Electrospinning Nanofibers

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Abstract With the rapid development of human technology, we are continuously facing new problems and challenges. On the one hand are the limited natural resources, and on the other hand are the increasing demands for convenient lifestyle. It is not a good idea to sacrifice one aspect to satisfy the other, but we should seek a balance between sustainable development and the comfortable living concept. Thus, it becomes a very crucial task to explore the low-cost, large-scale, and environmentally friendly fabrication methods for wide applications. Electrospinning is a top-down method in which polymeric or melt components are drawn out from a solution system onto a collector by electrostatic force. In comparison with other methods, including drawing, template synthesis, chemical vapor deposition, and so on, electrospinning offers some attractive features. One of the most important advantages is its industrial scalability, which makes it possible to directly transfer the results from laboratory research to the industry. In general, the unique advantages of electrospun nanostructures, including high spatial interconnectivity, high porosity, and large surface-to-volume ratio, make it a promising fabrication method in a wide range of applications. This chapter covers aspects of information relating to electrospinning nanofibers, including the materials for nanofiber fabrication, processing mechanism and parameters of electrospinning techniques, special electrospinning techniques, and potential applications of electrospun nanofibers.

Keywords Electrospinning techniques · Electrospun nanofibers · Materials parameters · Applications

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1 Introduction

Recently, fibers and textiles with multi-materials add-on or built-in multi-functional units have become a hot research area for researchers. Fiber- and textile-based flexible electronics have shown great possibilities in numerous applications including flexible circuits, skin-like pressure sensors, transistors, memory devices, and displays. But similar like other mainstream issues come across during the human society development and need to be addressed, how to guarantee low-cost and production scale simultaneously is the problem that constrains the application of fibers and textiles.

Electrospinning is an excellent solution to address these problems. Compared to other material processing methods, electrospinning is more suitable for large-scale commercial applications to produce long-lasting continuous polymer micro- and nanofibers (Huang et al. 2003), due to all the merits including easy accessibility, simple synthesis, well-controlled parameters, and low cost.

First raised in early twentieth century, electrospinning has been utilized to process materials for over a hundred years, but not until recent decades, has it been widely applied to various researching fields. With the well-developed techniques and versatile functionalities, electrospinning method is widely adopted in various applications, including energy conversion and storage, wearable smart devices, environment-related applications, and biomedical applications.

2 Main Body Text

Ultrathin one-dimensional structures like micro- and nanofibers, compared to three-dimensional bulk and two-dimensional film structures, possess numerous advantages, such as large surface-to-volume ratio, tensile strength, and good flexibility. And these amazing characteristics make fibers a competitive candidate for large quantity of applications, including energy harvesting, multi-functional sensing, bio-tissue growing, and many other fields.

There are many ways to fabricate one-dimensional structures, including fiber drawing, template growing, vapor growing, self-assembly, and electrospinning. Compared to other synthesis methods, electrospinning is more suitable for large-scale commercial applications to produce long-lasting continuous polymer micro- and nanofibers (Huang et al. 2003), due to all the merits mentioned in previous section.

The concept of electrospinning could retrospect to very early of the last century, first patented by Formhals (1943), and was developing slowly during the following decades. It was not until the mid-1990s that electrospinning started to regain the attention of an increasing number of researchers as a promising method to fabricate continuous micro- and nanofibers, and developed rapidly since the entry of this century as shown by Fig. 1. For the past two decades, this versatile synthesis technique has been applied to a wide range of researching fields, including energy conversion

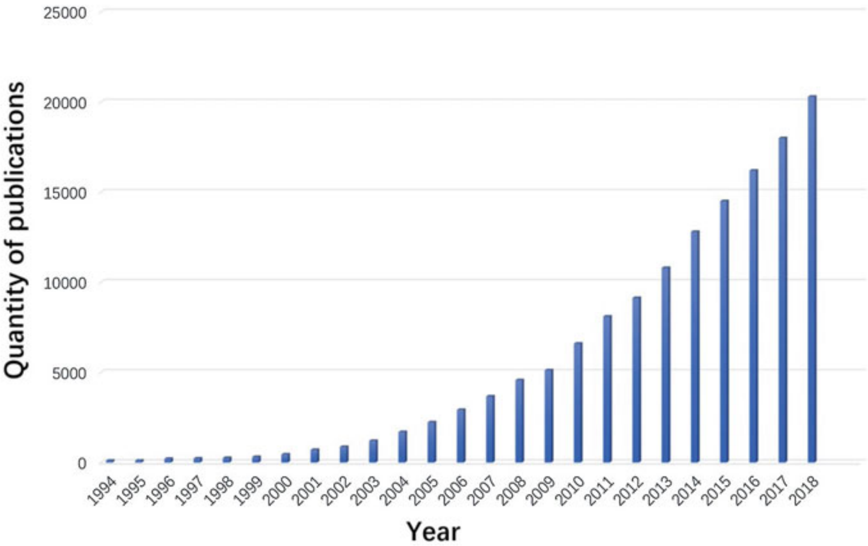

Fig. 1 Annual number of publications related to electrospinning

and storage, environment-related applications, and biomedical application and will be discussed in the following sections.

The apparatus for electrospinning is showed by Fig. 2. There are several necessary parts for a standard electrospinning setup, including a spinneret (usually a needle with a syringe), a pump that can maintain the feeding, a high-voltage power source (usually several tens of kilovolts), and a conductive collector to gather the resultant.

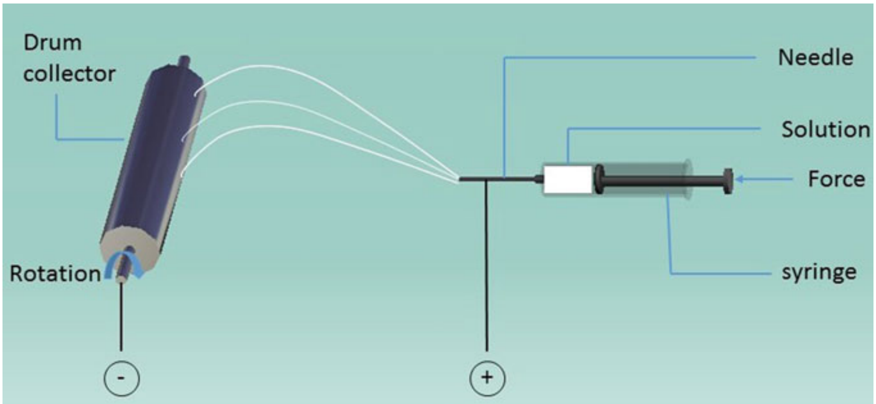

Fig. 2 An electrospinning apparatus with a rotating collector

There are several features that electrospinning process must fulfill, including (1) the solvent need to be selected properly to dissolve the polymer material; (2) suitable vapor pressure should be designed and maintained for the fiber integrity while avoiding over-harden; (3) the viscosity and surface tension of the solvent should be carefully balanced; (4) the power source must offer a voltage large enough to overcome the surface tension; and (5) the distance between spinneret and collector also need to be appropriate for full evaporation of the solvent. More specifics will be discussed in the coming sections.

2.1 Materials of Electrospinning

To understand electrospinning, the mechanism behind the process need to be investigated and learned. Different from the traditional fibers with relevant large diameter, which is fabricated by drawing method using a die involving an external mechanical force to form individual strand of fiber, electrospinning process adopt high voltage to generate a jet from polymer solution droplet. One great advantage of electrospinning is that it can process not only molten polymers but nearly all soluble polymers and materials that can be made into a suspension. Thus, there are many different types of polymers and precursors that can be electrospun for the formation of fibers. According to the application requirements, materials should be selected carefully. Some polymer and polymer composites nanofibers can be obtained directly while some ceramics and carbon nanotubes need further processing after electrospinning operation.

For each electrospinning application, proper materials must be selected and modified to obtain certain morphologies and properties to match the desired functions of the expected applications. The electrospinning technology can generate ultrathin fibers by using a wide variety of materials that contains, polymers such as polyacrylonitrile(PAN), polyvinylalcohol (PVA), polyvinylpyrrolidone (PVP), polyethylene glycol (PEG), polyvinylidene fluoride (PVDF), and polystyrene(PS); metal oxides/ceramics such as Fe_2O_3, CuO, NiO, and TiO_2; mixed metal oxides such as $TiNb_2O_7$, $NiFe_2O_4$, and $LiMn_2O_4$; composites such as carbon/SnO_2, PVA/TiO_2, Nylon-6/gelatin, graphene/TiO_2, and collagen/hydroxyapatite; and carbon-based materials such as carbon nanotubes, graphite, and graphene. Combined with controlled calcinations treatment, 1D hierarchical nanofibers can be synthesized easily by electrospinning.

The most commonly used materials for electrospinning are polymers. One great advantage of commercialization of polymers is that the cost of polymers is generally cheap because they are easy to synthesize. Polymers consist of repeating units of monomers bonded to one another, which form long molecular chains. For example, the polymer named polyethylene is made up of the repeating units of $[-CH_2CH_2-]_n$. One important value to describe a polymer is its molecular weight. As polymer chain consists of many repeating units, the molecular weight of the polymer is the sum of all the units. Higher molecular weight will make it harder to dissolve in solvents and cause a higher viscosity of the solution.

Electrospun polymer fibers are usually used as they are fabricated due to their processability and flexibility, but ceramic fibers that are hard and brittle must be electrospun from precursors followed by sintering process. Ceramics are a group of compounds composed of both metallic and non-metallic elements, usually oxides. Another common material for electrospun fiber is carbon. Carbon is the most fundamental element for organic compounds. Thus, many carbonaceous precursors can be made into pure carbon. Carbon nanofibers are known to be good conductor for electricity. And carbon nanotubes have also been applied in many electronics applications (McEuen 1998).

2.2 Electrospinning Process

After high electric potential difference is applied between the spinneret and the collector, the droplet at the needle tip will be charged and stretched under the combined forces of static electric force and liquid surface tension. With the increase of the electric potential difference, the static electric force will overcome the surface tension and the solution will form a Taylor cone (shown as Fig. 3), and a stream of

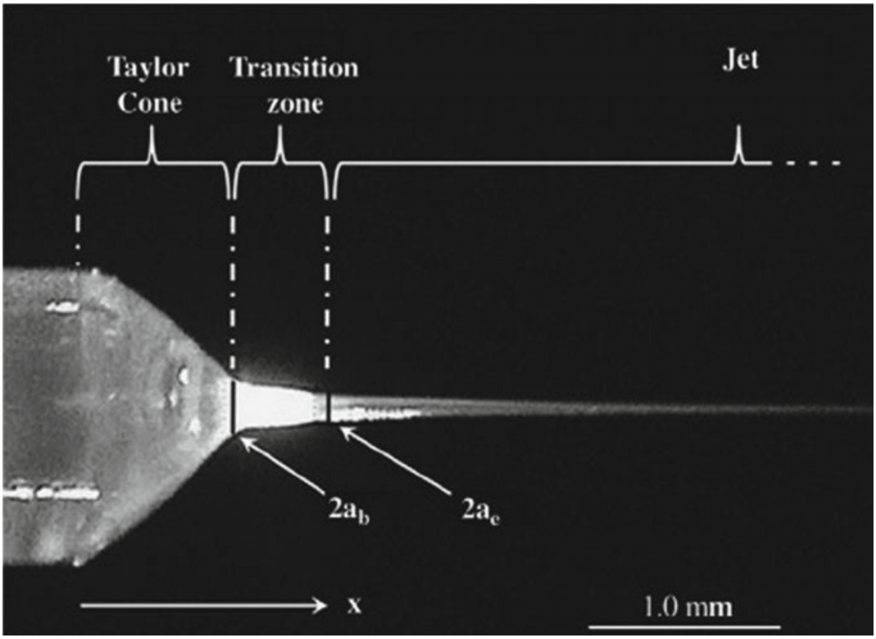

Fig. 3 Photograph of a Taylor cone in the process of electrospinning (Reneker 2008)

liquid will erupt from the surface. The liquid jet will stay in a single stream status if molecular cohesion overcomes electrostatic repulsion or break up into multiple streams otherwise. And with the evaporation of the solution solvent, the jet dries in flight and is then elongated with small bending due to the electrostatic repulsion, and finally reaches the collector to form micro- and nanoscale uniform fibers.

During the electrospinning process, there are a number of factors that can determine the final morphology and property of the resultant fibers, including the polymer solution parameter such as surface tension and viscosity, processing conditions including the voltage and distance, and the ambient condition like humidity. In the following sections, the factors that can affect electrospinning process will be introduced in detail.

2.2.1 Polymer Solution Parameters

Materials for electrospinning process must be maintained in a liquid form, molten or more commonly, dissolved in a solution. Thus, the properties of polymer solution play a crucial role in the electrospinning process and have a significant effect on the morphology of the products. When electrospinning process starts, the solution will be charged and drawn from the droplet at the spinneret under the force of electric field. The electrical property of the polymer solution, together with its viscosity and surface tension, will determine how the solution will be stretched. Meanwhile, the solution viscosity is also affected by the evaporation of the solvent and the solubility of the polymer in the solvent. The key factors of the solution include the surface tension, the polymer solubility, the viscosity, and the evaporation property and the conductivity of the solution.

Surface tension is the elastic tendency of a fluid surface, which makes it acquire the least surface area possible. At liquid–air interfaces, surface tension results from the greater attraction of liquid molecules to each other (due to cohesion) than to the molecules in the air (due to adhesion). In electrospinning process, after high electric potential difference is applied between the spinneret and the collector, the droplet at the needle tip will be charged and stretched under the combined forces of static electric force and liquid surface tension. With the increase of the electric potential difference, the static electric force will overcome the surface tension and the solution will form a Taylor cone (shown in Fig. 3), and a stream of liquid will erupt from the surface. The liquid jet will stay in a single stream status if molecular cohesion overcomes electrostatic repulsion or break up otherwise. If the resultant is collected as droplets, then the process should be called electrospraying instead of electrospinning where the liquid jet breaks up into multiple streams. And with the evaporation of the solution solvent, the jet dries in flight and is then elongated with small bending due to the electrostatic repulsion, and finally reaches the collector to form micro- and nanoscale uniform fibers (Li and Xia 2004a). For a pure liquid system, the surface tension of the solution is negatively correlated with temperature. But for an organic–aqueous mixture, the surface tension is more complicated as the small amount of organic molecules will significantly affect the surface tension due to hydrophobic behavior.

Another factor is the polymer solubility, since although electrospinning could use molten polymers, but for most cases, researches choose polymer solutions. As different solvent possesses different level of electro-spinnability (Jarusuwannapoom et al 2005), selecting the proper solvent is of great significance to dissolve the polymer and conduct the electrospinning process. Thus, the polymer solubility in a particular solvent is expected to have influence on the morphology of obtained electrospun fiber (Wannatong et al. 2004). As the molecular weight of polymer is far larger than low-molecular weight compounds, the size difference between polymer and solvent molecules is remarkable, which makes the solubility more complicated considering the viscosity and structure effects together. When the polymer is infiltrated in solvent, the solvent molecules will diffuse into polymer bulk slowly and generate a swollen gel. After the inter-bonds within the polymer molecules are broken, there will be a homogeneous polymer solution.

Another factor that has profound effect on electrospinning process and resultant morphology is solution's viscosity, which is usually related to the extent of molecule chains entanglement within the polymer solution. Too low viscosity will lead to electrospraying, and polymer particles will be obtained on the collector rather than fibers. Relatively lower viscosity caused by lower polymer chain entanglements can generate fibers probably accompanied by beads. Only solution with appropriate viscosity can produce desired smooth fibers. Therefore, the factors affecting solution's viscosity will have influence on electrospinning process and the resulting fibers, too. The intrinsic viscosity relates to the average molecular weight of polymers. The choosing of solvent is also important as in proper solvent, and the long-chain molecules of polymer are enclosure by solvent molecules, which can help reduce intercontact between polymer molecules, resulting in favoring uncurled configurations and decreasing the solution viscosity. Besides, the increasing of temperature also causes decrease in solution viscosity due to higher polymer chain mobility.

The effect of evaporation property on electrospinning resultant is obvious. The solvent of the jet will keep evaporating during the flight toward the collector. If the solvent is evaporated completely, the resultant should be well-formed fibers while incomplete evaporation will cause solvent residue and a thin film is likely to be obtained. Furthermore, solution conductivity is also important as the stretching of the polymer solution is caused by electrostatic repulsion. So, by adjusting the solution conductivity with extra ions, the carried charge could be increased, which can help in the stretching of polymer chains and avoiding beaded fibers.

2.2.2 Processing Conditions

During the electrospinning process, various of external parameters exerting on solution jet, including applied voltage, feed rate, distance between the spinneret and collector, and the type of collector, together determine how the morphology of the resultant fiber is.

First crucial element in electrospinning process is the high voltage applied between the spinneret and the collector. When the polymer solution is connected with a high voltage, charges will be induced. When the electrostatic force grows enough to overcome the surface tension, together with the electric field generated by the potential difference between the spinneret and the collector, electrospinning process starts to work. The voltage should be selected to match with the feed rate in order to form a stable Taylor Cone. Because higher voltage may induce more charges, accelerating the jet and draw larger amount of solution from the spinneret, which will cause smaller and unstable Taylor Cone.

Feed rate is the volume of solution being processed per unit time during electrospinning. For a certain voltage, there is a corresponding feed rate that can guarantee a stable Taylor Cone. With the increasing of feed rate, the diameter or beads size also increases since there is a greater volume drawn away from the spinneret. But there is a limitation of the upper feed rate, because increased volume brought by larger feed rate needs more charges for the stretching of solution, and more charges will accelerate the solution and decrease the flight time. However, greater volume requires more time for the evaporation of solvent, which contradicts the previous situation. Thus, a lower feed rate is more desirable for the electrospinning process as there will be long time for the completed evaporation of solvent.

The effect of temperature is simple and obvious. Higher temperature will increase the evaporation rate while reducing the viscosity of the solution. Meanwhile, the polymer solubility is also enhanced. Thus, the produced electrospun fibers tend to possess a smaller but more uniform diameter (Mit-uppatham et al. 2004).

To establish the electrospinning process, there must be an electrical field between the spinneret and the collector. So, the most commonly used collectors are chosen as conductive material like aluminum foil properly electrically grounded or connected to negative voltage. On a conductive collector, the distributed electrospun fibers are likely to be denser than that on an insulating collector, where the charges will accumulate and repulsion forces tend to drive fibers to form a loose structure. But this mechanism can be utilized to fabricate 3D fiber structures.

The final factor needed to be mentioned is the distance between the spinneret and the collector, as by changing the distance can vary the electrical field and flight time directly. If the distance is too small, the flight time will be possibly not enough for the completed solvent evaporation, especially when shorter distance will lead to larger electrical field, which will accelerate the jet meanwhile. In this case, extra residual solvent will exist when the resultant reaches the collector and the fibers may merge to form polymer nets or thin films instead of individually fibers. Decreasing the distance can be regarded as increasing the voltage supply.

2.2.3 Ambient Parameters

The effect of environmental on electrospinning process is a very complicated issue. The interaction between the surroundings and the polymer solution may be reflected on the morphology of the electrospun fibers. For example, high humidity level will possibly lead to the formation of pores on fiber surface. Because at normal atmosphere, water tends to condense on the fiber surface when humidity is high. This happens especially when the solvent is volatile. This has been verified by experiments using Polysulfone (PS) dissolved in Tetrahydrofuran (THF). When the humidity is over 50%, there will appear circular pores with the size and depth increasing with humidity until saturation (Casper et al. 2004). The environmental humidity also affects the evaporation rate of the solvent in the solution. When the humidity is very low, a volatile solvent is able to dry very soon, even faster than the solution removal from the spinneret. In this case, there may be only several minutes before the electrospinning process is terminated because the spinneret tip is clogged (Baumgarten 1971).

Besides the humidity, the atmosphere composition of the electrospinning environment also has effect on the processing. Under high electrostatic field, different behavior comes from different gases. Take helium as an example, under high electrostatic field, helium will break down that makes electrospinning not going to happen.

When the electrospinning process is carried within an enclosed environment, the pressure may become another factor that has influence. Generally speaking, reducing the atmosphere pressure does not good to electrospinning process. When the pressure is low, the polymer solution tends to flow out the spinneret automatically. Thus, the jet initiation becomes unstable. If the pressure keeps dropping, bubbles will occur at the tip of spinneret. At some extreme cases, electrospinning process is not able to establish due to the direst discharge of the electrical charges.

2.3 Special Electrospinning Techniques

Besides the conventional electrospinning method introduced above, there are many special electrospinning techniques, which can serve to fabricate specialty fibers. This greatly enriches the production of electrospun fibers and promotes the range of electrospun fiber application.

2.3.1 Highly Aligned Electrospun Fibers and Single Electrospun Fibers

First is the continuous electrospinning of aligned nanofibers. The approaches to gain highly aligned electrospun nanofibers are mainly by customizing collectors as Fig. 4 shows. One most commonly adopted way is to use high speed rotating drum as the collector, and the rotating speed range is from 2000 to 4000 rpm (Baniasad et al. 2015). Another approach is to replace the highly rotating drum with a rotating disk with an extremely sharp edge. Furthermore, the interdigital electrode is also an ideal substitute as the collector. By varying the configurations of the interdigital electrode, researchers can get parallel electrospun nanofibers with different length (Ke et al. 2017). Besides the frequently used methods above, the collector can also

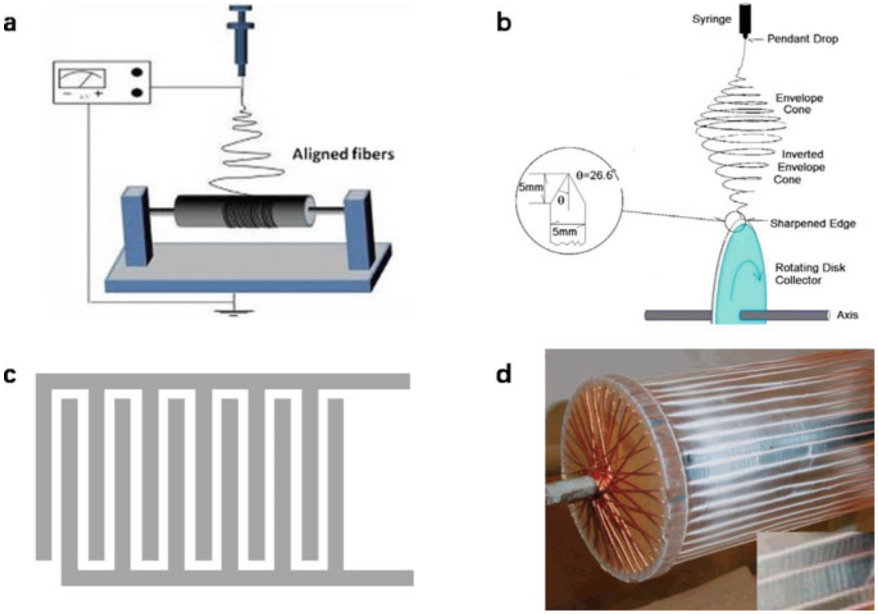

Fig. 4 Different approaches to acquire aligned electrospun nanofibers by **a** highly speed rotating drum (Prabhakaran et al. 2013), **b** sharp-edged rotating disk (Xu et al. 2004), and **c**, **d** parallel distributed electrodes (Ke et al. 2017; Katta et al. 2004)

be replaced by evenly distributed metal wire, parallel auxiliary electrodes, or U-shape collector. Similar methods of modifying collector are also used to get single electrospun fibers, including using cardboard frame, a substrate with micro-channels, and parallel electrodes.

2.3.2 Wet-Electrospinning

Sometimes, the electrospun fibers are preferable with 3-dimensional structure, so the wet-electrospinning system is established. If the collector of electrospinning process is immersed into solvent, or replaced by solvent container directly as Fig. 5 shows, this process is called wet-electrospinning.

In a previous study, pullulan nanofiber was fabricated by wet-electrospinning to explore how the solvent concentration can affect the fiber diameter. In this study, ethanol coagulation bath was used to collect the electrospun pullulan nanofibers (Kong and Ziegier 2014).

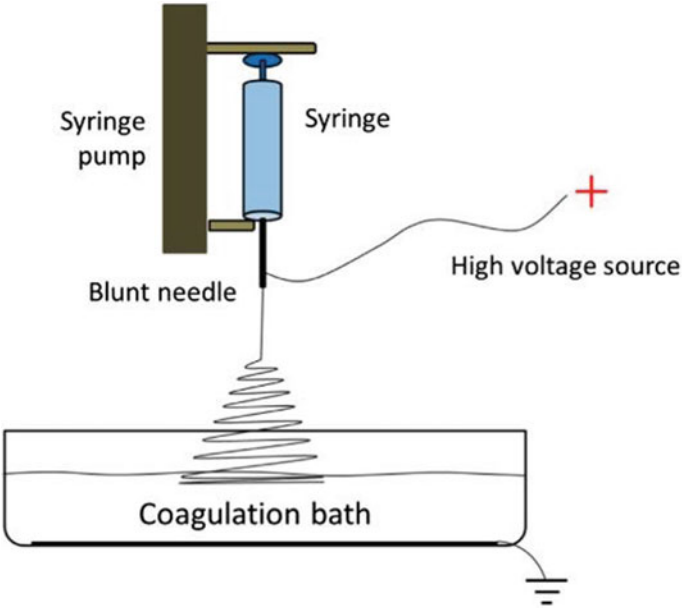

Fig. 5 Schematic drawing of the wet-electrospinning setup (Kong and Ziegier 2014)

2.3.3 Core–Shell Electrospinning

Except customizing the collector, the spinneret is another component that can be remolded to expand the morphology and functions of electrospinning products. For example, by using a special spinneret, as Fig. 6 shows, core–shell electrospun nanofiber is obtainable (Li and Xia 2004b). The special spinneret is made of two coaxial capillaries, through which two different, usually incompatible liquids are ejected to form a continuous coaxial jet simultaneously.

This core–shell electrospinning method is often used to process precursors of inorganic material. By calcining the electrospun core–shell nanofiber under high temperature condition, the as-spun nanofiber will convert into desired inorganic components (Zhang et al. 2012). And by adding functional particles into core liquid, which will be removed later, hollow nanofibers with decorated surfaces are obtained as Fig. 7 illustrates.

2.3.4 Melt Electrospinning

In some special cases like biomedical applications, the residual solvent is unwanted due to the potential toxicity to cells and tissues, or the residual repulsive charge may compromise the consistent density and thickness of electrospun fabrics. Then, melt electrospinning is a way to address these problems. The melt electrospinning setup

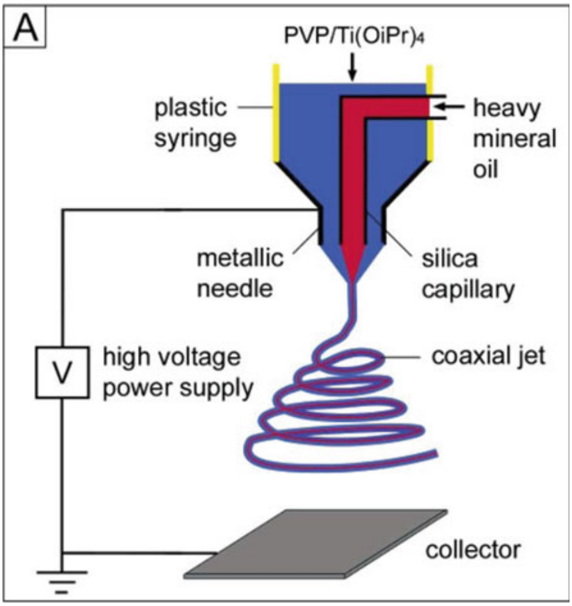

Fig. 6 Schematic illustration of the setup for core–shell electrospinning (Li and Xia 2004b)

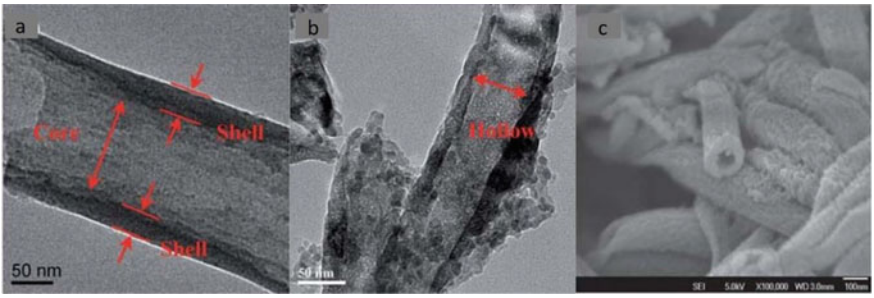

Fig. 7 TEM images of coaxial nanofibers when **a** as-spun and **b** calcined at 450° and**c** corresponding SEM image (Zhang et al. 2012)

is illustrated in Fig. 8 in which the key part is a heating module that can melt the polymer material.

Nowadays, melt electrospinning has been widely used in industry for many applications including filtration, reverse osmosis membranes, fuel cell catalyst technologies textiles, separator, and biomedical uses. Melt electrospinning can be further combined with core–shell electrospinning technology to explore its joint application.

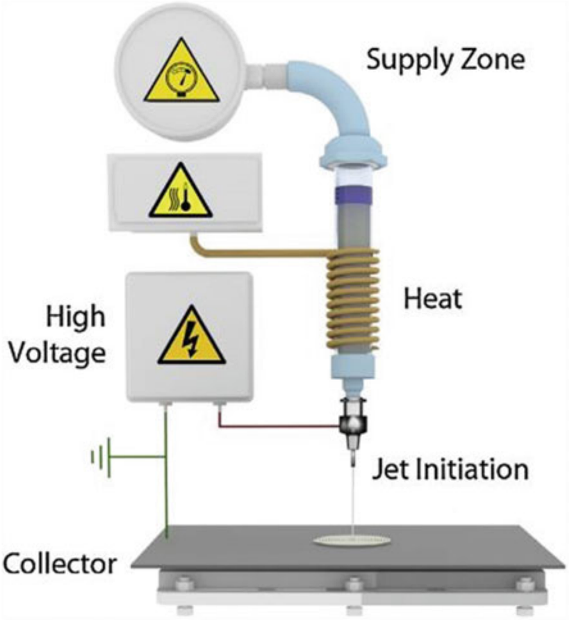

Fig. 8 Schematic of melt electrospinning onto a static collector (Brown et al. 2016)

2.3.5 Electrospray Technique

Electrospray, sharing the same mechanism and apparatus with electrospinning, also works on the principle of applied electric fields. Compared to electrospinning, the solution for electrospray is with less viscosity or smaller molecular weight, so that when applied with a high-voltage difference, the electrostatic repulsion overcomes the molecular cohesion and continuous liquid jet will break up into highly charged liquid droplets and radially disperses. By regulating the feed rate and applied voltage, the size of the electrosprayed droplets can be controlled precisely, from micro- to nanolevel (Fig. 9).

Due to its versatility and feasibility, electrospray has been involved in many nanoscience and nanotechnology area, especially in micro/nanoparticles fabrication for biomedical applications such as bone tissue engineering and drug delivery.

2.4 Application Examples of Electrospinning Nanofibers

As discussed in above sections, the electrospun nanofibers have been widely investigated in terms of the material science and engineering viewpoint. With the unique material properties and facile control of the fiber morphology/structure, various application fields of the electrospun nanofibers have been proposed by now, such as

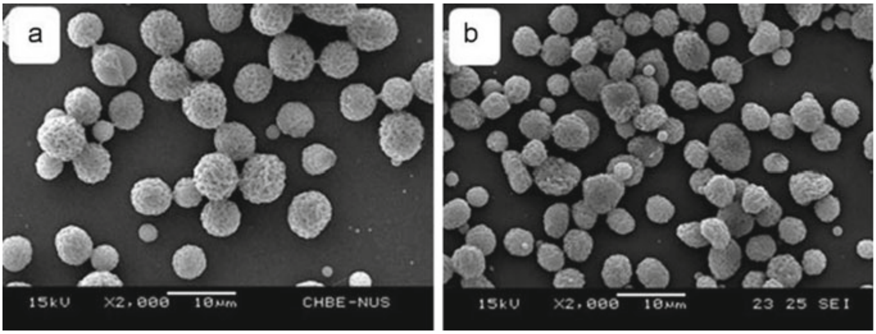

Fig. 9 Electrosprayed particles from **a** 5% w/v HMw PLGA and **b** 6% w/v LMw PLGA in pure DCM (5% w/v of BSA served as the core at a shell:core flow rate of 1.0:0.1 ml/h) (Zamani et al. 2014)

energy and electronics, bioengineering and biotechnology, defense and security, environmental engineering. Among these fields, the needing of electrospun nanofibers with enhanced mechanical, electrical, chemical, and physical properties have been inspired and they are believed to make the new era of the material research.

2.4.1 Energy Applications

Nowadays, the search for clean and sustainable energy sources is attracting increasing attention due to severe environmental issues raised from the massive usage of the traditional energy resources, such as coal, fossil fuels, and natural gas. Thus, human society have invested much time and effort to develop new energy techniques, such as batteries, catalysts, supercapacitors, fuel cells, and solar cells. Electrospun porous nanofiber mats made of functional material showed excellent energy storage and transfer behaviors in these research fields. The electrospun nanofibers have shown great potential in enhancing the performance of various batteries, increasing energy density of capacitors and fuel cells, and power conversion efficiency (PCE) of solar cells.

Batteries

According to a large amount of recent reports, the electrospun nanofiber mats can be used within various batteries to enhance their performance by introducing higher specific surface area, internal surface area, large pore volume, higher conductivity, and better 1D charge carrier transport. First, battery membranes made from electrospun fiber mats with tunable porosities have shown much enlarged specific areas to enhance the separation performance. For example, the electrospun sulfonated styrene nanofiber membranes expressed excellent affinity to liquid electrolytes and high ionic conductivity when acted as separators. Second, various morphologies (particles or nanoparticles) of transition metal oxide coated on the surface of carbon nanofibers (CNF) generate more access channels for Li^+ transport into the inner active sites of anodes and remarkably increase the electron transport rate. Furthermore, the coaxial nanofiber composite ($LiCoO_2$ core with MgO shell) electrodes fabricated by electrospinning, which exhibits excellent reversibility, small impedance growth, and better cyclability since the $LiCoO_2$ cannot directly contact electrolyte (Gu et al. 2007).

Catalysts

As far as we known, the catalysts' performance is determined by the number of active sites exposed to the precursors. The electrospinning method exbibits the facile production of the porous nanofiber mats with high specific area, which has shown great potential in novel catalysts fabrication. Electrospun TiO_2 nanofiber mats modified with Pt, Pd, and Ru nanoparticles have been successfully fabricated, their performance toward Suzuki coupling reactions has been tested, and the results showed the novel metal coated TiO_2 catalysts can shorten the reaction duration (Formo et al. 2009). The performance enhancement is attributed to the quasi-one-dimensional transport of the electron within the nanofibers as well as the dramatically reduction of the grain boundaries between the catalytic nanoparticles.

Supercapacitors

Supercapacitors are intensively investigated as an energy storage device due to their rapid charging/discharging capacity, long cycle lifetime, and high power density. They are widely used in large-range applications, from handheld devices to electric vehicles even to power station. For a supercapacitor, higher operating voltage and capacitance value are key points to increase the overall energy density of supercapacitors. Increase the surface contact area of the electrodes can be a simple method to obtain higher capacitance performance, and the electrospun nanofiber mats possess this advantage. High temperature activated electrospun CNFs have shown great potential to make high performance supercapacitor electrodes due to the porous surficial structures and 1D morphology. The commonly used precursors for the CNFs synthesis are some polymers (Kim et al. 2004), such as polyacrylonitrile (PAN), isotropic pitch precursor (IPP), poly(imide) (PI), (Kim 2005). polyamic acid (PAA), and polybenzimidazol (PBI). These polymer solutions are first loaded into a typical electrospinning setup to obtain the nanofibers and then carbonized under high temperature in inert atmospheres (N_2 or Ar) to obtain the CNFs. Ruthenium nanoparticles doped CNFs have been synthesized by electrospinning the PAN/Ruthenium acetylacetonate solution and the specific capacitance of the nanofiber-based device jumped from just 140 to 391 F/g. (Ju et al. 2007).

Fuel Cells

Platinum is extensively used in fuel cells for oxidation of fuels (such as hydrogen and methanol) due to its high activity and chemical stability, but the Pt in earth is very rare so the price of Pt-based materials is very high. To reduce the usage amount of Pt in fuel cells, the Pt nanoparticles can be coated on the surfaces of the electrospun carbon nanofibers to form a composite electrocatalyst, which can be used for the oxidation of methanol (Li et al. 2008). With enhanced specific surface area and porosity, the electrospun Pt and PtRh nanowires show better catalytic performance than the traditional Pt nanoparticle catalysts (Kim et al. 2009).

Thin Film Solar Cells

Thin film solar cells are fabricated by depositing several function layers, such as transparent metal oxides electrodes (fluorine-doped tin oxide and indium-doped tin oxide), light absorbers (perovskite and dyes), charge carrier transport layers, and metal electrodes, which can be used for converting sunlight into electricity. In order to fabricate high efficiency device, the efficiently transport/extraction of the photogenerated charge carriers (especially for electrons) should be achieved. Thus, high surface area, reduced crystal defects, and 1D pathway are urgent needed for the charge carriers transport layer synthesis. TiO_2 nanofiber mats are proposed for the high efficiency solar cell fabrication, and they are obtained by electrospinning polymers [PVP and polyvinyl acetate (PVAc)] and TiO_2 precursors (titanium isopropoxide) mixture in DMF. After high temperature annealing, the anatase TiO_2 nanofibers are grinded and fabricated into thin film electrodes to transport photogenerated electrons, the enlarged surface area, reduced crystal defects, and 1D electron pathway along the nanofiber will lead to the enhancement of light absorbers loading and sunlight harvesting efficiency (Chuangchote et al. 2008). Hollow rice grain-shaped TiO_2 nanostructures with abundant nanopores, reduced grain boundaries, direct electron transportation, and large surface area were prepared by simple electrospinning of PVAc ($Mw = 500{,}000$) and titanium isopropoxide mixture followed with high temperature calcination. Then, they were used as electron transport material in a perovskite solar cell and the champion PCE of 14.2% is achieved for 1 cm^2 device, which was 47.9% higher than its planar counterpart (with an efficiency of just 9.6%, Fig. 10) (Ma et al. 2019).

2.4.2 Electronic Applications

Nanofibers made of sensing materials have shown the high sensing behavior with fast response sensitivity. It is widely accepted that the electrospun nanofibers with good mechanical durability, high surface area, and aligned charge carrier transport can supply better structure reinforcement and achieve high sensing performance.

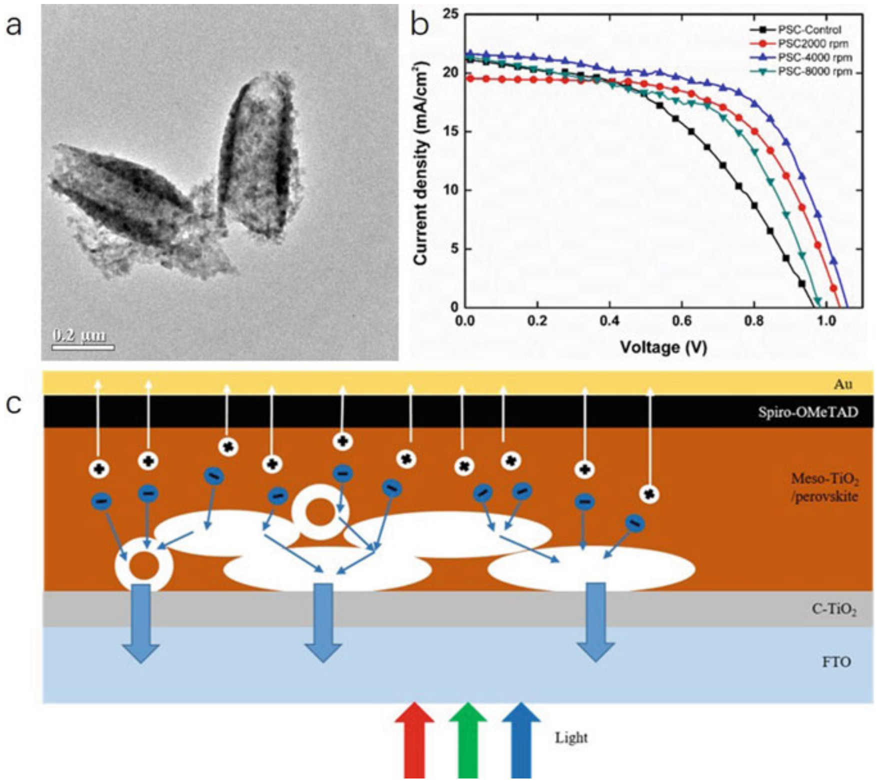

Fig. 10 **a** The TEM image of the fabricated rice grain-shaped TiO_2 nanostructures. **b** The photocurrent–voltage curve of the champion device with an active area of 1 cm^2. **c** The proposed mechanism for the enhanced performance of the rice grain-shaped TiO_2 nanostructure-based PSCs (Ma et al. 2019)

Motion Sensors

Piezoelectric materials, which can convert mechanical deformation into electric signals, are widely used to fabricate motion sensors,which are demanded for the wearable devices for power generation and body movement sensing. The electrospun fibers exhibit high mechanical endurance and enhanced piezoelectric property because of their unique morphologies. By applying the stretching-induced alignment method upon just-prepared poly[(vinylidenefluorid-co-trifluoroethylene)] P(VDF-TrFE) fibers, the highly oriented P(VDF-TrFE) fiber mat can be obtained. The 80% aligned electrospun P(VDF-TrFE) fibers show high output voltage of 84.96 mV (Fig. 11). The aligned electrospun P(VDF-TrFE) fiber bundle was integrated in daily cloth to monitor real-time body gestures (Ma et al. 2018).

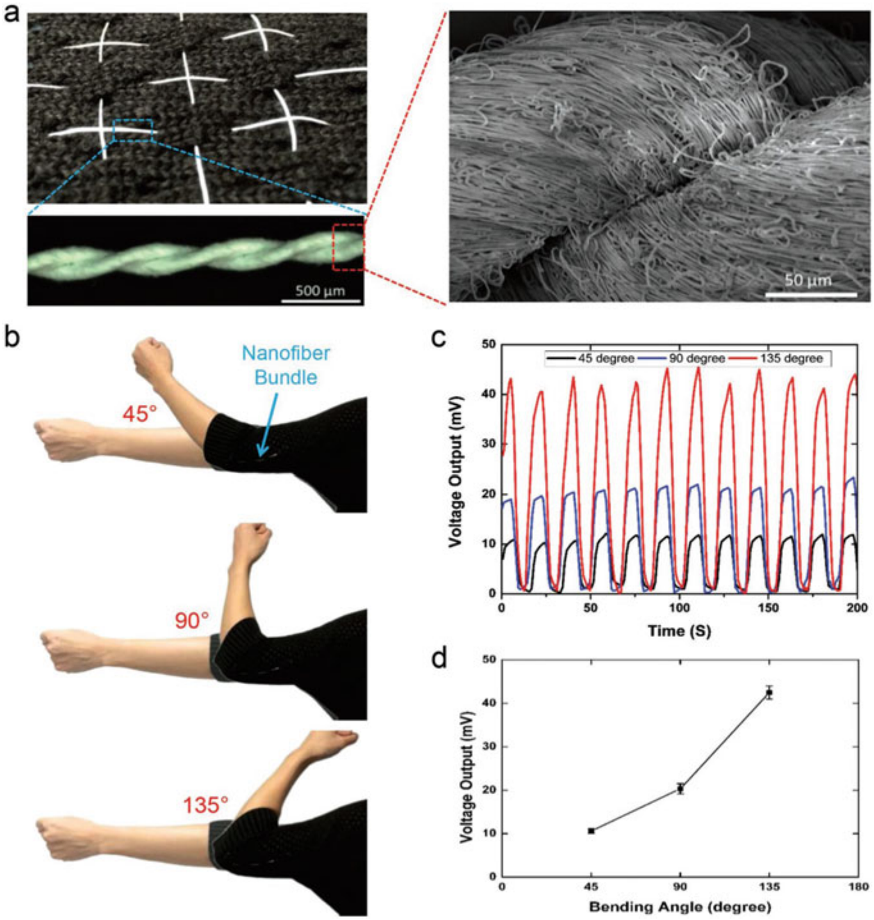

Fig. 11 **a** Twisted electrospun P(VDF-TrFE) fiber bundle integrated into cloth. **b** Monitoring different body movements (45°, 90°, and 135°). **c** Corresponding voltage outputs and **d** their average values for different body movements (Ma et al. 2018)

Chemical Sensors

When chemicals (usually liquid or gas) contacts with some nanostructured semiconductors, the charge transfer between the chemicals and the semiconductors will lead to resistance change of the semiconductors. One can get the information about the chemicals by fabricating chemical sensors based on these semiconductors by tracking the electric resistance change. It is commonly known that the size of the nanomaterials will affect the internal free charge carriers transport, so the chemical sensors fabricated with electrospun nanomaterials may exhibit faster and more sensitive response when compared to the conventional powder samples. For example, the electrospun SnO_2 and MoO_3 nanowires have been observed with higher sensitivity and faster response time in detecting H_2S and NH_3 than their thin film counterparts, respectively (Sawicka et al. 2005). Also, the detection threshold of the chemical sensors based on the electrospun nanomaterials is very low, such as electrospun ZnO nanowires can detect ethanol vapor with a concentration of just 10 ppm (Wu et al. 2009).

Actuators

Contrary to motion sensors, the actuators are a kind of devices designed to convert electrical energy into various mechanical motions. The electrospun flexible nanofiber mats can be used to enhance the mechanical properties of the device by increasing the strain since the electrolyte can better penetrate into the porous structure of the electrospun nanofiber membranes. The response rate of the electrospun nanofiber mat-based actuator can be increased since high ion mobility can be guaranteed. Some thermal sensitive nanofiber mats have been fabricated for the construction of unique thermal response actuators.

Optoelectronics

With regard to the optoelectronics, the 1D electrospun nanofibers with high conductivity can efficiently transport the photogenerated charge carriers. When compared to the traditional thin film, an electrospun Al doped ZnO nanowire shows higher sensitive photoresponse under below bandgap light illumination. Intrinsic p-type quasi-1D CuO nanofibers fabricated with rotating electrospinning method have been used to construct low-cost and photo-sensitive field-effect transistors (Wu et al. 2006).

2.4.3 Bioengineering and Biotechnology

The nanofibers made of biocompatible materials are widely investigated for implanting into patient’s body for the purpose of repairing the diseased tissues (Fig. 12, Yang et al. 2012). The well-designed bio-friendly nanofiber mats have shown the capacity to separate the bio-interfaces by using different chemical ligands to functionalize the nanofiber surfaces. The separation efficiency can be remarkably enhanced due to the high surface area of the electrospun nanofibers. The electrospun nanofibers are also regarded as drug carrier with controllable release function. That is, the electrospun nanofiber mats loaded with specific drug can be used for surgery wound recovery and controllable deliver the required amount of drug through patient’s digestive system by encapsulating into capsules.

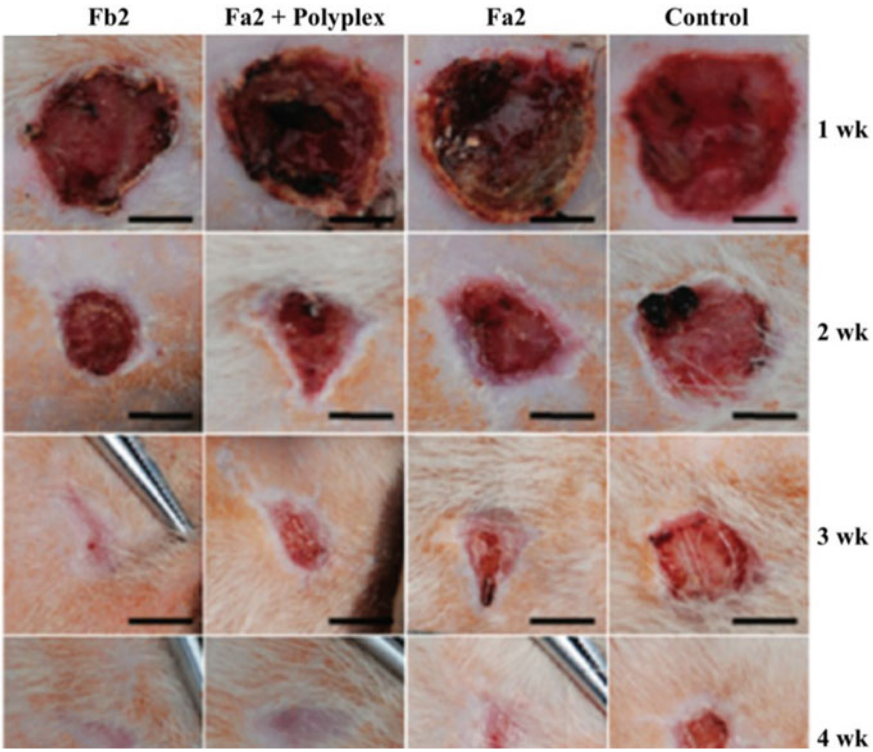

Fig. 12 Diabetic skin wound using a rat model for comparison of control and those subjected to delivery of pbFGF polyplexes from electrospun poly(ethylene imine)/PEG (2 kDa) core/shell fibers (Fa2: blank fibers and Fb2: fibers with pbFGF polyplexes in the core) (Yang et al. 2012)

2.4.4 Defense and Security

The electrospun nanofiber mats can be used as protective clothing for the soldiers' safety. By incorporating the nanofiber mats, the protective cloth can kill/degrade the biological warfare agents and harmful chemicals. Work together with the chemical sensors, the protective clothing can perception the danger in advance to avoid body injure from chemical weapons.

2.4.5 Environmental Engineering

In the aspect of environmental engineering, the electrospun nanofiber mats can be used to filter dusts and hazardous substances. Polluted air or solutions can be purified by these nanoscale porous membranes. Also, the bacteria or organic groups within the air or solutions can be killed or degraded by the functionalized nanofibers by surficial decorated with some functional chemical groups, and this technique has

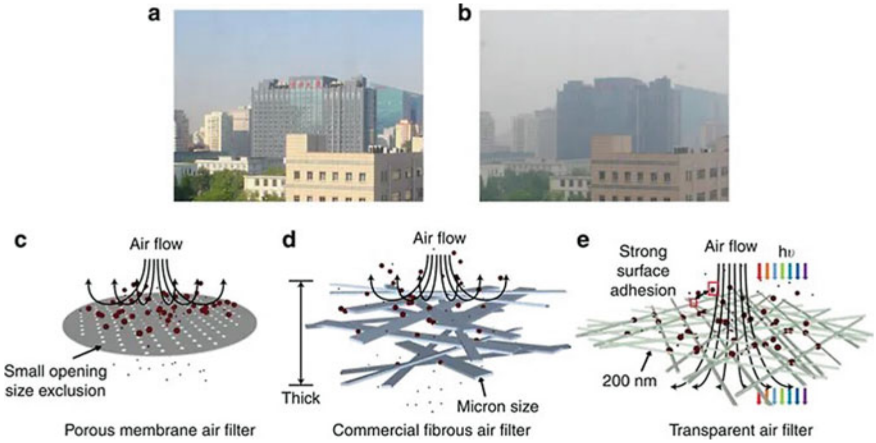

Fig. 13 **a**, **b** Photographs of a place in Beijing during sunny and hazy day with high PM2.5 level. **c**–**e** Schematics of different air filters that capture PM particles (Liu et al. 2015)

shown great potential to protect people outside/inside a room (Fig. 13, Liu et al. 2015).

3 Conclusion

In this chapter, information about electrospinning nanofibers is comprehensively introduced, including the materials for nanofiber fabrication, processing mechanism and parameters of electrospinning techniques, special electrospinning techniques, and potential applications of electrospun nanofibers.

The electrospinning technology can generate ultrathin fibers by using a wide variety of materials that contain the most commonly used polymers, metal oxides/ceramics, and composites. There are several necessary parts for a standard electrospinning setup, including a spinneret (usually a needle with a syringe), a pump that can maintain the feeding, a high-voltage power source (usually several tens of kilovolts), and a conductive collector to gather the resultant. During the electrospinning process, there are a number of factors that can determine the final morphology and property of the resultant fibers, including the polymer solution parameter such as surface tension and viscosity, processing conditions including the voltage and distance, and the ambient condition like humidity. Besides the conventional polymer fibers, nanofibers with special morphology and property can be customized with special electrospinning techniques such as wet- electrospinning, melt electrospinning, core–shell electrospinning, and electrospray technique. The resulted electrospun nanofibers can be applied in various situations like energy harvesting and storage, all kinds of sensing applications, biomedical applications, and environmental protection.

Electrospinning is an old technique that has existed for nearly one century, but it still has so many possibilities in potential innovation and can facilitate the large-scale fabrication of nanofibers. Electrospun nanofibers have attracted extensive interest as their diverse applications. And with the problems being continuously addressed and new modules being developed, this technique is expected to be applied on a broader platform and contributed to the improvement of daily life in the foreseeable future.

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