferences efficiently.

Recently, needleless electrospinning appeared as an alternative electrospinning technology with the aim of producing nanofibers on a large scale from a compact space. Needleless electrospinning is featured as electrospinning of nanofibers directly from an open liquid surface. Numerous jets are formed simultaneously from the needleless fiber generator without the influence of capillary effect that is normally associated with needle-like nozzles. Because the jet initiation in needleless electrospinning is a self-organized process which happens on a free liquid surface, the spinning process is hard to control. Spinnerets in needleless electrospinning play

essential roles in determining the electrospinning process, fiber quality, and productivity, which is the main focus of this paper.

2. Brief History of Needleless Electrospinning

Although the electrospinning technique was invented as early as 1934 by Anton [31], it took 45 years when a needleless electrospinning system using a ring spinneret was patented for the electrostatic production of fiber fleece [32]. However, it took another 25 years when needleless electrospinning technique began to exhibit its potential in the mass production of nanofibers.

In 2004, a magnetic-field-assisted needleless electrospinning was reported [33], which used a magnetic field to induce the formation of spikes on the solution surface and then initiated an electrospinning process. In 2005, a rotating roller was invented as a fiber generator for the mass electrospinning of nanofibers [34], and this technique was rapidly commercialized by Elmarco Co. with the brand name "Nanospider." In 2007, air bubbles were employed to initiate electrospinning [35]. A conical wire coil was used as a fiber generator to prepare nanofibers in 2009. In this setup, the polymer solution was conveyed to the spinning sites under the action

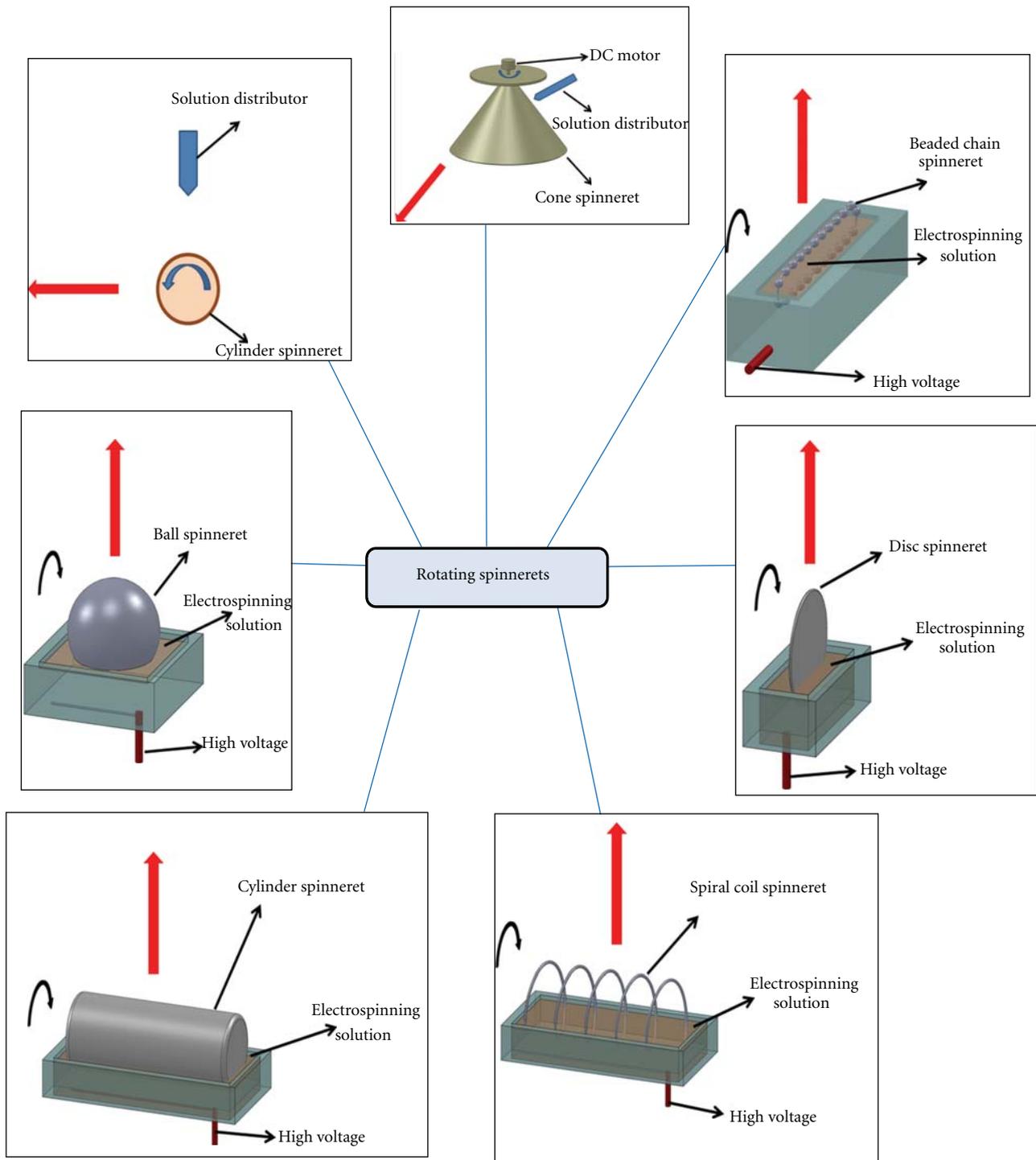


FIGURE 3: Schematic summary of needless rotating spinnerets (electrospinning direction along the red arrow).

of gravity and guided by the coil structure. This system can produce high-quality nanofibers with a significantly increased production rate compared with needle electrospinning [36]. Later on, a few fiber generators, for example, metal plate [37], splashing spinneret [38], rotary cone [39], cylinder [40], and bowel edge [41], were reported.

The influences of spinneret geometry on electrospinning process and fiber quality were examined by Niu et al. [42] who also proved the crucial role of spinneret shape on needleless electrospinning. They found that a disc spinneret formed higher intensity electric field thus exhibiting a better electrospinning performance when compared to a cylinder

spinneret. Inspired by these results, the same group also invented a spiral coil setup and proved that spiral coil had higher fiber production rate and better control toward the fiber morphology compared to disc and cylinder electrospinning [43]. More recently, a moving bead chain has been used as a spinneret to electrospin nanofibers needlelessly [44].

According to the working states, spinnerets for needleless electrospinning can be classified into two categories: rotating or stationary spinnerets. Rotating spinnerets can introduce mechanical vibration to the polymer solution, which assists in initiating jets. Rotating spinnerets mostly work continuously. For electrospinning using a stationary spinneret, an auxiliary force (e.g., magnetic field, gravity, and gas bubble) is often applied to initiate electrospinning process.

3. Needleless Electrospinning Using Rotating Spinnerets

Figure 3 lists the rotating spinnerets that have been reported for needleless electrospinning. These spinnerets are all connected with a high voltage power supply and a spinning solution. For cylinder, ball, disc, coil, and beaded chain electrospinning, spinnerets are immersed in the spinning solutions. Nanofibers are electrospun upward, which effectively prevents the polymer fluid from dropping onto the fiber mats collected, warranting the production of high-quality nanofibers. The rotation of spinnerets conveys polymer solutions to the electrospinning sites, ensuring the production continuously. For roller and cone electrospinning, the spinning solutions are fed from separated solution containers.

Although rings were first invented as a needleless electrospinning spinneret [32], needleless electrospinning began to attract attentions since Jirsak et al.'s invention on using a metal roller as spinneret [34]. The main advantage of this technology is that the jets are initiated naturally in the optimal positions. The jet formation in needleless electrospinning has been proposed to follow four steps: (1) a thin layer of polymer solution is formed on the spinneret surface as a result of its partial immersion in the solution and rotation; (2) the rotation also causes perturbations on the solution layer thus inducing the formation of conical spikes on the solution surface; (3) when a high voltage is applied, the spikes concentrate electric forces thus intensifying the perturbations to form "Taylor cones"; (4) jets are stretched out from the "Taylor cones" and finally result in fibers (Figure 4). Nanospider has shown the capability of producing nanofibers from both polymer solutions and polymer melts.

Rotating cylinder, ball, and disc spinnerets have been compared by Niu et al. [45] using polyvinyl alcohol (PVA) as the model polymer (Figure 5). In their setup, the high voltage was connected with the system by inserting a metal wire inside the solution vessel. When the electric force was high enough, numerous jets were generated from the spinneret surface and fibers electrospun were finally deposited onto the grounded drum collector (Figure 5). In comparison with the needle electrospinning, these spinnerets had much higher productivities (cylinder 8.6 g/hr, disc 6.2 g/hr, and ball 3.1 g/hr). Under the same working conditions, the disc produced finer nanofibers (257 ± 77 nm) with a narrower diameter

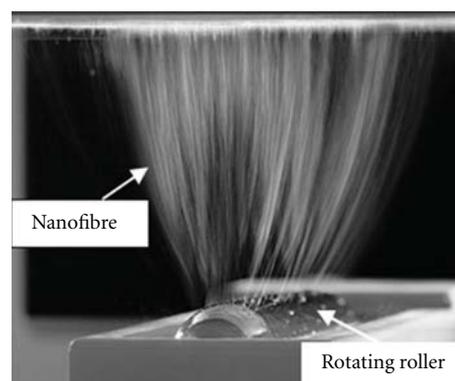


FIGURE 4: Spinneret of nanospider [34].

distribution compared to the ball (344 ± 105 nm) and the cylinder (357 ± 127 nm) spinnerets. In this work, electric field was analyzed by a finite element method, and high electric field was found to be narrowly distributed on the disc top, which led to a high stretching rate to the solution jets. The cylinder spinneret had a large surface area, but the electric field distributed unevenly on the fiber-generating surface. The ball formed an electric field with low intensity thus generating fewer jets when compared to the disc and the cylinder spinnerets. These experimental results and theoretical analysis provided a new insight into the design of fiber generators for needleless electrospinning.

Lin et al. [43] recently patented a new needleless electrospinning setup using a spiral coil as a spinneret. Figure 6 shows the coil spinneret and the electrospinning process. Numerous polymer jets are generated from the wire surface. The nanofibers produced from the coil spinneret were much thinner with a narrower fiber diameter distribution when compared with those from needle electrospinning. However, for disc, ball, and cylinder spinnerets, they normally produced coarser nanofibers than the needle electrospinning. The spiral coil had a higher fiber production rate than the cylinder spinneret of the same dimension. For a coil with a diameter of 8 cm and a length of 16 cm (6 turns), the productivity of PVA nanofibers changed from 2.94 g/hr to 9.42 g/hr when the applied voltage increased from 45 kV to 60 kV.

Rotating needleless electrospinning has been used to process different polymers, such as poly(vinyl alcohol) [36, 42], polyacrylonitrile [46], polyurethane [47], carbon nanotube/poly(vinyl alcohol) [48], and polyamic acid [49]. It was reported that the solution concentration played a vital role in the electrospinning process [50]. When the polymer concentration was low, the chain entanglement was insufficient, which resulted in beads or beaded fibers instead of uniform fibers. However, if the polymer concentration was too high, the high viscosity restricted stretching of polymer fluid into fine filaments. In the range that a polymer solution could be successfully electrospun into uniform nanofibers, the variation of polymer concentration had a small effect on the fiber diameter [42].

Molecular weight is another important factor that affects the electrospinning process. It was found that when the molecular weight of PVA was lower than 67,000, no fibers



FIGURE 5: Photographs of cylinder, disc and ball electrospinning processes (Cylinder diameter 80 mm, rim radius 5 mm; ball diameter 80 mm; disc diameter 80 mm, thickness 2 mm) [45].

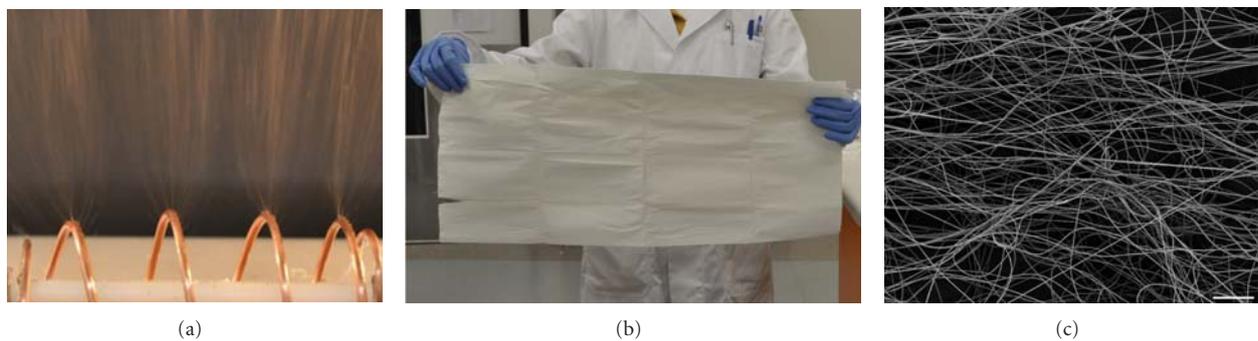


FIGURE 6: (a) Photograph of the spiral coil spinneret and electrospinning process, (b) photograph of polyacrylonitrile (PAN) nanofiber mat produced by coil electrospinning, and (c) SEM image of coil electrospun PAN nanofibers (scale bar: 10 μm).

could be electrospun. Fibers were electrospun from the PVA with a molecular weight in the range of 80,000–150,000 [51]. In addition, needleless electrospinning can also be affected by other factors, including solution conductivity and surface tension, applied voltage, collecting distance, and ambient environment (e.g., temperature, gas environment, and humidity).

The flow rate in needleless electrospinning cannot be controlled precisely but could be adjusted just in a very limited range through changing the rotating speed of the spinneret. The rotating speed of a spinneret can be varied in large range from few rpm up to 200 rpm [42, 46], depending on the spinning solution, spinneret dimension, and operating parameters. When the rotating speed was low, a thin solution layer was formed on the spinneret surface. Electrospinning exhausted the solution layer until it reached a state of which the solution was too thin to be electrospun [40]. Increasing the rotating speed leads to a thicker solution layer, and solution processing can be thus increased. When the rotating speed is too high, the solution could be thrown out from the fiber generator surface. On the other hand, increasing the spinneret rotating speed also decreases the life span of “Taylor cones,” resulting in a reduced productivity. In addition, the increase in the rotating speed of cylinder spinneret was reported to decrease the fiber diameter [46].

More recently, a horizontal bead chain was used to produce nanofibers in an upward fashion [44]. In this setup, the rotating bead chain comprised two parallel parts. The

lower part was dipped in a polymer solution, while the higher part functioned to produce fibers. When a high voltage was applied, the beads on the top part of the chain generated fine fibers. The small beads can generate high strength electric field thus improving the electrospinning performance.

In addition, rotating spinnerets were also used for electrospinning nanofibers in other fashions. In this case, the solution was conveyed to the electrospinning sites through the action of both the spinneret rotation and the gravity. Tang et al. [38] reported an electrospinning setup using a rotating roller as a fiber generator. During electrospinning, the spinning solution was dropped to the roller from a solution distributor. When the solution droplets attached to the electrically charged metal roller, jets were ejected and nanofibers were thus produced (Figure 7). The solution concentration, applied voltage, distance between the roller spinneret and the collector, and rotational speed of roller spinneret are the key factors to the electrospinning process and the fiber diameter. This setup had a 24–45 times higher fiber productivity than a conventional needle electrospinning system.

Lu et al. [39] reported a needleless electrospinning system using a rotary cone as a spinneret. The rotating cone spinneret and electric field were reported to be the crucial parameters affecting the nanofiber production. Polyvinylpyrrolidone (PVP) solution was supplied to the cone by a glass pipe to ensure electrospin continuously (Figure 8(a)). The PVP solution flowed down to the fiber generating sites

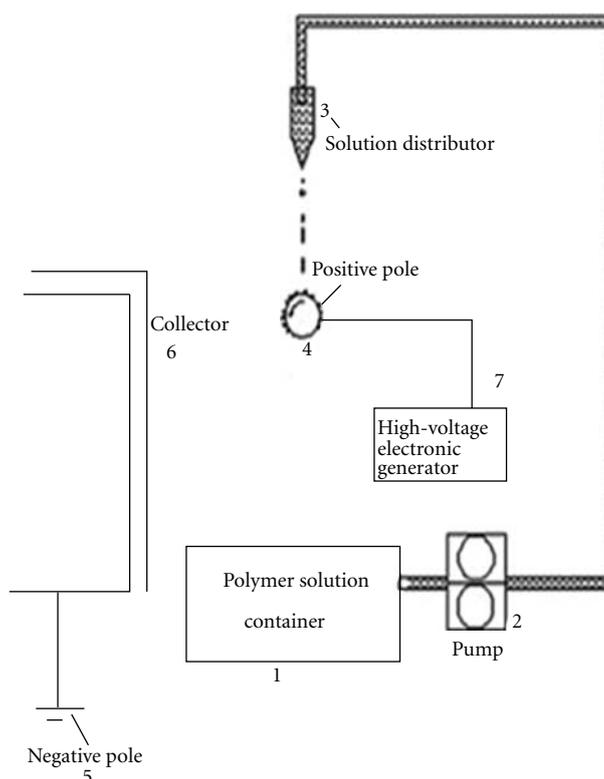


FIGURE 7: Schematic illustration of the downward needleless electrospinning setup using a rotating roller spinneret [38].

(cone edge) along the cone surface under the gravity. When a high voltage was applied and cone rotating speed was over 50 rpm, solution jets were generated from the cone edge and stable electrospinning was performed. Compared to the conventional needle system, this system produced fibers of a similar quality with 1000 times larger production rate (Figures 8(b) and 8(c)). When a higher applied voltage was employed, more uniform nanofibers with smaller diameter were obtained.

When the polymer solution is conveyed under the action of gravity, the downward electrospinning becomes more dependent on the solution properties (e.g., viscoelasticity and surface tension) than that in the upward rotating electrospinning.

4. Needleless Electrospinning Using Stationary Spinnerets

Needleless electrospinning is heavily relied on the initiation of jets from an open liquid surface. How to concentrate electric forces on the solution surface where jets are expected to generate is the key to a successful electrospinning process. When stationary spinnerets are employed, conical spikes are often created with the aid of an external force, such as magnetic force, high pressure gas flow, and gravity. Figure 9 lists the stationary spinnerets reported.

In 2004, Yarin and Zussman [33] reported a needleless electrospinning system that used a magnetic field to initiate

the jet formation. The setup comprised a bottom layer of ferromagnetic fluid and an upper layer of polymer solution (Figure 10(a)). When an external magnetic field was applied to the fluid system and an electric field was added simultaneously to the polymer solution layer, the ferromagnetic fluid triggered the formation of steady vertical spikes, which perturbed at the interlayer interface. Under the action of a strong electric field, these spikes were drawn into fine solution jets (Figure 10(b)). Compared with the multineedle electrospinning, the production rate of poly(ethylene oxide) (PEO) nanofibers was 12 times higher. Nevertheless, the electrospinning setup is complicated to build and nanofibers electrospun are relatively coarse with a large diameter distribution.

Blowing gas into a polymer solution was also used to initiate jet formation from a flat open solution surface. Such an electrospinning mode is also called “bubble electrospinning.” During bubble electrospinning, when gas was introduced into a solution reservoir and at the same time a high voltage was applied, bubbles were then generated on the solution surface. The gas bubbles made electric forces concentrate on the bubble surface, where initiated the formation of multiple jets [35]. The gas pressure, solution properties, and applied voltage should have a considerable influence on the fiber production rate. However, no details on the fiber properties and productivity were provided.

Unlike the above-mentioned needleless electrospinning systems that fibers are electrospun upward, some setups produced nanofibers downward and in these cases the gravity

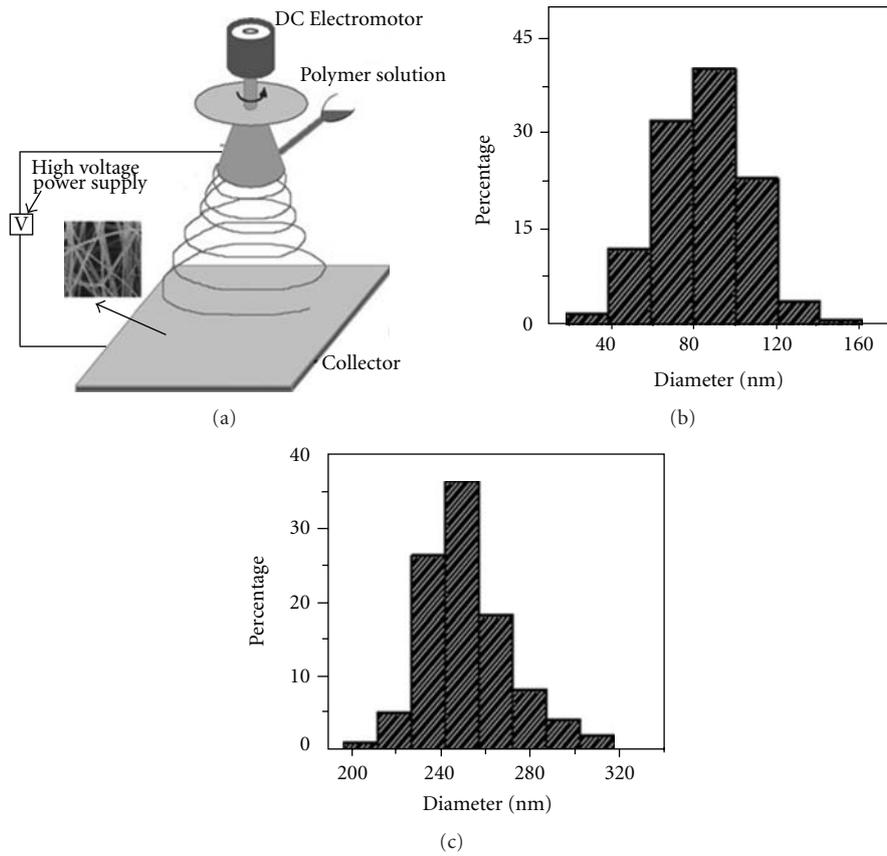


FIGURE 8: (a) Schematic illustration of the rotary cone electrospinning setup (inset: SEM image of collected PVP nanofibers, rotational speed of cone = 100 rpm, applied voltage = 30 kV, collecting distance = 20 cm, and solution throughput = 10 g/min), (b) diameter distribution of needle electrospun fibers, and (c) diameter distribution of rotary cone electrospun fibers [39].

is utilized to assist in conveying the solution to the spinning sites. Wang et al. [36] reported a conical coil spinneret that functioned as both the solution container and fiber generator (Figures 11(a) and 11(b)). When a high voltage was applied to the wire coil, solution was stretched out from both the wire surface and the gap between wires to form solution jets (Figure 11(c)). This setup was able to work at up to 70 kV without causing corona discharges. It can improve the electrospinning productivity by 13 times and produce finer nanofibers compared with the conventional needle electrospinning (Figure 11(d)). The only drawback of this electrospinning technique is the discontinuous fiber production.

In another setup reported by Thoppey et al. [37], a plate with a certain horizontal angle was used for retaining the spinning solution, and nanofibers were generated from the plate edge (Figure 12(a)). In this work, the jet initiation was observed. An electrically insulated reservoir connected with one or more plastic pipettes was used to provide polymer solution to the plate, wherein each pipette formed a solution stream as a jet initiation site. Because of the high viscoelasticity, the polymer solution maintained its fluid shape (Figure 12(b)). When it reached the plate edge, it formed a neck (Figure 12(c)) and became elongated (Figure 12(d)).

Under the influence of strong applied electric field at the plate edge, jet initiation happened (Figure 12(e)). The production rate of this electrospinning was over 5 times higher than that of the conventional needle electrospinning, even using a single spinning site (one pipette). Nanofibers produced by this method had the same quality as those produced by the conventional needle electrospinning at the same working conditions.

The utilization of gravity simplifies the needleless electrospinning setups and this makes the devices easy to implement. Because viscosity and surface tension are both important properties affecting the solution flow under the gravity, they should have considerable influences on electrospinning process and fiber morphology.

Wu et al. [40] reported an upward needleless electrospinning system using a stationary cylinder spinneret. It works in a similar way to rotating spinnerets, except that the process is performed discontinuously. PEO nanofibers produced by this setup were reported to be more than 260 times larger in the production rate than that of the conventional needle electrospinning (0.02 g/h). It was proposed that “Taylor cones” in this setup were formed on the surface of an open solution surface by sucking up the solution from around. Since no

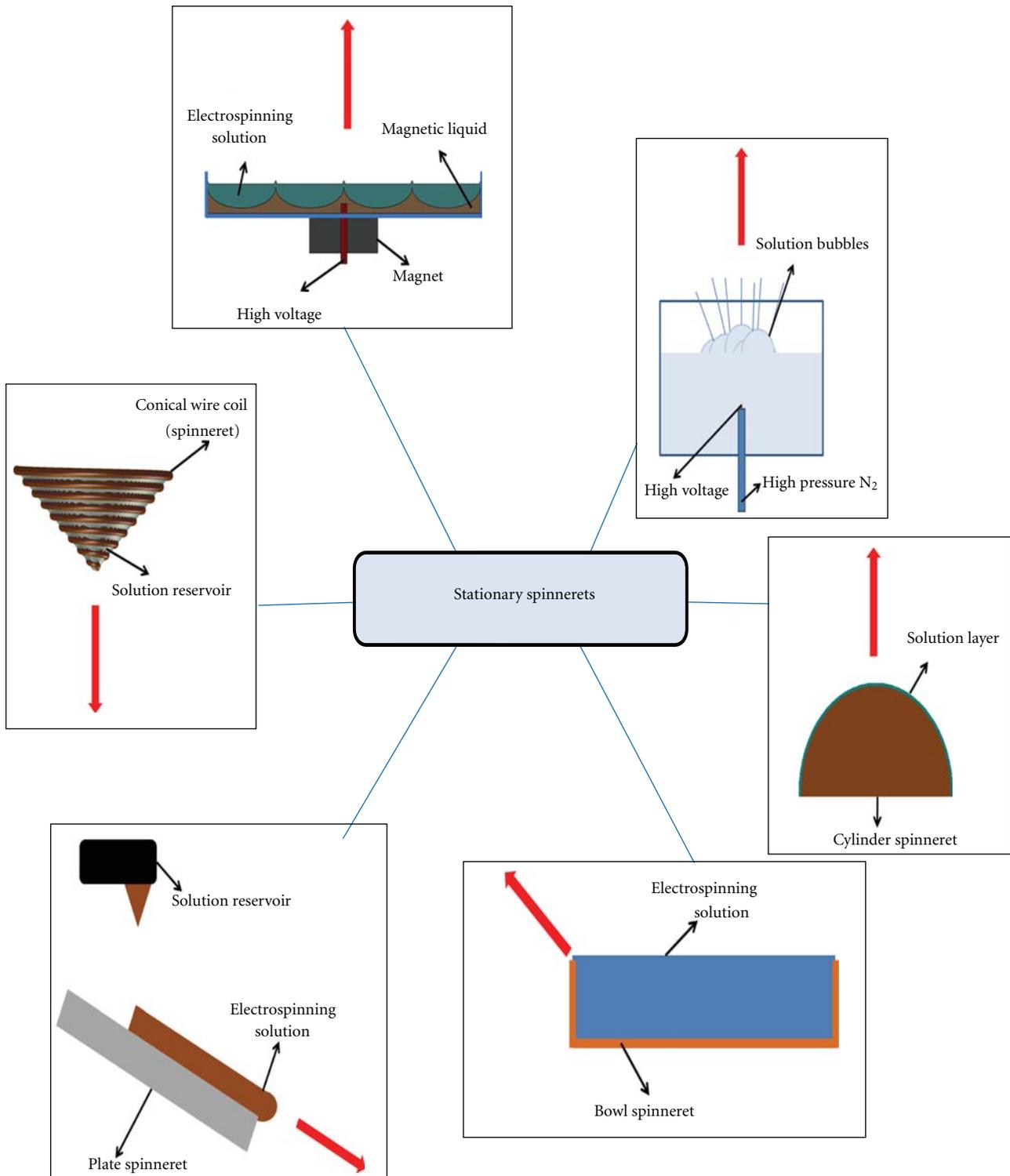


FIGURE 9: Schematic summary of stationary needleless spinnerets (electrospinning direction along the red arrow).

polymer solution was further supplied to the generator, the solution layer on the spinneret surface declined in thickness gradually. As a consequence, the jet diameter reduced from 1.2 mm to 0.3 mm throughout the electrospinning process.

More recently, an aluminum bowl was used as a spinneret to electrospin nanofibers (Figure 13(a)) [41]. The jet initiation on the bowl surface was quite similar to that on the needle electrospinning. Nanofibers generated from the edge

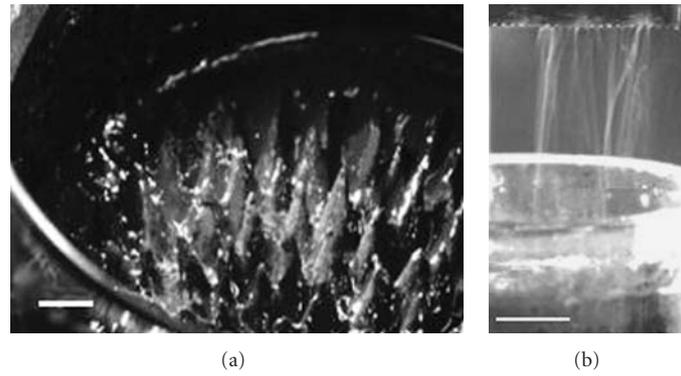


FIGURE 10: (a) Magnetic-field-assisted needleless electrospinning setup and (b) multiple jets ejected toward the counterelectrode [33].

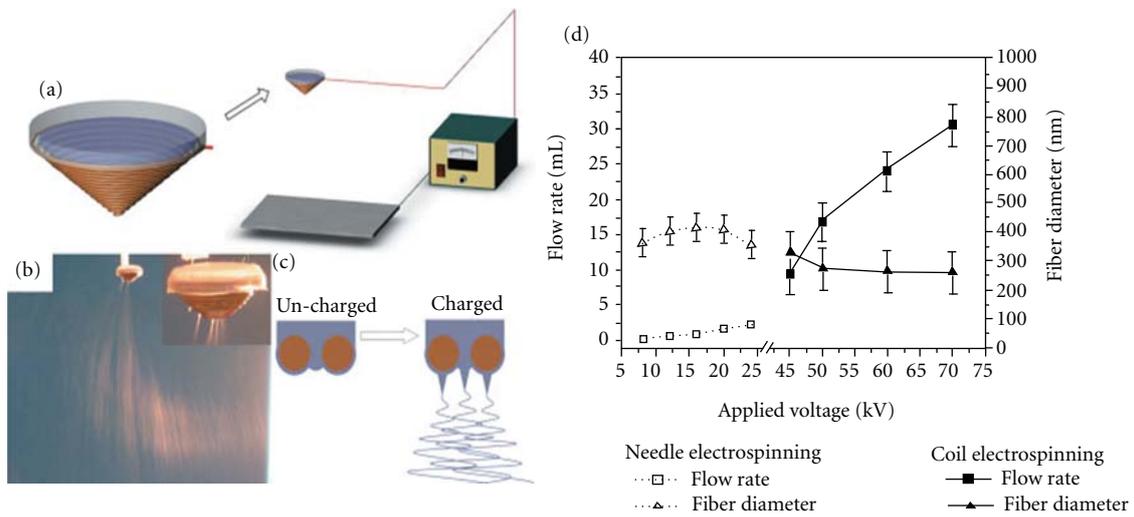


FIGURE 11: (a) Schematic illustration of the conical wire coil electrospinning setup, (b) photograph of the electrospinning process, (c) illustration of the jet formation, and (d) comparison between needle electrospinning and coil electrospinning [36].

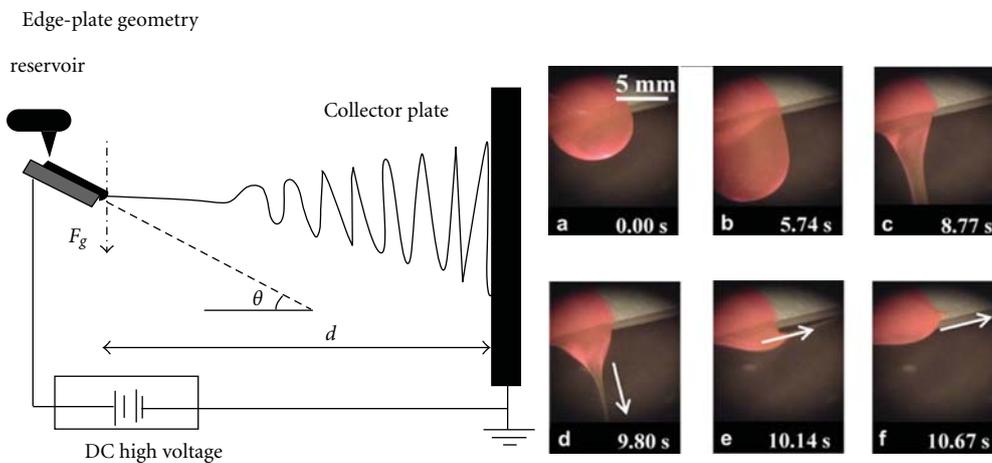


FIGURE 12: (Left) schematic illustration of the plate edge electrospinning setup and (right) jet initiation in the electrospinning of PEO solution [37].

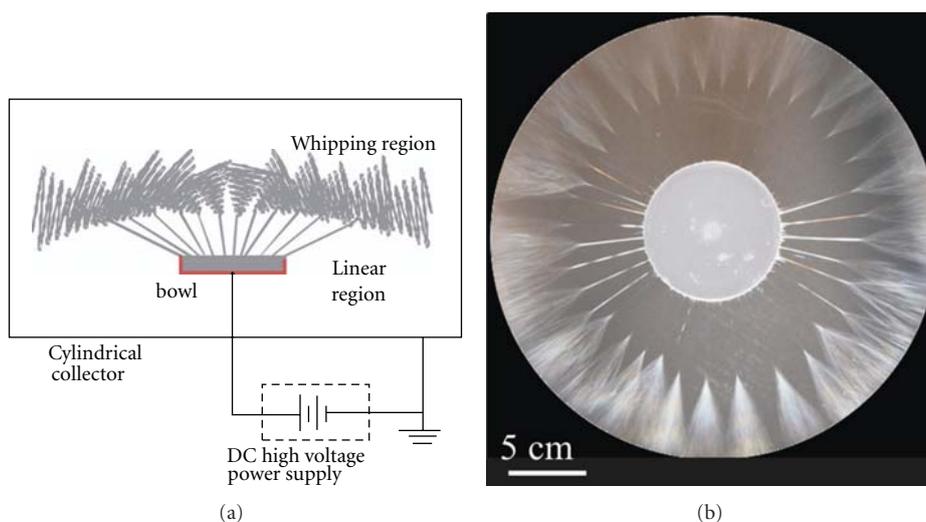


FIGURE 13: (a) Schematic illustration of the bowl electrospinning setup in a side view and (b) the top view of bowl electrospinning process [41].

of the bowl were deposited on a concentric cylindrical collector (Figure 13(b)). When a high voltage was applied, the solution on the bowl surface deformed immediately, forming conelike protrusions at the bowl edge. A few seconds later, solution jets were ejected from these protrusions. Nanofibers produced by this electrospinning system exhibited the same quality as those produced by conventional needle electrospinning, but the production rate was about 40 times higher. Again, it is a discontinuous spinning process and the fiber production stops once the solution level is below the bowl edge.

5. Concluding Remarks

This paper introduces the recent development in needleless electrospinning spinnerets and the influences of spinnerets on fiber properties and the production rate. Indeed, needleless spinnerets show great potential in electrospinning nanofibers on large scales. Although diversely different spinnerets could be chosen for the mass production, they may not be ideal and some of them still need further experimental verification in terms of the ability to control the fiber quality and electrospinning process. It still lacks an extensive understanding on how the polymer types and solution properties, especially for those using organic solvent systems, affect the electrospinning process and productivity.

Needleless electrospinning is still in infant stage. It still remains a challenge to electrospin bicomponent nanofibers using a needleless electrospinning spinneret. The control of fiber morphology through using specific polymer, polymer solution using a specific solvent, or the solution in a specific state has not been demonstrated in needleless electrospinning. It is expected that further development of needleless electrospinning technology will make these happen. High-quality, low-cost nanofibers will be electrospun needlelessly on large scale and widely used in our daily life in the not far future.

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