Review Article

Ran Chen, Junfeng Liu, Zeyong Sun, Dong Chen*

Functional Nanofibers with Multiscale Structure by Electrospinning

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Abstract: Electrospinning can produce nanofibers with extremely high surface-to-volume ratio and well tunable properties. The technique has been widely used in different disciplines. To fabricate fibers with required properties, parameters of fabrication should be well controlled and adjusted according to specific applications. Modification of electrospinning devices to align fibers in highly ordered architectures could improve their functions. Enhanced efficiency have also been obtained through the upscaling modification of spinnerets. With the outstanding efficiency, electrospinning has exhibited huge potentials to construct various nanostructures, such as artificial vessel, membrane for desalination and so on.

Keywords: Electrospinnig; Parameter control; Fiber alignment; Upscaling

1 Introduction

Nanofibers of different properties are widely used in tissue engineering, drug delivery, battery, sensors and filtrations [1–26]. To make nanofibers with properties that meet the requirement for these applications, various methods have been developed, including drawing, electrospinning, self-assembly and so on. Among them, electrospinning is the most commonly used method to fabricate nanofibers due to its straightforward setup, the ability to mass-produce continuous nanofibers from various polymers, and the capability to generate nanofibers with controllable diameters, compositions and orientations. In addition, the flexibility of electrospinning allows for controlling the structure (e.g. hollow fibers) and arrangement (e.g. well-ordered fiber arrays) of the fibers so that nanofibers of desired properties can be fabricated depending on the intended applications.

The diameters of electrospun fibers can be easily varied from tens of nanometers to microns, and thus the fibers possess extremely high surface-to-volume ratio, making them suitable for activities requiring a high degree of physical contact, such as providing sites for chemical reactions. Membranes consisted of electrospun fibers possess relatively uniform pore size distribution and significantly high porosity and thus are good filter to capture small-sized particulates by physical entrapment [22,23,27–29]. In addition, the nanofibers fabricated by electrospinning possess a relatively defect-free structure at the molecular scale, showing enhanced mechanical properties. Because of these advantages, electrospun fibers have been widely used in various applications. For example, in biomedical applications, by using biocompatible materials, electrospun fibrous scaffold have been considered as suitable substrates for tissue engineering [13–16] and artificial blood vessels [18], and also used to study the differentiation of stem cell [24]. While in the field of electromechanics, various sensors, such as tactile sensors [8,9], chemical sensors [3,5,6,10,11,17,19] and optical sensors [12], are using electrospun fibers as substrates or sensing elements.

In this review, we provide an overview of electrospinning technologies, which have been developed to prepare nanofibers of different materials, ranging from inorganic ceramics to organic polymers, and systematically summarize the techniques to adjust the system parameters and thus tailor the properties of the fibers, including the fiber diameter and its surface morphology. We also highlight the advance of electrospinning techniques in creating complex structures with desired properties, such as well-aligned fiber arrays and specifically patterned fiber structure on the collector. Construction of nanofibers with more complex internal structure, such as core-

***Corresponding author: Dong Chen,** State Key Laboratary of Fluid Power and Mechatronic Systems, Zhejiang University, Zheda Rd. 38, Hangzhou, China, E-mail: chen_dong@zju.edu.cn
Ran Chen, State Key Laboratary of Fluid Power and Mechatronic Systems, Zhejiang University, Zheda Rd. 38, Hangzhou, China
Ran Chen, Junfeng Liu, Zeyong Sun, Dong Chen, Institute of Process Equipment, Zhejiang University, Zheda Rd. 38, Hangzhou, China

shell structure, is also described. Finally, we discuss the industrial applications of the electrospun fibers with a focus on their scale-up. Overall, the electrospinning technologies offer a promising approach to fabricate nanofibers with tunable properties and structures that could meet the requirements of various applications.

2 Fundamentals of electrospinning

A typical electrospinning system consists of three components: a conductive spinneret to infuse the polymer solution, a conductive grounded collector to collect the nanofibers and a high voltage power supply to generate a strong electric field between the spinneret and the collector, as shown in **Figure 1a**. Under the electric field, the drop tip becomes charged and the electric force pulls the polymer solution downstream while the surface tension holds the polymer solution to the tip. At a critical point when the electric force is strong enough to overcome the surface tension, a tiny jet of the polymer solution is drawn from the tip and the conical drop tip at this point is generally known as the Taylor cone, as shown in **Figure 1b**. As the solvent of the jet evaporates in air, the charge migrates to the surface and the jet is further elongated by a whipping process due to the bending instability associated with the electrostatic repulsion initiated as small bends [30], eventually forming solidified nanofibers randomly distributed on the collector [31,32], as shown in **Figure 1c**.

3 Relation between system parameters and nanofiber properties

The set-up of the electrospinning system is simple; however, the properties of electrospun nanofibers are influenced by a lot of factors. These factors can be categorized into three groups: the properties of the solution fed into the spinneret, such as the viscosity, the surface tension and the dielectricity; the operating

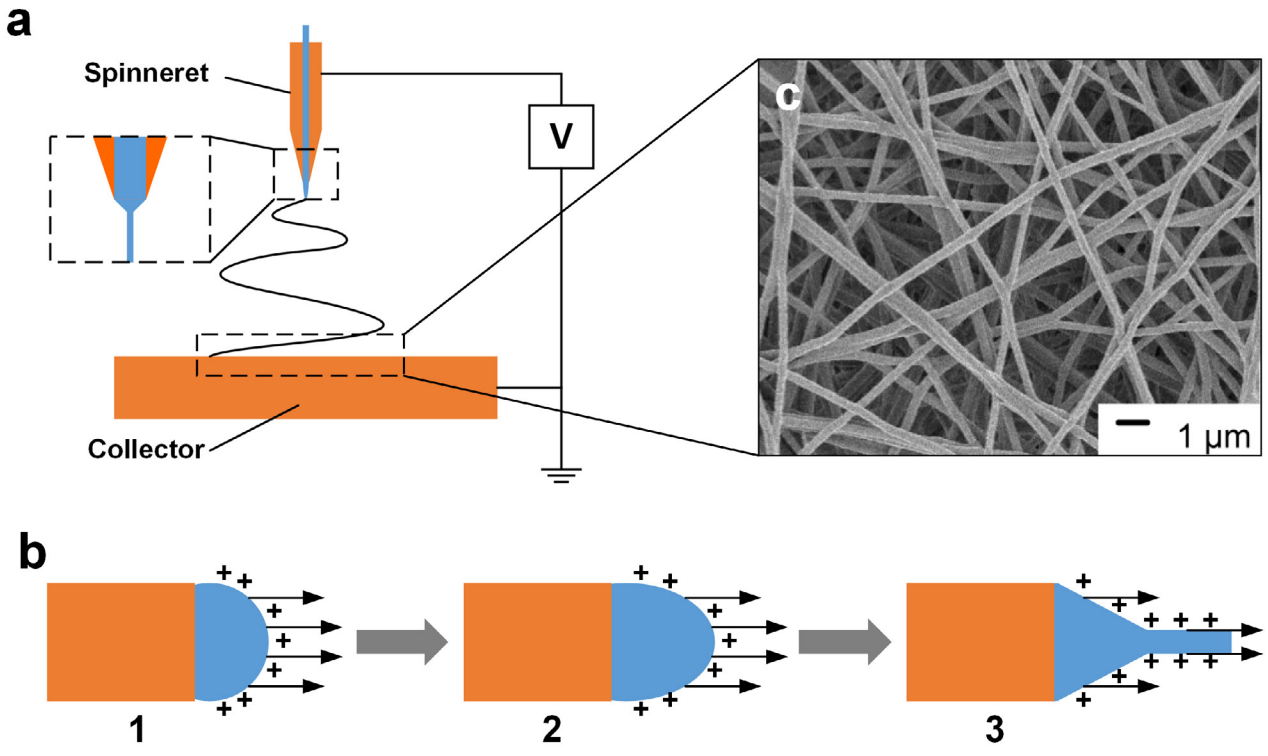

Figure 1. Schematic diagram of a typical electrospinning system. (a) Model of a typical electrospinning system consisting of three components: a conductive spinneret to infuse the polymer solution, a grounded conductive collector and a high voltage between the spinneret and the collector. (b) Formation of the Taylor cone under electric field. When the electric force that pulls the polymer solution downstream is strong enough to overcome the surface tension that holds the polymer solution to the tip, a tiny jet of the polymer solution is drawn from the tip of the Taylor cone and its solvent evaporates quickly in air, forming solidified polymer fibers on the collector. (c) SEM image of typical electrospun polymer nanofibers randomly distributed on the collector. The figure (c) is reproduced from Ref. [33] with permission from Elsevier.

conditions of the electrospinning systems, such as the feed rate of the solution, the voltage and the distance between the spinneret and the collector; the ambient conditions, such as the temperature and the humidity. Therefore, to control the properties of the electrospun nanofibers, such as their diameters and surface morphology, it is important to understand the relations between the properties of the nanofibers and the control parameters. For example, the diameter of electrospun nanofibers generally increases when the polymer concentration increases. In this section, we summarize the laws between the control parameters and the properties of electrospun nanofibers and then suggest some strategies to easily optimize the parameters and achieve nanofibers with required properties.

3.1 Solvent

Solutions used for electrospinning could be polymer solutions, particulate suspensions or polymer melts, among which polymer solutions are most widely used. Varieties of polymer could be used in electrospinning, such as polyurethane [33,34], nylon [35,36], polyvinyl alcohol [37], cellulose acetate [28], poly(caprolactone) [15,38–41], polyesterurethane [14,42–46], poly(L-lactic acid) [16,24,47–50] and so on. The selection of polymer is generally determined according to the practical application. Therefore, the choice of the solvent is one of the most important parameters, which strongly influence the spinnibility and the morphology of electrospun nanofibers. In electrospinning, nanofibers are drawn from the solution under the competing force between the electric force that pulls the polymer solution downstream and the surface tension that holds the polymer solution to the tip. While the surface tension is barely affected by the polymer concentration [51], it is directly determined by the type of solvent and can be tuned by mixing different solvents at some ratio. For example, defects, such as beads which are usually observed on electrospun nanofibers, could be minimized by changing the ratio between two different solvents and thus reducing the surface tension of the polymer solution [52].

The volatility of the solvent also plays an important role. When the volatility of the solvent is low, the solvent of the polymer solution does not evaporate completely when electrospun nanofibers are deposited on the collector, resulting in wet nanofibers and subsequent coagulation between nanofibers. In contrast, when the solvent evaporates too fast, small pores are usually formed on the surface of electrospun nanofibers, due to the rapid phase separation and subsequent solidification [53]. In the worst case, the whole electrospinning system will malfunction as the polymer will solidify at the tip of the spinneret and clog the spinneret.

3.2 Concentration

The concentration of the polymer in the solution, which directly determines the viscosity, also strongly influences the properties of electrospun nanofibers. The viscosity of the polymer solution generally increases as the polymer concentration increases. When a tiny jet of the solution is drawn from the Taylor cone, the jet would break into tiny drops when the viscosity is too low. Therefore, nanofibers can only be drawn from the solution within a certain range of viscosity, depending on the polymer concentration and the solvent. For example, nanofibers can be drawn from a solution of poly(ethylene oxide) (PEO) dissolved in ethanol/water mixture with a viscosity in the range of 1–20 poises [54] and nanofibers can be electrospun from a solution of cellulose acetate (CA) dissolved in acetone/dimethylacetamide mixture with a viscosity in the range of 1.2–10.2 poises [28].

The concentration of polymer in the solution also influences the diameter of fabricated nanofibers. The increase of polymer concentration generally leads to a higher viscosity and thus a larger diameter of spinning jet from the spinneret [52,54]. Since the diameter of the jet increases and the concentration of polymer in the jet also increases, nanofibers of larger diameter are obtained when the polymer solidifies from the jet [34,55].

3.3 Other system parameters

Other parameters that influence the properties of electrospun nanofibers are summarized as follows: 1) **Doping**. Adding some dopants into the polymer solution may change the properties of the solution and thus influence the morphology of nanofibers. For example, with the addition of 1 wt% salt in the poly(D,L-lactic acid) solution, the charge density on the surface of the jet of the polymer solution increases, which results in higher elongation forces and thinner nanofibers [27]. 2) **Feeding rate**. When the feeding rate is too low, the jet of polymer solution breaks easily, forming fragmented nanofibers. When the feeding rate is too high, infused polymer solution could not be spurted out sufficiently and thus excess polymer solution slowly accumulates at the tip of the spinneret. 3) **Voltage and distance**. The applied voltage and the distance between the spinneret

and the collector directly determine the strength of the electric field, which pulls the tiny jet out of the Taylor cone. Generally, a higher electric field will drive more fluid in the jet [34] and cause a larger electrostatic force that stretches the nanofibers [56]. However, when the strength of the electric field is too low, the jet is only intermittently drawn from the spinneret. When the strength is too high, the polymer solution may directly be sprayed out of the spinneret [57]. 4) **Temperature**. When the temperature increases, the volatility of the solvent generally increases while the viscosity of the polymer solution usually decreases, both of which will influence the properties of electrospun nanofibers. 5) **Humidity**. The humidity of the surrounding environment strongly affect the evaporation of solvent in air. For example, when the humidity is high, the absorption of surrounding water in the solution of poly(vinylpyrrolidone) in ethanol could result in slower solidification, larger elongation and thinner nanofibers [58]. In some special case, the evaporation of the solvent interacts with the condensation of water, resulting in breath figure patterns of pores on the surface of electrospun nanofibers [59]. During the electrospinning process, the solvent evaporates from the jet of polymer solution. Meanwhile water condenses on the surface of nanofibers due to evaporative cooling, forming an array of water droplet on the surface. When nanofibers are eventually dry, an array of pores is left on the surface [60].

3.4 Optimizing the performance of electrospinning

To fabricate nanofibers with desired properties, it is important to optimize the performance of the electrospinning system. Because the properties of nanofibers are affected by multiple system parameters coupled with each other, here we summarize the relations between the performance of the electrospinning system and the system parameters, as shown in **Table 1**. A strategy to optimize the operating condition and achieve nanofibers with desired properties is suggested as below. The performances of electrospinning are discussed in order of priority.

1) **Spinnibility**. Spinnibility is the priority to prepare electrospun nanofibers. Since polymer solution is mostly used, the solvent used to dissolve the polymer is first determined and must be chosen carefully to ensure the spinnibility of electrospinning. The concentration of polymer in the solution should also be considered when the formation of a stable jet from the solution is difficult.

2) **Stability**. Solvent and polymer concentration, which directly determine the properties of a polymer solution, are the two most important variables that influence the stability of electrospinning. The stability to continuously fabricate nanofibers is also affected by other parameters, such as the applied voltage, the distance between the spinneret and the collector, the feeding rate of the polymer solution and humidity. For example, when the humidity is too high, electrospun nanofibers are difficult to dry before being deposited on the collect, resulting in wet nanofibers and causing coagulation of nanofibers.

3) Uniformity. Defects such as beads could sometimes form on electrospun nanofibers, generally due to the capillary breakup of the spinning jet, i.e. contraction of the radius of the jet driven by surface tension [54]. Therefore, beads on the nanofibers can be reduced by adjusting the strength of the electric filed or choosing the right solvent.

4) Porosity. Pores can appear on the surface of electrospun nanofibers when the solvent evaporates too fast or the evaporation of solvent interact with the condensation of water. To achieve nanofibers with desired surface morphologies, the humidity of the electrospinning environment needs to be well controlled, i.e. higher humidity, more pores and larger pore size.

5) Diameter. Diameter is one of the basic parameters of electrospun nanofibers and is generally tailored by changing the polymer concentration, i.e. higher polymer concentration, larger diameter. Sometimes, the diameters is adjusted by changing the strength of the electric field.

Table 1. Relations between the performance of the electrospinning system and the system parameters. Parameters that influence the performance are listed in order of priority.

4 Alignment of nanofibers

Because of the bending instability, electrospun nanofibers are randomly spread on the collector; the disordered distribution of nanofibers thus could not meet the requirements of some applications, such as the electronic and photonic devices that require well-aligned and highly ordered architectures [61,62]. Therefore, a lot of efforts have been dedicated to develop effective methods to align the nanofibers in desired patterns. Since the bending instability causes complicated whipping of nanofibers in space, one widely used strategy is to use external electric field to guild the distribution of charged nanofibers on the collector through electrostatic interaction.

Table 1. Relations between the performance of the electrospinning system and the system parameters. Parameters that influence the performance are listed in order of priority.

Performance	Parameters	Reference
Spinnibility	Solvent, Concentration	[28] [53] [54]
Stability	Solvent, Concentration, Voltage and Distance, Feeding Rate, Humidity, Temperature	[28] [54] [57] [58]
Uniformity	Solvent ,Voltage and Distance	[34] [52] [54] [56]
Porosity	Solvent, Humidity, Temperature	[53] [59]
Diameter	Concentration, Voltage and Distance	[34] [52] [54-56]

4.1 Alignment of nanofibers by electrostatic guiding

In electrospinning, a high voltage is applied to pull a charged jet of polymer solution from the spinneret and the charge migrates to the surface as the solvent of the jet evaporates in air. The as-spun nanofibers are thus highly charged. When an external electric field is applied, the electrostatic force exerted on the highly charged nanofibers could drive and align them on the collector. For example, a simple way of aligning the polymer fibers along one parallel direction is to use a pair of grounded electrodes as the collector [36,63,64], as schematically illustrated in **Figure 2a**. The high voltage between the spinneret and the collector generates an ordered electric field, pointing towards the two grounded electrodes, as shown in **Figure 2b**. Therefore, the positively charged nanofibers are attracted to the two grounded electrodes by the electrostatic forces resulted from the electric field (F1) and the Coulomb interaction (F2) between the positive charges on the fiber and the negative image charges on the electrodes (**Figure 2c**). Under the bending instability, the fibers are thus whipping between the two electrodes. Since the electron on the nanofibers could not be transferred immediately, the nanofibers remains highly charged even when deposited on the collector and the electrostatic repulsion between them could further enhance the parallel alignment across the two electrodes, eventually forming nanofibers well aligned along one direction, as shown in Figure 2d and magnified in Figure 2e [64]. Similarly, to achieve two layers of orthogonally aligned nanofibers, two pairs of electrodes are deposited on the same collector, as shown in Figure 2f. When the 1 and 3 electrodes are grounded, a layer of nanofibers is aligned along the horizontal direction. Alternatively, another layer of nanofibers is deposited along the vertical direction when the 2 and 4 electrodes are grounded, as shown in Figure 2g. To provide better control over the orientation of nanofibers on the collector, multiple pairs of electrodes have also been developed [65].

When the collector is a flat substrate, such as the pair of electrodes, the distribution of nanofibers on the collector only spans across a small area, generally less than 40 mm x 40 mm. Thus, it is challenging to weave nanofibers with homogeneous distribution over a large area using a single pair of electrodes. To solve the problem, an array of electrodes is developed on a rotating cylinder [19]. When the cylinder rotates slowly, each pair of electrodes in the array is consecutively exposed under the spinneret. Therefore, uniaxially aligned nanofibers could be homogeneously deposited on the collector over a large area.

Similar to electric field, magnetic field could also be used to guide the alignment of electrospun nanofibers. However, the method requires that the nanofibers could be magnetized under magnetic field and thus a small amount of magnetic nanoparticles are generally added to the solution. Under a pair of magnets with the N and S poles facing against each other on a grounded collector, nanofibers are magnetized and driven back and forth across the N and S poles, forming well-aligned patterns [66]. Compared with electric field, the use of magnetic field allows the deposition of nanofibers over a slight larger area. Most importantly, only a thin layer of nanofibers could be aligned between a paired electrodes, as the deposition of highly charged nanofibers on the collector could shield the electric field, while the magnetic electrospinning is able to weave a thick layer of nanofibers on the collector.

4.2 Alignment of nanofibers guided by the motion of collector

Besides electric and magnetic fields, alignment of electrospun nanofibers could also be guided by the

relative motion between the spinneret and the collector. Different from the grounded paired electrodes, which align nanofibers over a small area on a 2D substrate, electrospun nanofibers are collected on a grounded rotating cylinder [67–71], as shown in **Figure 3a**. Though the bending instability causes the electrospun nanofibers to whip vigorously in air, the rotating cylinder is able to pull the nanofibers along its perimeter and subsequently align them on the cylinder, when the rotation of the cylindrical collector is fast enough, for example several thousand rpm, as shown in **Figure 3b**. Ideally, nanofibers are better aligned on a cylinder rotating at a higher speed and the diameter of nanofibers is generally smaller due to the stretching of nanofibers by the rotating cylinder [69]. However, too fast stretching of nanofibers by the rotating cylinder could tear off the nanofibers and thus an appropriate choice of the rotation speed of the cylinder according to the operation condition is important to ensure the continuous collection of nanofibers. A variation of the cylinder collector is the use of a plate with a sharp edge, as shown in **Figure 3c**. When the sharp edge is grounded, the high voltage between the spinneret and the collector produces a strong electric field that converges towards the edge of the plate. The charged nanofibers are thus better aligned along the edge under the electrostatic force, as shown in **Figure 3d** [72,73].

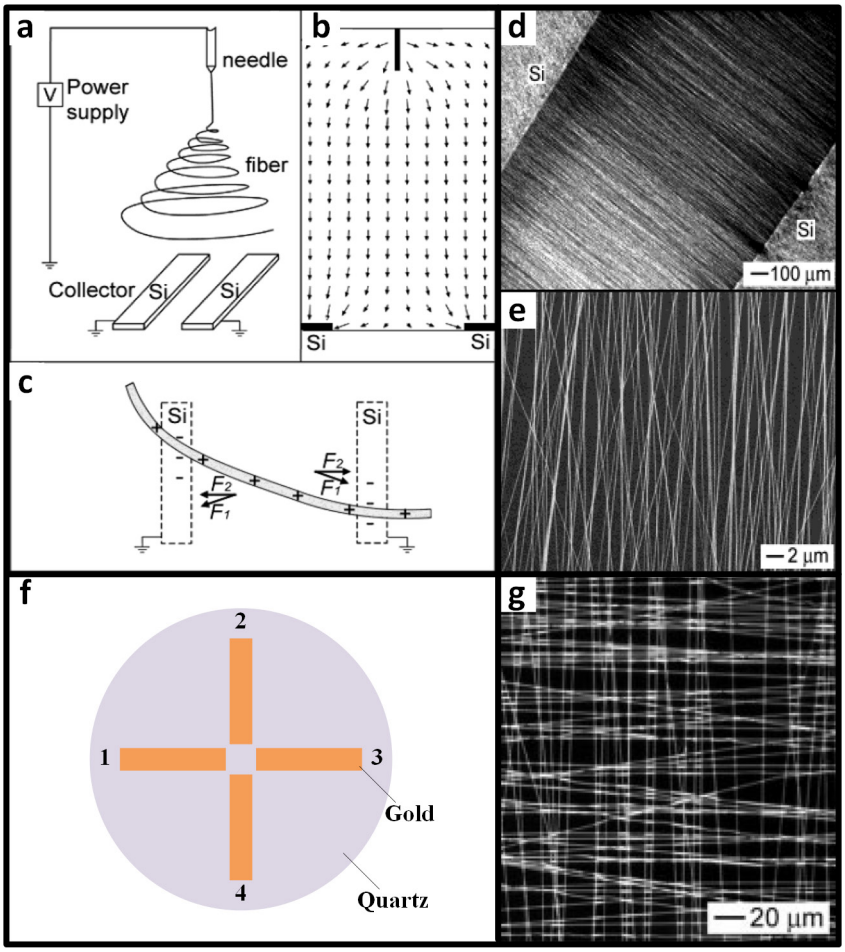

Figure 2. Alignment of electrospun polymer fibers through electrostatic guiding. (a) To align the polymer fibers along one parallel direction, a pair of grounded electrodes is used as the collector. (b) The electric field generated by the high voltage between the spinneret and the collector splits into two fractions pointing toward opposite edges of the gap between the electrodes. (c) The positively charged fibers are attracted to the two grounded electrodes due to the electrostatic forces resulted from the electric field (F_1) and the Coulomb interaction (F_2) between the positive charges on the fiber and the negative image charges on the electrodes. (d) SEM image of parallel aligned fibers between the two electrodes and enlarged in (e). (f) Schematic illustration of four electrodes deposited on quartz wafers. (g) Two layers of orthogonally aligned fibers are achieved, when the pairs of 1-3 and 2-4 electrodes are alternatively grounded for ~5 s. The figure (a-e) is reproduced from Ref. [64] with permission from American Chemical Society. The figure (g) is reproduced from Ref. [65] with permission from John Wiley and Sons.

Another strategy to align nanofibers is to overcome the bending instability through near-field electrospinning and achieve different patterns on a moving collector, as schematically illustrated in **Figure 3e**. Different from traditional far-field electrospinning, the spinneret-to-collector distance of near-field electrospinning is extremely short, i.e. less than 3 mm. Therefore, the critical voltage required to draw polymer jet from the Taylor cone in near-field electrospinning is much small than that required in traditional far-field electrospinning. In this case, the polymer jet is pulled almost straight downwards [75]. By moving the collector on an X-Y stage, specially designed 2D pattern of nanofibers could be drawn, as shown in **Figure 3f** [74]. One advantage of the near-field electrospinning is its ability to draw complex pattern on a large area under delicate control of the moving collector. However, its drawing speed of nanofibers is much slower than that of conventional electrospinning [74,76].

5 Construction of nanofibers with complex internal structure

Recent developments of the electrospinning technique have enabled the construction of nanofibers with complicated internal structures, which further expand

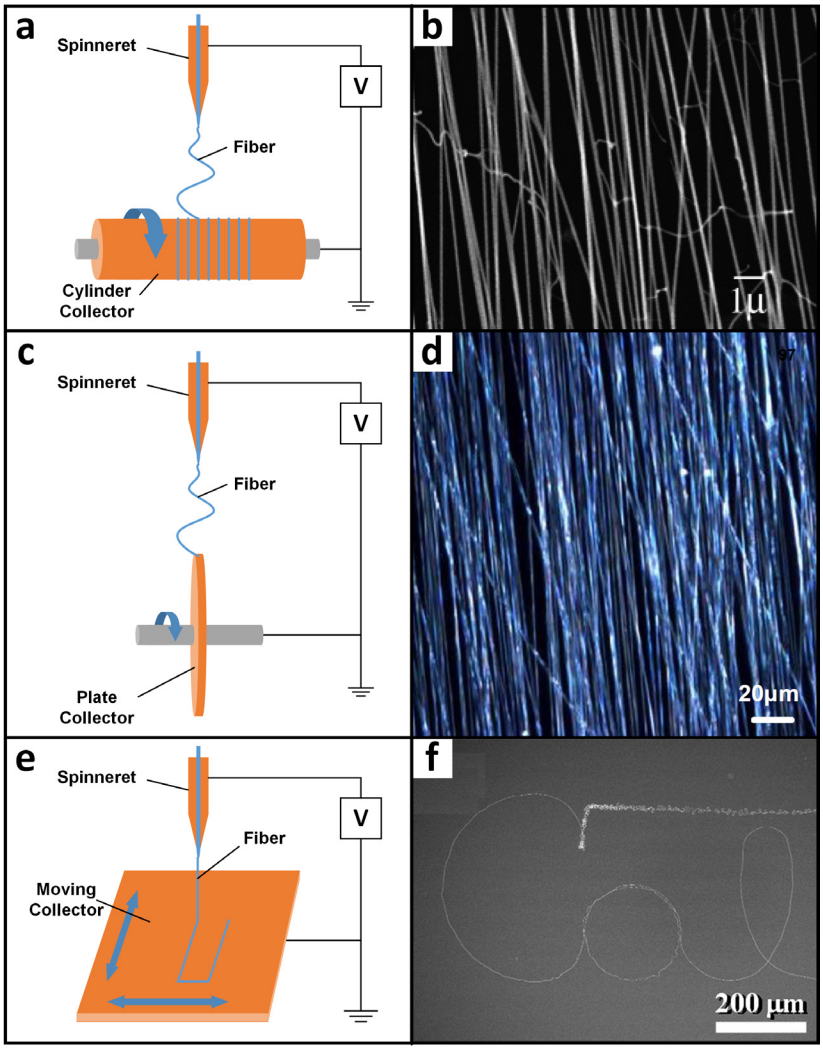

Figure 3. Patterning of electrospun fibers based on the relative motion between the spinneret and the collector. (a) Schematic diagram and (b) SEM image of fibers aligned using a rotating cylindrical collector. (c) Schematic diagram and (d) Optical image of highly ordered fibers prepared using a rotating disk with a sharp edge. (e) Schematic illustration and (f) SEM image of fibers prepared by near-field electrospinning and patterned on a moving collector. The figure (b) is reproduced from Ref. [69] with permission from American Chemical Society. The figure (d) is reproduced from Ref. [72] with permission from Elsevier. The figure (f) is reproduced from Ref. [74] with permission from American Institute of Physics.

their applications in various fields. For example, when the spinneret consists of two coaxial channels, one inner channel surrounded by an outer channel, two different solutions are delivered independently through the inner and outer channels and nanofibers drawn from the spinneret also possess a core-shell structure [77–90], as schematically illustrated in Figure 4a. As the inner and outer solutions are fed into the spinneret, a compound Taylor cone is stabilized at the tip when a high voltage is applied across the outer channel of the spinneret and the collector. In this case, the outer solution is highly charged and a jet is drawn from the Taylor cone. Meanwhile, the inner solution is dragged simultaneously along with the outer solution via viscous dragging and/or contact friction, forming core-shell nanofibers. The internal core-shell structure could directly be visualized under TEM, such as the nanofibers with thermoplastic polyurethane as the core and collagen as the shell shown in Figure 4c. With careful design of the solutions in the inner and outer channels, nanofibers with a hollow core could also be fabricated through coaxial electrospinning [81,91–93]. For example, a coaxial jet of heavy mineral oil in the core and ethanol solution containing PVP and $Ti(OiPr)_4$ in the shell are spun from the system. After hydrolization in air and calcination at 500 °C, the PVP and the oil are removed and $Ti(OiPr)_4$ is turned into TiO_2, forming nanofibers with a hollow core, as shown by the SEM image of **Figure 4d**. The fabrication of functional nanofibers with different materials and different internal structures simultaneously will further broaden their applications.

6 Scale-up of electrospun nanofibers

Electrospun nanofibers have been widely used in various areas such as porous membranes, biomedical scaffolds, sensors and so on. To meet the increasing demands for applications, different techniques have been developed to scale up the production of nanofibers. In a traditional

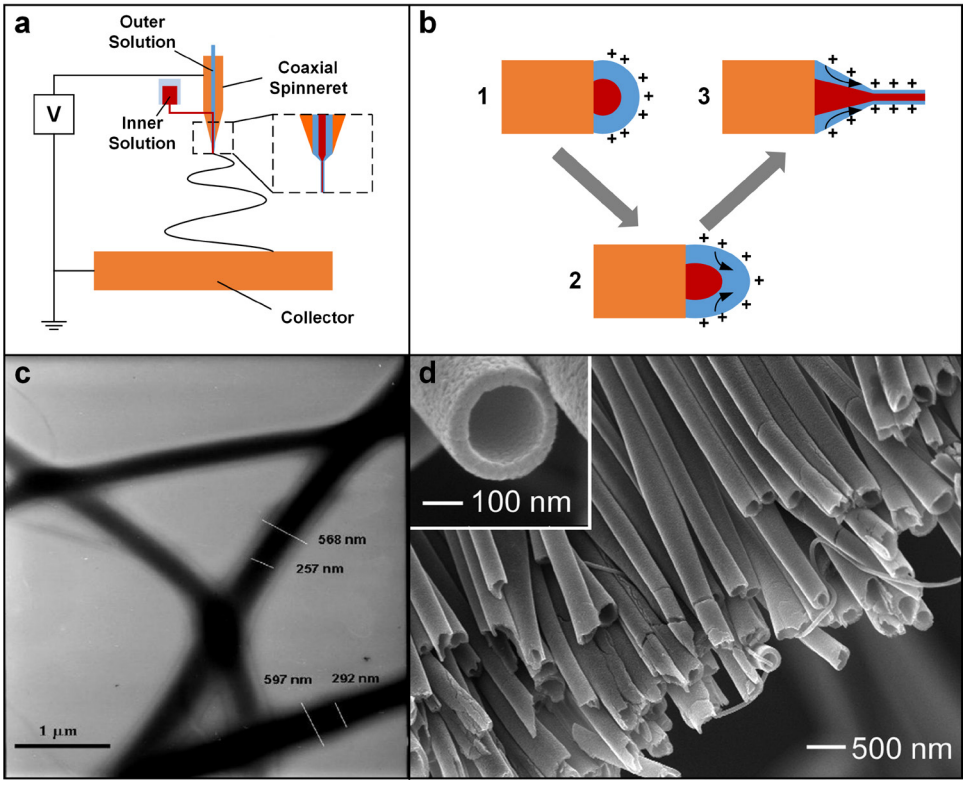

Figure 4. Preparation of nanofibers with a core-shell microstructure. (a) Schematic illustration of an electrospinning system with the spinneret containing two coaxial channels. Two different solutions are delivered independently through the inner and outer channels, respectively. (b) A compound Tylor cone forms at the tip when a high voltage is applied between the outer channel of the spinneret and the collector. A jet of the outer solution is subsequently stretched by the electrostatic force and the inner solution is simultaneously drawn along the outer solution via viscous dragging and/or contact friction, forming core-shell nanofibers. (c) TEM image of core-shell nanofibers with thermoplastic polyurethane as the core and collagen as the shell. (d) SEM image of nanofibers with a hollow core. The figure (c) is reproduced from Ref. [82] with permission from Elsevier. The figure (d) is reproduced from Ref. [94] with permission from American Chemical Society.

setup, there is only one single needle in the spinneret and only one stream of nanofiber is drawn from the setup, as shown in **Figure 5a**. A simple approach to scale up the production is to parallelize the electrospinning of nanofibers from the spinneret, such as an array of parallel needles shown in **Figure 5b**. Since nanofibers are electrospun from each needle, the production rate of nanofibers increases linearly as the number of needles increases. Further increasing the number of needles on a rectangular or circular array has also been practiced [95–98]. However, to ensure the homogeneity of nanofibers drawn from different needles, the density of needles in the spinneret is strictly limited. The high voltage applied between the spinneret and the collector raises a strong electric field around each needle, which eventually draws nanofibers from the tip of each needle. However the electric field around each needle is strongly influenced by the presence of neighboring needles, especially when they are close to each other, thus affecting the electrospinning conditions.

Instead of an array of needles, alternative techniques have been developed to produce conical tips in the spinneret, which are equivalent to those produced by needles. Generally, a sharp conical tip is preferred and under the high voltage a strong electric field is raised near the tip, which draws nanofibers from the solution. One simple method to generate sharp conical tips in the polymer solution reservoir is using magnetic fluids as template [99]. When a magnetic fluid is subjected to a strong vertical magnetic field, its surface forms a regular pattern of sharp conical tips due to the normal-field instability, as shown in **Figure 5c**. The profile of the sharp conical tips can be replicated by a layer of polymer solution on top of the magnetic field. When a high voltage is applied between the spinneret and the collector, tens of streams of nanofibers are drawn simultaneously from the sharp conical tips. Another widely used approach to scale up the production of nanofibers is to dynamically generate sharp conical tips using a rotating cylinder with a rough surface [100,101], as shown in **Figure 5d**. Half of

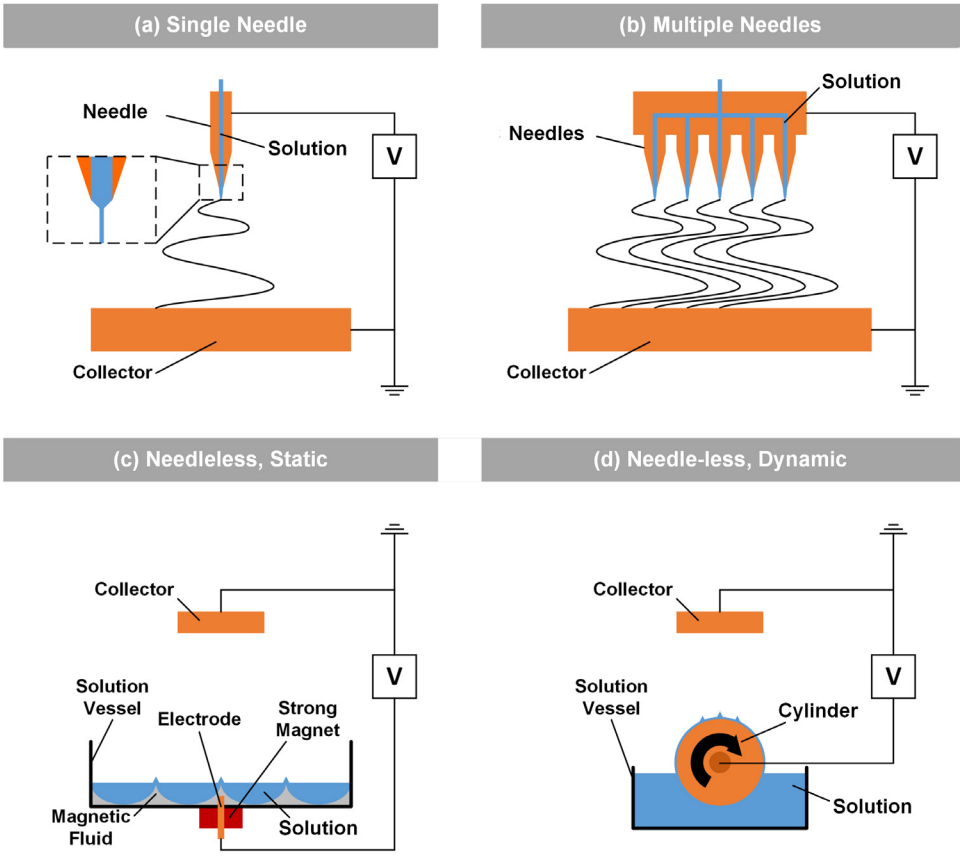

Figure 5. Scale-up of electrospun nanofibers. (a) A typical electrospinning system with a single needle in the spinneret. (b) Parallel scale-up of nanofibers drawn from an array of needles in the spinneret. (c) Instead of using needles, numerous static sharp conical tips are built up in the polymer solution reservoir by using a magnetic fluid as template. (d) Dynamic generation of multiple sharp conical tips through a rough rotating cylinder. In needleless electrospinning, a strong electric field is raised near each sharp conical tip under the high voltage, which draws nanofibers from each tip.

the cylinder is submerged in the polymer solution. When the cylinder rotates, the polymer solution is loaded onto the rough surface and both the rough surface and the centrifugal force assist the formation of sharp conical tips on the edge of the cylinder. Numerous nanofibers are thus simultaneously drawn from the spinneret under an applied high voltage. Though it avoids the use of complicated needle array and is able to mass produce nanofibers, running of needleless electrospinning is often less stable and nanofibers produced are usually less homogeneous.

7 Applications of electrospun nanofibers

Electrospinning is an effective technique to produce fibers with diameters ranging from tens of nanometers to microns. Fabricated fibers usually possess an extremely high surface-to-volume ratio and well tunable properties. The control over the alignment and the internal structure of nanofibers and the scale-up of the production also pave the way to a whole range of new applications. So far, electrospun nanofibers have been used in a variety of fields and are developed into different functional materials, such as filters [102–106], battery electrodes [2,107–112], tissue scaffolds, sensors and so on.

In tissue, cells are embedded in the extra cellular matrix (ECM), as shown in **Figure 6a**. The porous structure of electrospun nanofibers strongly resembles that of ECM in tissue and nanofibers prepared from biocompatible polymeric materials, such as poly(caprolactone) [15,38–41], polyesterurethane [14,42–46], poly(L-lactic acid) [16,24,47–50] and polyethylene terephthalate [18], provide a satisfactory microenvironment for cell culture

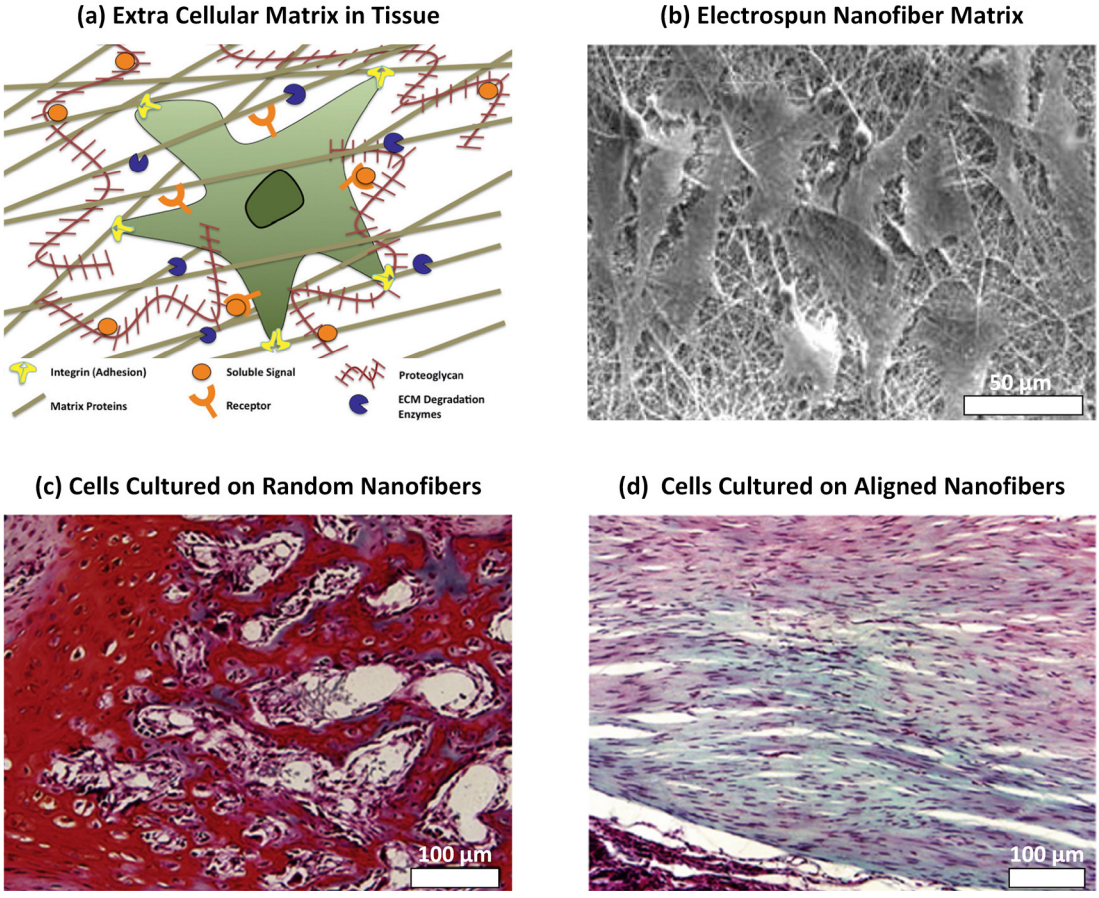

Figure 6. Biomedical applications of electrospun nanofibers. (a) Schematic illustration of extra cellular matrix (ECM). Cells are embedded in the fibrous matrix. (b) Endothelial cells cultured on the matrix of electrospun nanofibers of gelatin-grafted polyethylene terephthalate. The porous scaffold of electrospun nanofibers strongly resembles that of extra cellular matrix in tissue. Safranin O staining images of cells (c) grown in random scaffold cells and (d) grown in aligned scaffold of poly(L-lactic acid) nanofibers at 8 weeks post-surgery. More chondrocyte-like cells are observed in the randomly-oriented versus aligned nanofibers. The figure (a) is reproduced from Ref. [113] with permission from Elsevier. The figure (b) is reproduced from Ref. [18] with permission from Elsevier. The figure (c) (d) are reproduced from Ref. [24] with permission from Elsevier.

and proliferation, as shown in **Figure 6b**. While the behavior of cells strongly depends on the morphology of electrospun nanofibers, more chondrocyte-like cells are observed in the randomly-oriented nanofibers (**Figure 6c**) as compared to cells grown on aligned scaffolds at 8 weeks post-surgery (**Figure 6d**). The results of X-ray images of repaired tendons of mice at 8 weeks post-transplantation also indicate that randomly-oriented topographic scaffolds have significantly higher potential to induce ectopic bone formation when compared to aligned scaffolds.

Electrospun nanofibers are also used in mechanical [8,9,114–116] and chemical sensors [3,5,6,11,17,19,117,118], due to their larger surface area, flexibility and tunable material properties. For example, well-aligned nanofibers of conductive poly(3-hexylthiophene) have been used as a flexible tactile sensor, as shown in **Figure 7a**. When a small pressure is exerted on the nanofiber array, more contacts between neighboring nanofibers are created, reducing the resistance and thus increasing the current under a constant voltage [9]. When the fiber materials are chemical sensitive, for example NH_3 sensitive, electrospun nanofibers can be developed into a gas sensor, as shown in **Figure 7b**. A layer of well-aligned polyaniline (PANI) nanofibers is deposited on four gold electrodes [11]. When exposed to NH_3 gas, NH_3 is adsorbed by the PANI nanofibers, which reduces the charge-carrier concentration and thus decreases the conductivity. Due to the large surface area, the gas sensor based on nanofibers could respond quickly, as shown in **Figure 7c**. When exposed to H_2 gas, the nanoscale palladium layers coated on the nanofibers undergo a large deformation and subsequently an irreversible cracking in one minute [19]. Besides the applications briefly mentioned above, there are a lot of other applications of electrospun nanofibers and a lot of more applications are under exploration.

8 Conclusions

Electrospinning is a powerful technology to fabricate functional nanofibers with designed alignment and internal structure. However, to achieve nanofibers with desired properties, a delicate control over the system parameters is required. In this review, we briefly summarize the relationship between the system parameters and the nanofiber properties and provide a guidance to optimize the performance of the electrospinning system. The advance in the technology of electrospinning has enabled the fabrication of nanofibers with highly ordered architectures, such as parallel nanofiber arrays aligned by external electric field, and complex internal structures, such as core-shell nanofibers using a coaxial spinneret, which greatly broaden their applications. The scale-up of the production of electrospun nanofibers is also indispensable. So far, electrospun nanofibers have been widely used in various disciplines, such filters, sensors,

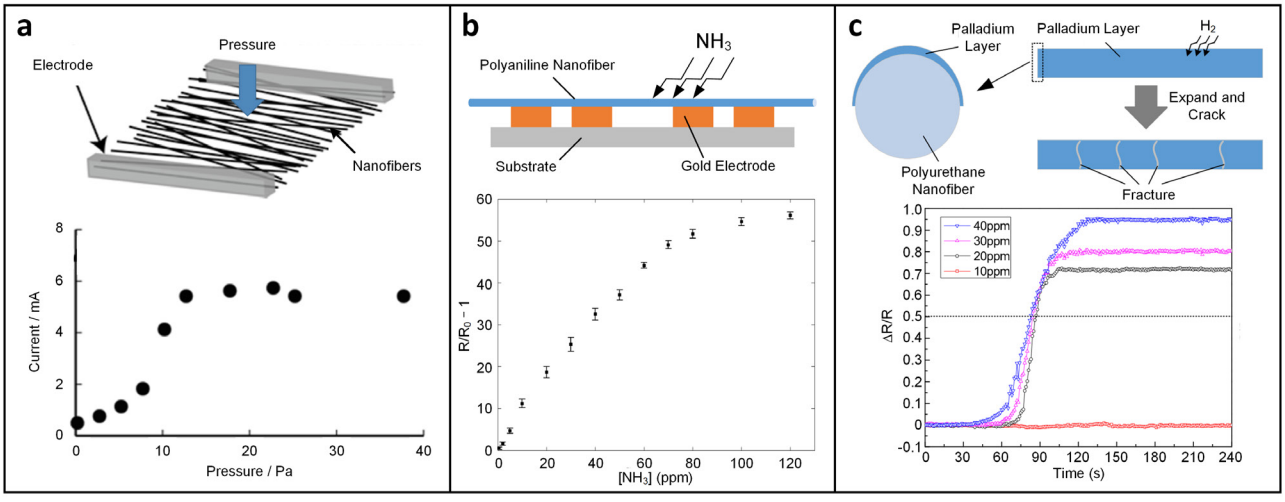

Figure 7. Applications of electrospun nanofibers as mechanical and chemical sensors. (a) Schematic illustration of a tactile sensor. When conductive nanofibers is compressed by an external pressure, the current across the device increases. (b) Model of an NH_3 gas sensor. The resistance of the sensor increases as the concentration of NH_3 increases. (c) Fast response of a H_2 gas sensor. When exposed to H_2, the palladium layer coated on the polyurethane nanofibers cracks, dramatically increasing the resistance. The figure (a) is reproduced from Ref. [8] with permission from American Chemical Society. The figure (b) is reproduced from Ref. [11] with permission from American Chemical Society. The figure (c) is reproduced from Ref. [19] with permission from Elsevier.

tissue scaffolds and so on.

Most of the applications based on electrospun nanofibers are limited in 2D, i.e. generally a thin layer of deposited nanofibers. The development of complex 3D patterns is desired to meet the requirements, for example encountered in 3D tissue engineering. In addition, the properties of electrospun nanofibers are easily affected by ambient environment, especially the humility, while the industrial application of nanofibers requires a very strict quality control, such as consistent nanofiber diameter. Therefore, the system parameters need to be precisely controlled.

Future improvements of electrospinning may benefit from the development of other technologies, such as 3D printing and microfluidics. The implementation of 3D printing could provide better control over the alignment of nanofibers in 3D space and is able to construct more complex 3D architectures. While combined with microfluidics [119], nanofibers with complex internal structures could be developed, such as those decorated with separated beads along the fiber [120,121]. These hybrid technologies are able to fabricate complex ordered 3D networks of nanofibers and develop new functional materials, such as bionic materials with periodic twisting microstructure [122,123]. We believe that electrospinning will play an even more important role in future research.

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