INTRODUCTION AND HISTORICAL OVERVIEW

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1.1 INTRODUCTION

1.1.1 NANOFABRICATION: THE ROAD TO EXCELLENCE

Nanofabrication, the technology of the future, is the most advanced manufacturing technology in today's world. Because this technology lets scientists reach nearly the theoretical limit of accuracy, i.e., the size of a molecule or atom, it is also believed to be the "extreme technology" (Mamalis et al., 2004). Indeed, it is basically the manipulation of matter at the nanoscale, which can develop a variety of materials and devices far superior, in terms of performance, efficiency, and durability, to those produced by conventional processes. This manipulation at the nanoscale alters the material characteristics without compromising the fundamental properties of the substrate and makes them intrinsically different and relatively much better compared with their bulk counterparts (Biswas et al., 2012). In addition, it also meets both of the major demands of the manufacturing industry, i.e., ultraprecision and miniaturization; thus this technology is a roadway to excellence in the field of manufacturing.

1.1.2 POTENTIAL APPLICATIONS OF ONE-DIMENSIONAL NANOMATERIALS

Nowadays, nanomaterials are at the center of attention of engineers and scientists because of their ability to alter the performance and capabilities of materials in a number of commercial sectors (Fang et al., 2008, 2011; Zhang and Fang, 2010; Xiao et al., 2011; Wang et al., 2013). Nanomaterials are believed to be at the forefront of the fundamental materials because they provide additional features and aptitudes while maintaining the basic characteristics of the materials. Among all nanomaterials, one-dimensional (1D) nanostructured materials have firmly gained tremendous attraction in recent decades owing to their fundamental features, unique shapes, and potential applications in various fields (Lu et al., 2011; Yuan et al., 2011; Xia et al., 2003). These materials have enough potential to be applied to a very wide range of applications (Fig. 1.1).

Their characteristic features, such as high volume-to-surface area, facilitate the production of lighter weight materials, which is one of the key demands of all manufacturing fields; their ability to be

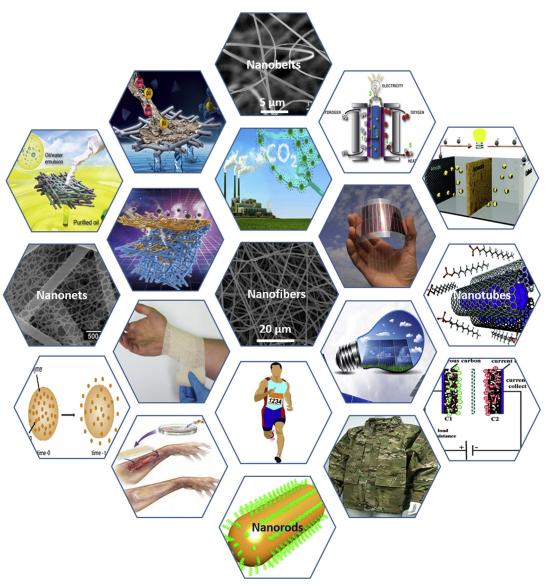


FIGURE 1.1

Application potential of 1D nanomaterials.

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highly hydrophobic and breathable is extremely desired for protective clothing; and their highly porous structure makes them ideal candidates for energy and environmental applications. Hollow fibers with multiple numbers of channels are a value addition in the field of biomedical and tissue engineering. The controlled structures of nanofibers developed from biodegradable and biocompatible sources such as polysaccharides and proteins are very useful in biomedical applications and regulated drug-delivery applications. Moreover, their individual fibers as well as resultant membrane structure can be custom-made to meet the needs of a number of applications. In addition, the growing interest of scientists in using nanofibers in various applications highlights the significance of their potential (Li and Yang, 2016; Kaur et al., 2014), which may also be credited to the easier fabrication with a variety of structural architectures and relatively reasonable production cost.

1.1.3 ONE-DIMENSIONAL NANOFABRICATION TECHNIQUES

The 1D nanoscale materials, such as wires, belts, rods, tubes, spirals, and fibers, owe the most vital importance due to their high length-to-width ratio and huge surface area, and can be produced with various commercial fabrication techniques such as template synthesis, drawing, phase separation, self-assembly, hand-spinning, and electrohydrodynamics (EHD) techniques (Lu et al., 2009; Lauhon et al., 2002; Zach et al., 2000; Hu et al., 1999, 2006; Huang et al., 2001; Barth et al., 2010; Xiao et al., 2010; Shojaee et al., 2010; Jiang et al., 2004; Taylor, 1966; Wang et al., 2006, 2008, 2011; Du and Hsieh, 2008; Dzenis, 2004; Sarkar et al., 2010; Kim et al., 2006).

The drawing technique of nanofabrication is similar in nature to the traditional dry-spinning technique and capable of producing very long single nanofibers. This technique involves three very simple steps, i.e., (1) a drop of polymer solution nearly 1 mL in volume is placed on the substrate, (2) a micropipette is touched to the edge of the drop, and (3) it is pulled back (Fig. 1.2); this backward motion of the micropipette draws the polymer solution enough to turn it into a nanofiber. The standard speed of the up—down moment of the micropipette is about 104 ms⁻¹, and the diameter of the drawn fiber may range from a few micrometers to several nanometers. Solvent evaporation, polymer nature, and drawing velocity are the parameters that determine the quality of the resultant fibers. The technique is easy to control, is relatively very economical, and also does not require any expert personnel supervision; however, its low production rate and unacceptability for all polymers are major restrictions to its commercial application. A variety of polymeric nanofibers, such as polyvinyl butyl,

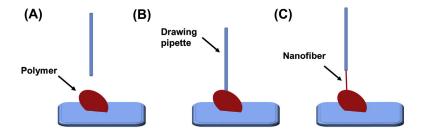


FIGURE 1.2

Schematic demonstration of 1D nanofiber fabrication via mechanical drawing. (A) A drop of polymer solution is placed on the substrate, (B) a micropipette is touched to the drop, and (C) the micropipette is pulled back.

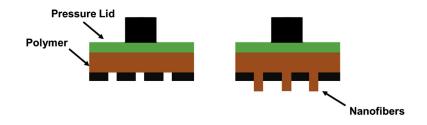


FIGURE 1.3

Schematic demonstration of 1D nanofiber production via template synthesis.

polymethylmethacrylate, polyvinyl alcohol, polycaprolactone, polyethylene oxide, and hyaluronic acid, have been developed via this technique. In addition, nanofibers from melt have also been reported.

The template synthesis technique involves nanosized pores and a variety of materials. The solution is forced through a fibril-shaped solid or hollow tubule and is immediately solidified by a solidification solution (Fig. 1.3). The concept of this technique may be credited to the traditional wet spinning technique in which the polymer solution drawn out through spinnerets is directly passed through a trough containing the fiber solidification solution. A variety of materials, including metal oxides (alumina), metals, semiconductors, or carbons, can be processed via this technique for synthesizing membranes for targeted applications, even without any expert supervision. High production times and inability to develop single nanofibers limit its application at the megascale.

The phase-separation technique of nanofiber fabrication consists of dissolution, gelation, and extraction using a suitable solvent, followed by freezing and drying techniques. A polymer solution in a Teflon trough is converted into a gel with the help of heat treatment and this resultant gel is dried via a freeze-drying process (Fig. 1.4). Polymer concentration and gelation temperature mostly affect the duration of gel. Low and high gelation temperatures lead to the formation of nanoscale fiber networks and platelet-like structures. Fabricated nanofibers are 50–500 nm in diameter and have a porous

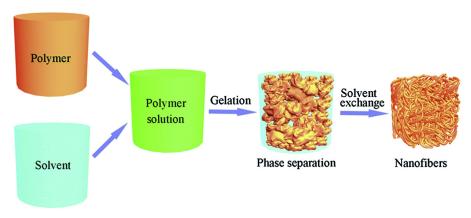


FIGURE 1.4

Schematic demonstration of 1D nanofiber development via the phase-separation technique.

Reprinted with permission from He, C., Nie, W., Feng, W., 2014. Engineering of biomimetic nanofibrous matrices for drug delivery and tissue engineering. Journal of Materials Chemistry B 2, 7828–7848. © 2014 Royal Society of Chemistry.

structure with a network of "endless" filaments. The type of polymer, type of solvent, gelation temperature, gelation duration, and thermal treatment also affect the nanofibers' morphology. This technique is simple, inexpensive, and widely used for the fabrication of nanofibers. It makes one by one continuous nanofibers, and mass production is also possible through this technique. However, it suffers some major limitations such as a time-consuming process, laboratory-scale production, lack of structural stability, and difficulty in maintaining porosity and is not applicable for all polymers (He et al., 2014).

1.2 ELECTROSPINNING

1.2.1 OVERVIEW

Electrospinning is simple, and is potentially the most effective and advanced EHD technique being used for the production of continuous fibers with diameters down to a few nanometers. It shares the characteristic features of two conventional processes, i.e., electrospraying and conventional dry or melt spinning. The process involves the use of high voltage for inducing the formation of a liquid jet, which is soon solidified either by evaporating the solvent or by freezing the melt to ensure nanofiber fabrication (Fig. 1.5). This versatile process can be applied to natural as well as synthetic polymers, polymer alloys, metals, and ceramics (Greiner and Wendorff, 2007). A variety of fibrous architectures, such as porous fibers, core—shell fibers, hollow fibers, and helical fibers, etc. can be produced by the

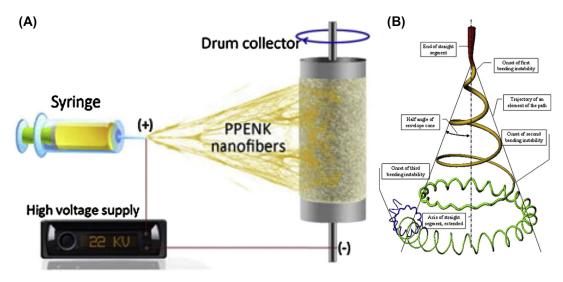


FIGURE 1.5

(A) Schematic illustration of the basic electrospinning setup. (B) Schematic drawing of the looping part of the jet showing a sequence of bending instabilities. *PPENK*, poly(phthalazinone ether nitrile ketone).

(A) Reprinted with permission from Wang, G., Zhang, H., Qian, B., Wang, J., Jian, X., Qiu, J., 2015. Preparation and characterization of electrospun poly(phthalazinone ether nitrile ketone) membrane with novel thermally stable properties. Applied Surface Science 351, 169–174. © 2015 Elsevier. (B) Reprinted with permission from Reneker, D.H., Yarin, A.L., 2008. Electrospinning jets and polymer nanofibers. Polymer, 49, 2387–2425. © 2008 Elsevier.

electrospinning technique using certain special tools. Moreover, the process is capable of producing a diverse range of single-fiber structures as ordered arrangements of fibers. Depending on the physical, biological, or chemical attributes, fibers produced using electrospinning are of great interest for a range of applications, including filtration, biomedicine, sensors, protective clothing, and so on. Since the late 1990s, the electrospinning process has not only been intensively reexamined by laboratories to ensure its acceptability at the megascale, but has also been extensively applied in industry (Thavasi et al., 2008; Dong et al., 2011; Bhardwaj and Kundu, 2010).

1.2.2 HISTORY OF ELECTROSPINNING

Electrospinning, also known as electrostatic spinning, is not a very new but yet is a very powerful nanofiber fabrication technique. It is versatile enough to produce fibers on micro- and nanoscales and is believed to be a variant of the electrospray process. The first record claiming the electrostatic attraction of liquids is traced back to the 16th century, reported by Gilbert, the president of the Royal College of Physicians (Wendorff et al., 2012; Tucker et al., 2012). He claimed that if a properly charged piece of amber and a water droplet are brought close enough to each other, the latter would form a cone shape, and small droplets would be ejected from the tip of the cone. About 270 years later, Bose synthesized aerosols using high electric potentials in 1745 (Lin et al., 2012; Greiner and Wendorff, 2007). Later on, in 1882, Rayleigh calculated the maximum amount of charge that causes a liquid drop of definite size to burst by overcoming the surface tension of the droplet. He also explained that the stability of an ascending liquid jet would first increase with increasing electric charge; however, when the electric charge exceeds a certain limit, then it will destabilize the liquid jet (Wang, 2008; De Vrieze and De Clerck, 2009).

In the early 20th century, Morton and Cooley demonstrated the phenomenon of the electrospinning process and discovered the possibility of fabricating tiny fibers via electrospinning, and in addition, they first patented the devices using electric charge to spray liquids: four types of indirectly charged spinning heads, a conventional head, a coaxial head, an air-assisted model, and a spinneret featuring a rotating distributor, were proposed (Ding and Yu, 2014; Morton, 1902; Cooley, 1902, 1903). W.B. Wiegand and E.F. Burton further described the relationship between charge and surface tension to examine electrical effects on water streams (Burton and Wiegand, 1912; Wang et al., 2006). John Zeleny, a physicist working at the University of Minnesota, published a series of papers between 1907 and 1920 describing electrical discharge from liquid as well as solid surfaces. He determined that the diameter of the electrodes was the primary factor, rather than the shape of the electrodes, that influenced the discharge current. He also analyzed the effect of humidity and concluded that an increase in humidity required more potential to maintain the predefined current flow. Later on, he examined fluid droplet behavior at the end of metal capillaries and determined the distortion tendency of a hemispherical liquid droplet under high voltage, which helped in developing the mathematical model for determining fluid behavior under electrostatic forces. This is also believed to be the initiation of modern needle electrospinning (Lin et al., 2012; Zeleny, 1914, 1917).

K. Hagiwara, Professor at Imperial University Kyoto, reported on the use of electricity for regulating the molecular structure of a colloidal liquid viscose precursor that could align colloidal components leading to highly lustrous fibers, i.e., free of irregular aggregation of the particles. In addition to viscose, other substrates, such cellulose acetate and nitrocellulose, gelatin, albumen, and natural silk solutions, were also run through Professor Hagiwara's equipment (Kiyohiko, 1929). W. A. Macky from

New Zealand explained that it is the ionized gas or vapor particles that make a flow of current that breaks the liquid drop during flight, rather than the flight of the charged liquid drop (Macky, 1931, 1937).

Further progress toward commercialization was made by A. Formhals (United States), who published a series of 22 patents from 1931 to 1944, which are believed to be a key contribution to the development of electrospinning (Anton, 1934). Anton explained the physical setup for producing polymer filaments using electrostatic force. He intended to develop yarns by gathering up the fibers for further processing, which was a very critical job. Initially, Anton designed a machine having a sawtoothed rotating fiber emitter dipped in a polymer solution trough (Formhals, 1934). Fibers were emitted from the wetted tips with the help of an electric charge toward the rotating collector. Later on, Anton planned tapered nozzle—shaped fiber emitters and aimed to collect short staple fibers; staple fibers with controlled length were produced by disrupting the current flow to the spinning heads of the machine (Formhals, 1937; Anton, 1938). In addition, Anton also proposed cospinning of fibers with opposite charge to produce a product with no net charge, and made serious efforts to devise winding devices to gather up the fiber in a usable form (Anton, 1939, 1940, 1943).

Charles Ladd Norton, an American physicist, who had experience of powering Crookes tubes with high voltage, was the first to introduce melt spinning using a combined electrostatic and air-jet assist method, and also made efforts to prepare lofted fibers for insulation or packaging applications (Williams, 1940). Following this, Games Slayter produced glass wool fiber using melt spinning, which was later commercialized by the Owens Corning fiberglass company and was used by naval ships for fire protection (Slayter, 1938).

In the 1930s, N.A. Fuchs (USSR) and his coworkers introduced the theory of ultrafine fibrous materials and developed electrospun fibers for filter materials. For this contribution they were awarded the Stalin Prize. Based on their work, a factory was installed to fabricate electrospun fibers for gas masks using cellulose acetate and a solvent mixture of ethanol and dichloromethane. In the 1950s, using the Petryanov filter, a particulate filter mask, the "Lepestok," was developed for the nuclear industry. B. Vonnegut (Vonnegut and Neubauer, 1952) and V. Drozin (Drozin, 1955; Vonnegut and Neubauer, 1952) investigated liquid jet production under electrostatic force and observed that uniform-sized droplets of about 1 µm were formed during the process, which repelled one another in the case of having like charges. The generation of these droplets was attributed to the dielectric constant of fluid droplets; moreover, dipole moment, conductivity, and refractive index were observed as process-limiting factors.

The output of spun filtration materials had reached as much as 20 million m² per annum by the 1960s. Polymer substrate was pushed through spinnerets under the exceptionally high voltage of 100 kV, and the resulting liquid stream was bifurcated, leading to high volume throughput. It was then Sir Geoffrey Ingram Taylor who made a significant advancement in the theoretical underpinning of the electrospinning process during 1964–65. Taylor designed a mathematical model of the conical shape of the fluid droplet in an electric field. This characteristic droplet shape is now known as the Taylor cone. In 1971 Baumgarten found that fiber diameter depends on process and substrate parameters such as solution viscosity, jet radius and length, and applied voltage. Taylor also reported, with the help of his devised method for photographing electrospun fibers during flight, that only a single fiber is spun at a time and that the filament forms many loops, which fall to the electrical ground. In addition, he described the electrospinning of acrylic, whereas Larrondo and S.J. Manley published a series of articles on the subject of electrospinning of polymer melts. They also launched a melt electrospinner, in which a dead weight was used to push the polymer through a barrel to the spinning tip, which was

then drawn rapidly using electrostatic force. In the meantime, certain efforts in the commercialization of the electrospinning process were also undertaken in the 1970s. A series of patents was submitted by Simm, from the Bayer Company, on the electrospinning of plastics, and the first practical application advised for electrospinning was for the nonwoven industry.

The electrospinning process became popular only after the 1990s, when numerous research groups, especially those of Reneker (University of Akron) and Wendorff, picked up the process. It was then established that several organic polymers could be electrospun into nanofibers. Since then, a number of researchers have entered this field and the quantity as well as quality of research papers has exponentially increased, from just a few papers per annum to over 4000 in 2017 (Fig. 1.6). Increasing numbers of patents, books, and review papers about electrospinning applications have been reported in recent years, and over 500 research institutes and universities around the globe working in the field of electrospinning signify its popularity and provide insight into the most prominent aspects of the process. Increasing interest and active involvement of certain commercial companies, such as Nano Technics, eSpin Technologies, Elmarco Ltd., and Kato Tech, witness the huge impact and significance of electrospinning in the field of materials science. Some companies such as Freudenberg and Donaldson Company have been earning significant capital by reaping the benefits of electrospun nanofibers since the late 1990s or even earlier.

In short, this rapid and intensive research carried out since the beginning of the 21st century in the field of electrospinning can be summarized as follows: (1) an extensively enhanced number of polymers and composites are being electrospun; (2) the comprehensive in-depth comprehension of nanofiber fabrication has increased; (3) a very broad range of fiber and membrane structures, including

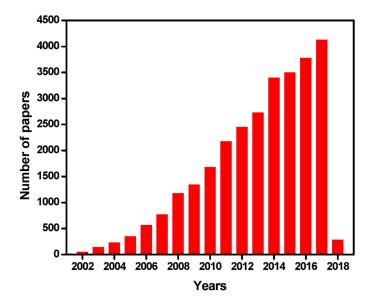


FIGURE 1.6

Number of publications from 2001 to January 24, 2018, with the keyword "electrospinning."

From ISI Web of Science.

those inspired from nature, have been made possible; (4) it is possible to develop multicomponent, composite, and inorganic fibers; and (5) the focus of research has been transformed from fabrication to application, and now it is being centered on the industrialization of this process.

1.2.3 MODERN ELECTROSPINNING TECHNOLOGY

The versatile maneuverability of electrospinning to produce nanofibers with regulated individual fibers as well as resultant membrane structures, the controlled inter- and intrafiber porosity, and the ability to produce meticulous fiber orientations and dimensions make it a simple but powerful fiber manufacturing technique. In addition, easier process control and lower production costs are potential reasons for its global attention. Randomly oriented structures of fibers obtained from electrospinning are being utilized in numerous fields. However, this random orientation of electrospun nanofibers limits their broader acceptability in the fields of biomedical and electronic devices (Supaphol et al., 2011). Therefore, it is extremely necessary to fabricate nanofibers with controlled fiber structure and ordered fiber orientation via electrospinning to make full use of their potential and enhance their acceptability in electronic devices and biomedical applications, which require well-arranged fiber alignment and special fiber structures (Greiner and Wendorff, 2007).

Many groups are engaged in developing aligned fiber arrays produced via electrospinning with the help of custom-made collectors. As a result, various patterned fiber architectures (Fig. 1.7) have been successfully synthesized by various groups with certain process modifications, such as insulation gaps introduced between conducting collectors demonstrated in uniaxially aligned fiber mats (Rasel, 2015). It is also reported that high-speed rotating rollers can also produce aligned fibers; however, the collector rotation speed and fiber orientation strongly influence the resultant nanofiber properties.

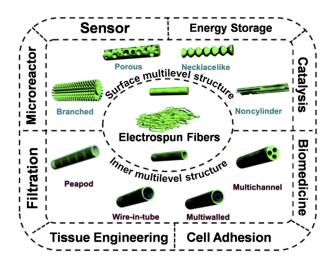


FIGURE 1.7

Schematic demonstration of some electrospun nanofiber architectures and their corresponding applications.

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In addition, this approach facilitates the direct integration of tailorable configured nanofibers, which may be a key support for manufacturing nanofiber-based devices (Wang et al., 2013; Woodruff and Hutmacher, 2010; Pan et al., 2008).

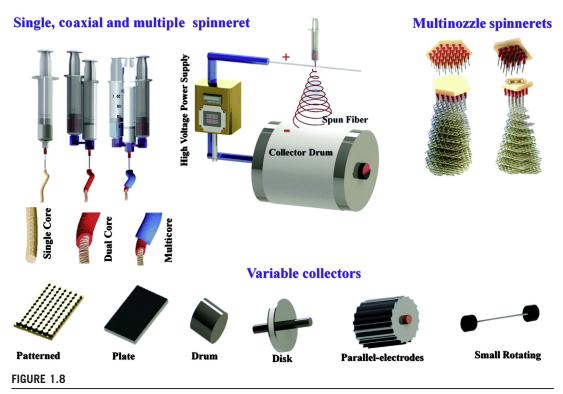
In addition to aligned or patterned nanofibers, the process is also capable of producing a very wide range of fibrous structures, including core—shell (Sun et al., 2003; Zhang et al., 2009), tube-in-tube (Mou et al., 2010), multicore cablelike (Hiroshi et al., 2007), rice grain shape (Shengyuan et al., 2011), helical (Kessick and Tepper, 2004; Shin et al., 2006), ribbon-like (Koombhongse et al., 2001), necklace-like (Jin et al., 2010; Lu et al., 2006), multichannel tubular (Zhao et al., 2007), nanowire-in-microtube (Chen et al., 2010), firecracker shape (Chang, 2011), and hollow (Li and Xia, 2004) fiber structures (Wu et al., 2013). Moreover, the provision of high specific surface area and feasibility to control pore size along with certain chemical, physical, thermal, and mechanical characteristics of fabricated nanofibers indicate the significance of the process (Huang et al., 2003; Zhu et al., 2008).

The versatile nature of the electrospinning process and its ability to synthesize numerous fiber structures from all kinds of materials (i.e., organic as well as inorganic polymers or the combination both) and various input forms, including melts, solutions, emulsions, and mixtures, have recommended it for use in different fields ranging from the hottest fields of energy generation, defense, and security to complicated fields like health care, biomedicine, biotechnology, and environmental engineering (Tran et al., 2011). Several modifications in the basic electrospinning process have been made to meet the desired needs of these applications (Fig. 1.8). These modified electrospinning techniques include tipless electrospinning, edge electrospinning, multijet electrospinning, and electroblowing to enhance the throughput rate of the process to render the electrospun nanofibers acceptable on a larger scale. In addition, the enormous amount of research since 2008 has concluded that nanofibers offer huge potential for various fields; however, fiber diameters yet need to be reduced to tens of nanometers (<50 nm), which is very critical and challenging task, to achieve ultrasensitive sensors, ultrafiltration, catalysis, etc. Therefore, as of this writing, researchers are focused on developing such a process that offers not only high throughput, but also fibers with extremely small diameter along with controlled fiber morphology.

1.3 NANOFIBERS: SOLVING GLOBAL ISSUES

As discussed earlier, intensive research is being carried out on electrospun nanofibers to comprehend the theoretical and practical aspects of their fabrication process and the characteristics of the resultant nanofibers. Thus, after long and untiring efforts, scientists are successfully able to tailor the fiber morphology and aggregate structures, which has resulted in numerous applications for electrospun nanofibers reported by various research institutes via scientific publications. Still, intensive research is being carried out to learn more and more about nanofibers and their corresponding possible applications for solving various issues around the globe (Mongwaketsi, 2014).

Electrospun nanofibers, when applied in the fields of energy and environmental engineering, play a vital role in solving the current energy and environmental issues that are alarming threats to the world today. Owing to their delicate fabrication, specially designed functional electrospun nanofibers have been employed in the energy sector, including in fuel cells (Chevalier et al., 2017), organic and hybrid solar cells (Mohamed et al., 2017), lithium ion batteries (Aravindan et al., 2015), dye-sensitized solar cells (Singh et al., 2017), hydrogen storage (Kharel et al., 2017), carbon dioxide capture (Iqbal et al., 2017), and supercapacitors (Iqbal et al., 2016, 2017a,b). In addition to these



Various needle-based spinneret designs and collector shapes for synthesizing typical fiber structures.

Reprinted with permission from Aravindan, V., Sundaramurthy, J., Suresh Kumar, P., Lee, Y.-S., Ramakrishna, S., Madhavi, S., 2015. Electrospun nanofibers: a prospective electro-active material for constructing high performance Li-ion batteries. Chemical

Communications 51, 2225–2234. © 2015 Royal Society of Chemistry.

energy-related applications, nanofibers have been widely utilized in the field of environmental engineering to fulfill the need for clean water and air, the biggest threat to human health around the globe (Vaseashta et al., 2008). Thus, functional nanofiber use has been reported for air filtration, liquid filtration, sensors, oil spill cleanup, photocatalysis, electromagnetic shielding, adsorbents, self-cleaning products, etc.

Moreover, the application range of nanofibers is not limited to the energy and environmental engineering fields; they also provide value additions in the most critical fields of defense, security, and health care. Since security, firefighter, and medical personnel, among others, are always exposed to known and unknown hazardous attacks, they require an extreme level of protection from both hazardous chemicals and microorganisms (Ratner and Ratner, 2004). Nanostructures have enabled the design of lighter and more effective protective suits by virtue of their light weight, high surface area, and breathable porous nature (Sheng et al., 2016, 2017; Li et al., 2015, 2016; Yang et al., 2016). Nanofiber-enabled protective structures have taken personnel protection to the next level because of their ability to filter and destructively decompose harmful toxins without compromising the comfort of the protective garment (Turaga et al., 2012; Babar et al., 2017, 2018). Similarly, nanofiber employment

has been reported to be very efficient and economical in a very wide range of applications in field of health care, which include medical implants, controlled drug delivery, tissue engineering, wound dressings, and medical textiles (Song et al., 2017; Ceylan et al., 2017; Irani et al., 2017; Laha et al., 2017; Zilberman and Elsner, 2008; Dash et al., 2011; Tansaz et al., 2017; Grande et al., 2017; Aragon et al., 2017; Zhou et al., 2017; Perumal et al., 2017).

1.4 **OUTLOOK**

This chapter summarized the electrospinning process and the history of its development, with a brief discussion about the potential applications of electrospun nanofibers. Recent progress in electrospinning technology provides significant evidence for the potential role of electrospun nanofibers in defense and security, biomedicine, environmental protection, energy conversion, and storage applications (Fig. 1.9). Electrospun fibrous mats used as protective clothing would not only provide excellent protection from both chemical and biological attacks but also maintain the comfort of the garment, which plays a very critical role in the performance of the wearer. The use of functional nanofibers in electronic devices would enhance the performance, efficiency and cycle life of the fabricated devices. Moreover, nanofiber based filters for fluid filtration have given excellent protection to the environment and public health, which was never possible with conventional filtration materials.

Furthermore, the large-scale production of nanofibers has become possible to some extent; however, it is yet a very challenging job to fabricate bead-free fibers with diameters less than 50 nm.

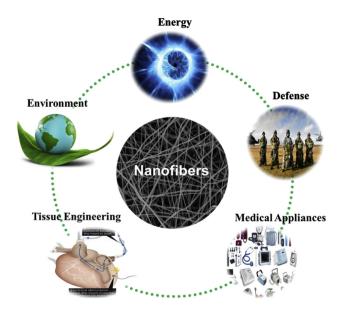


FIGURE 1.9

Some of the major potential application categories of nanofibers.

Therefore, extensive research is being carried out on developing nanofibers with <50-nm diameters. Their successful fabrication on a large scale would open new doors to achieving extraordinary performance in numerous applications such as ultrasensitive sensors, ultrafiltration, catalysis, etc.

ACKNOWLEDGMENTS

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REFERENCES

- Anton, F., 1934. Process and Apparatus for Preparing Artificial Threads. Google Patents.
- Anton, F., 1938. Artificial Fiber Construction. Google Patents.
- Anton, F., 1939. Method and Apparatus for the Production of Artificial Fibers. Google Patents.
- Anton, F., 1940. Artificial Thread and Method of Producing Same. Google Patents.
- Anton, F., 1943. Production of Artificial Fibers from Fiber Forming Liquids. Google Patents.
- Aragon, J., Navascues, N., Mendoza, G., Irusta, S., 2017. Laser-treated electrospun fibers loaded with nano-hydroxyapatite for bone tissue engineering. International Journal of Pharmaceutics 525, 112–122.
- Aravindan, V., Sundaramurthy, J., Suresh Kumar, P., Lee, Y.-S., Ramakrishna, S., Madhavi, S., 2015. Electrospun nanofibers: a prospective electro-active material for constructing high performance Li-ion batteries. Chemical Communications 51, 2225–2234.
- Babar, A.A., Wang, X., Iqbal, N., Yu, J., Ding, B., 2017. Adv. Mater. Interfaces 4, 1700062. https://doi.org/10.1002/admi.201700062.
- Babar, A.A., Miao, D., Ali, N., Zhao, J., Wang, X., Yu, J., Ding, B., 2018. ACS Appl. Mater. Interfaces 10, 22866—22875. https://doi.org/10.1021/acsami.8b07393.
- Barth, S., Hernandez-Ramirez, F., Holmes, J.D., Romano-Rodriguez, A., 2010. Synthesis and applications of one-dimensional semiconductors. Progress in Materials Science 55, 563–627.
- Bhardwaj, N., Kundu, S.C., 2010. Electrospinning: a fascinating fiber fabrication technique. Biotechnology Advances 28, 325–347.
- Biswas, A., Bayer, I.S., Biris, A.S., Wang, T., Dervishi, E., Faupel, F., 2012. Advances in top—down and bottom—up surface nanofabrication: techniques, applications & future prospects. Advances in Colloid and Interface Science 170, 2—27.
- Burton, E., Wiegand, W., 1912. Effect of Electricity on Streams of Water Drops. University Library.
- Ceylan, Z., Unal Sengor, G.F., Sağdiç, O., Yilmaz, M.T., 2017. A novel approach to extend microbiological stability of sea bass (*Dicentrarchus labrax*) fillets coated with electrospun chitosan nanofibers. Lebensmittel-Wissenschaft und -Technologie- Food Science and Technology 79, 367–375.
- Chang, Z., 2011. "Firecracker-shaped" ZnO/polyimide hybrid nanofibers via electrospinning and hydrothermal process. Chemical Communications 47, 4427—4429.
- Chen, H., Wang, N., Di, J., Zhao, Y., Song, Y., Jiang, L., 2010. Nanowire-in-microtube structured core/shell fibers via multifluidic coaxial electrospinning. Langmuir 26, 11291–11296.
- Chevalier, S., Lavielle, N., Hatton, B.D., Bazylak, A., 2017. Novel electrospun gas diffusion layers for polymer electrolyte membrane fuel cells: Part I. Fabrication, morphological characterization, and in situ performance. Journal of Power Sources 352, 272–280.
- Cooley, J.F., 1902. Apparatus for Electrically Dispersing Fluids. Google Patents.

- Cooley, J.F., 1903. Electrical Method of Dispersing Fluids. Google Patents.
- Dash, M., Chiellini, F., Ottenbrite, R., Chiellini, E., 2011. Chitosan—a versatile semi-synthetic polymer in biomedical applications. Progress in Polymer Science 36, 981–1014.
- De Vrieze, S., De Clerck, K., 2009. 80 years of Electrospinning. International Conference on Latest Advances in High-tech Textiles and Textile-based Materials. Ghent University, Department of Textiles, pp. 60–63.
- Ding, B., Yu, J., 2014. Electrospun Nanofibers for Energy and Environmental Applications. Springer.
- Dong, Z., Kennedy, S.J., Wu, Y., 2011. Electrospinning materials for energy-related applications and devices. Journal of Power Sources 196, 4886–4904.
- Drozin, V.G., 1955. The electrical dispersion of liquids as aerosols. Journal of Colloid Science 10, 158-164.
- Du, J., Hsieh, Y.-L., 2008. Nanofibrous membranes from aqueous electrospinning of carboxymethyl chitosan. Nanotechnology 19, 125707.
- Dzenis, Y., 2004. Spinning continuous fibers for nanotechnology. Science 304, 1917–1919.
- Fang, X., Bando, Y., Gautam, U.K., Ye, C., Golberg, D., 2008. Inorganic semiconductor nanostructures and their field-emission applications. Journal of Materials Chemistry 18, 509–522.
- Fang, X., Zhai, T., Gautam, U.K., Li, L., Wu, L., Bando, Y., Golberg, D., 2011. ZnS nanostructures: from synthesis to applications. Progress in Materials Science 56, 175–287.
- Formhals, A., 1934. Process and Apparatus for Preparing Artificial Threads. US Patent, 1975504.
- Formhals, A., 1937. Production of Artificial Fibers. Google Patents.
- Grande, D., Ramier, J., Versace, D.L., Renard, E., Langlois, V., 2017. Design of functionalized biodegradable PHA-based electrospun scaffolds meant for tissue engineering applications. New Biotechnology 37 (Part A), 129–137.
- Greiner, A., Wendorff, J.H., 2007. Electrospinning: a fascinating method for the preparation of ultrathin fibers. Angewandte Chemie International Edition 46, 5670–5703.
- He, C., Nie, W., Feng, W., 2014. Engineering of biomimetic nanofibrous matrices for drug delivery and tissue engineering. Journal of Materials Chemistry B 2, 7828–7848.
- Hiroshi, K., Bin, D., Takayuki, N., Hiroki, T., Seimei, S., 2007. Multi-core cable-like TiO 2 nanofibrous membranes for dye-sensitized solar cells. Nanotechnology 18, 165604.
- Hu, J., Odom, T.W., Lieber, C.M., 1999. Chemistry and physics in one dimension: synthesis and properties of nanowires and nanotubes. Accounts of Chemical Research 32, 435–445.
- Hu, M.-S., Chen, H.-L., Shen, C.-H., Hong, L.-S., Huang, B.-R., Chen, K.-H., Chen, L.-C., 2006. Photosensitive gold-nanoparticle-embedded dielectric nanowires. Nature Materials 5, 102–106.
- Huang, Y., Duan, X., Wei, Q., Lieber, C.M., 2001. Directed assembly of one-dimensional nanostructures into functional networks. Science 291, 630–633.
- Huang, Z.-M., Zhang, Y.-Z., Kotaki, M., Ramakrishna, S., 2003. A review on polymer nanofibers by electrospinning and their applications in nanocomposites. Composites Science and Technology 63, 2223–2253.
- Iqbal, N., Wang, X., Babar, A.A., Yu, J., Ding, B., 2016. Highly flexible NiCo₂O4/CNTs doped carbon nanofibers for CO₂ adsorption and supercapacitor electrodes. Journal of Colloid and Interface Science 476, 87–93.
- Iqbal, N., Wang, X., Yu, J., Ding, B., 2017. Robust and flexible carbon nanofibers doped with amine functionalized carbon nanotubes for efficient CO₂ capture. Advanced Sustainable Systems 1, 1600028.
- Iqbal, N., Wang, X., Babar, A.A., Zainab, G., Yu, J., Ding, B., 2017a. Scientific Reports 7, 15153. https://doi.org/ 10.1038/s41598-017-15535-x.
- Iqbal, N., Wang, X., Babar, A.A., Yan, J., Yu, J., Park, S.-J., Ding, B., 2017b. Adv. Mater. Interfaces 4, 1700855. https://doi.org/10.1002/admi.201700855.
- Irani, M., Sadeghi, G.M.M., Haririan, I., 2017. The sustained delivery of temozolomide from electrospun PCL-Diol-b-PU/gold nanocomposite nanofibers to treat glioblastoma tumors. Materials Science and Engineering: C 75, 165–174.
- Jiang, L., Zhao, Y., Zhai, J., 2004. A lotus-leaf-like superhydrophobic surface: a porous microsphere/nanofiber composite film prepared by electrohydrodynamics. Angewandte Chemie 116, 4438–4441.
- Jin, Y., Yang, D., Kang, D., Jiang, X., 2010. Fabrication of necklace-like structures via electrospinning. Langmuir 26, 1186-1190.

- Kaur, S., Sundarrajan, S., Rana, D., Sridhar, R., Gopal, R., Matsuura, T., Ramakrishna, S., 2014. Review: the characterization of electrospun nanofibrous liquid filtration membranes. Journal of Materials Science 49, 6143–6159.
- Kessick, R., Tepper, G., 2004. Microscale polymeric helical structures produced by electrospinning. Applied Physics Letters 84, 4807–4809.
- Kharel, K., Gangineni, R., Ware, L., Lu, Y., Wujcik, E.K., Wei, S., Günaydın-Şen, Ö., 2017. Dehydrogenation properties of ammonia borane—polyacrylamide nanofiber hydrogen storage composites. Journal of Materials Science 52, 4894—4902.
- Kim, I.-D., Rothschild, A., Lee, B.H., Kim, D.Y., Jo, S.M., Tuller, H.L., 2006. Ultrasensitive chemiresistors based on electrospun TiO₂ nanofibers. Nano Letters 6, 2009–2013.
- Kiyohiko, H., 1929. Process for Manufacturing Artificial Silk and Other Filaments by Applying Electric Current. Google Patents.
- Koombhongse, S., Liu, W., Reneker, D.H., 2001. Flat polymer ribbons and other shapes by electrospinning. Journal of Polymer Science Part B: Polymer Physics 39, 2598—2606.
- Laha, A., Sharma, C.S., Majumdar, S., 2017. Sustained drug release from multi-layered sequentially crosslinked electrospun gelatin nanofiber mesh. Materials Science and Engineering: C 76, 782–786.
- Lauhon, L.J., Gudiksen, M.S., Wang, D., Lieber, C.M., 2002. Epitaxial core—shell and core—multishell nanowire heterostructures. Nature 420, 57—61.
- Li, D., Xia, Y., 2004. Direct fabrication of composite and ceramic hollow nanofibers by electrospinning. Nano Letters 4, 933–938.
- Li, H., Yang, W., 2016. Electrospinning technology in non-woven fabric manufacturing. In: Jeon, H.-Y. (Ed.), Non-woven Fabrics. InTech, Rijeka.
- Li, Y., Yang, F., Yu, J., Ding, B., 2016. Hydrophobic fibrous membranes with tunable porous structure for equilibrium of breathable and waterproof performance. Advanced Materials Interfaces 3, 1600516.
- Li, Y., Zhu, Z., Yu, J., Ding, B., 2015. Carbon nanotubes enhanced fluorinated polyurethane macroporous membranes for waterproof and breathable application. ACS Applied Materials & Interfaces 7, 13538–13546.
- Lin, J., Wang, X., Ding, B., Yu, J., Sun, G., Wang, M., 2012. Biomimicry via electrospinning. Critical Reviews in Solid State and Materials Sciences 37, 94–114.
- Lu, X., Wang, C., Wei, Y., 2009. One-dimensional composite nanomaterials: synthesis by electrospinning and their applications. Small 5, 2349–2370.
- Lu, X., Zhang, D., Zhao, Q., Wang, C., Zhang, W., Wei, Y., 2006. Large-scale synthesis of necklace-like single-crystalline PbTiO₃ nanowires. Macromolecular Rapid Communications 27, 76–80.
- Lu, X., Zhang, W., Wang, C., Wen, T.-C., Wei, Y., 2011. One-dimensional conducting polymer nanocomposites: synthesis, properties and applications. Progress in Polymer Science 36, 671–712.
- Macky, W., 1931. Some investigations on the deformation and breaking of water drops in strong electric fields. Proceedings of the Royal Society of London Series A: Containing Papers of a Mathematical and Physical Character 133, 565–587.
- Macky, W., 1937. Some Comparisons of the Invigorating Effect of the Climate in Different Parts of New Zealand, NZMS.
- Mamalis, A.G., Vogtländer, L.O.G., Markopoulos, A., 2004. Nanotechnology and nanostructured materials: trends in carbon nanotubes. Precision Engineering 28, 16–30.
- Mohamed, I.M.A., Dao, V.-D., Yasin, A.S., Barakat, N.A.M., Choi, H.-S., 2017. Design of an efficient photoanode for dye-sensitized solar cells using electrospun one-dimensional GO/N-doped nanocomposite SnO₂/TiO₂. Applied Surface Science 400, 355–364.
- Mongwaketsi, N.P., 2014. Studies on Porphyrin-based Nanorods for Artificial Light Harvesting Applications. Stellenbosch University, Stellenbosch.
- Morton, W.J., 1902. Method of Dispersing Fluids. Google Patents.
- Mou, F., Guan, J.-G., Shi, W., Sun, Z., Wang, S., 2010. Oriented contraction: a facile nonequilibrium heat-treatment approach for fabrication of maghemite fiber-in-tube and tube-in-tube nanostructures. Langmuir 26, 15580—15585.

- Pan, Z.-J., Liu, H.-B., Wan, Q.-H., 2008. Morphology and mechanical property of electrospun PA 6/66 copolymer filament constructed of nanofibers. Journal of Fiber Bioengineering and Informatics 1, 47–54.
- Perumal, G., Pappuru, S., Chakraborty, D., Maya Nandkumar, A., Chand, D.K., Doble, M., 2017. Synthesis and characterization of curcumin loaded PLA—hyperbranched polyglycerol electrospun blend for wound dressing applications. Materials Science and Engineering: C 76, 1196—1204.
- Rasel, S.M., 2015. An Advanced Electrospinning Method of Fabricating Nanofibrous Patterned Architectures with Controlled Deposition and Desired Alignment.
- Ratner, D., Ratner, M.A., 2004. Nanotechnology and Homeland Security: New Weapons for New Wars. Prentice Hall Professional.
- Reneker, D.H., Yarin, A.L., 2008. Electrospinning jets and polymer nanofibers. Polymer 49, 2387–2425.
- Sarkar, K., Gomez, C., Zambrano, S., Ramirez, M., De Hoyos, E., Vasquez, H., Lozano, K., 2010. Electrospinning to Forcespinning [™]. Materials Today 13, 12–14.
- Sheng, J., Xu, Y., Yu, J., Ding, B., 2017. Robust fluorine-free superhydrophobic amino-silicone oil/SiO₂ modification of electrospun polyacrylonitrile membranes for waterproof-breathable application. ACS Applied Materials & Interfaces 9, 15139–15147.
- Sheng, J., Zhang, M., Xu, Y., Yu, J., Ding, B., 2016. Tailoring water-resistant and breathable performance of polyacrylonitrile nanofibrous membranes modified by polydimethylsiloxane. ACS Applied Materials & Interfaces 8, 27218–27226.
- Shengyuan, Y., Peining, Z., Nair, A.S., Ramakrishna, S., 2011. Rice grain-shaped TiO₂ mesostructures-synthesis, characterization and applications in dye-sensitized solar cells and photocatalysis. Journal of Materials Chemistry 21, 6541–6548.
- Shin, M.K., Kim, S.I., Kim, S.J., 2006. Controlled assembly of polymer nanofibers: from helical springs to fully extended. Applied Physics Letters 88, 223109.
- Shojaee, N., Ebadzadeh, T., Aghaei, A., 2010. Effect of concentration and heating conditions on microwave-assisted hydrothermal synthesis of ZnO nanorods. Materials Characterization 61, 1418–1423.
- Singh, N., Salam, Z., Sivasankar, N., Subramania, A., 2017. ZnSe quantum dots sensitized electrospun ZnO nanofibers as an efficient photoanode for improved performance of QDSSC. Materials Science in Semi-conductor Processing 64, 16–23.
- Slayter, G., 1938. Method and Apparatus for Making Glass Wool. Google Patents.
- Song, J., Klymov, A., Shao, J., Zhang, Y., Ji, W., Kolwijck, E., Jansen, J.A., Leeuwenburgh, S.C.G., Yang, F., 2017. Electrospun nanofibrous silk fibroin membranes containing gelatin nanospheres for controlled delivery of biomolecules. Advanced Healthcare Materials 1700014.
- Sun, Z., Zussman, E., Yarin, A.L., Wendorff, J.H., Greiner, A., 2003. Compound core—shell polymer nanofibers by co-electrospinning. Advanced Materials 15, 1929—1932.
- Supaphol, P., Suwantong, O., Sangsanoh, P., Srinivasan, S., Jayakumar, R., Nair, S.V., 2011. Electrospinning of biocompatible polymers and their potentials in biomedical applications. Biomedical Applications of Polymeric Nanofibers 213–239. Springer.
- Tansaz, S., Liverani, L., Vester, L., Boccaccini, A.R., 2017. Soy protein meets bioactive glass: electrospun composite fibers for tissue engineering applications. Materials Letters 199, 143—146.
- Taylor, G., 1966. Studies in electrohydrodynamics. I. The circulation produced in a drop by electrical field. Proceedings of the Royal Society of London: Mathematical, Physical and Engineering Sciences 159–166. The Royal Society.
- Thavasi, V., Singh, G., Ramakrishna, S., 2008. Electrospun nanofibers in energy and environmental applications. Energy & Environmental Science 1, 205–221.
- Tran, H.D., D'arcy, J.M., Wang, Y., Beltramo, P.J., Strong, V.A., Kaner, R.B., 2011. The oxidation of aniline to produce "polyaniline": a process yielding many different nanoscale structures. Journal of Materials Chemistry 21, 3534–3550.

- Tucker, N., Stanger, J.J., Staiger, M.P., Razzaq, H., Hofman, K., 2012. The history of the science and technology of electrospinning from 1600 to 1995. Journal of Engineered Fabrics & Fibers 7.
- Turaga, U., Singh, V., Lalagiri, M., Kiekens, P., Ramkumar, S.S., 2012. Nanomaterials for defense applications. In: Intelligent Textiles and Clothing for Ballistic and NBC Protection. Springer.
- Vaseashta, A., Reisfeld, R., Mihailescu, I.N., 2008. Green nanotechnologies for responsible manufacturing. In: MRS Proceedings. Cambridge Univ Press. 1106-PP03-05.
- Vonnegut, B., Neubauer, R.L., 1952. Production of monodisperse liquid particles by electrical atomization. Journal of Colloid Science 7, 616–622.
- Wang, G., Zhang, H., Qian, B., Wang, J., Jian, X., Qiu, J., 2015. Preparation and characterization of electrospun poly(phthalazinone ether nitrile ketone) membrane with novel thermally stable properties. Applied Surface Science 351, 169–174.
- Wang, J., Wang, M., Li, Z., 2006. Lattice Poisson—Boltzmann simulations of electro-osmotic flows in microchannels. Journal of Colloid and Interface Science 296, 729—736.
- Wang, M., Liu, J., Chen, S., 2008. Electric potential distribution in nanoscale electroosmosis: from molecules to continuum. Molecular Simulation 34, 509—514.
- Wang, X., Ding, B., Sun, G., Wang, M., Yu, J., 2013. Electro-spinning/netting: a strategy for the fabrication of three-dimensional polymer nano-fiber/nets. Progress in Materials Science 58, 1173–1243.
- Wang, X., Ding, B., Yu, J., Wang, M., 2011. Engineering biomimetic superhydrophobic surfaces of electrospun nanomaterials. Nano Today 6, 510–530.
- Wang, Z.M., 2008. One-Dimensional Nanostructures. Springer Science & Business Media.
- Wendorff, J.H., Agarwal, S., Greiner, A., 2012. Electrospinning: Materials, Processing, and Applications. John Wiley & Sons.
- Williams, R.S., 1940. Charles Ladd Norton (1870-1939). Proceedings of the American Academy of Arts and Sciences 74. JSTOR.
- Woodruff, M.A., Hutmacher, D.W., 2010. The return of a forgotten polymer—polycaprolactone in the 21st century. Progress in Polymer Science 35, 1217–1256.
- Wu, J., Wang, N., Zhao, Y., Jiang, L., 2013. Electrospinning of multilevel structured functional micro-/nanofibers and their applications. Journal of Materials Chemistry 1, 7290—7305.
- Xia, Y., Yang, P., Sun, Y., Wu, Y., Mayers, B., Gates, B., Yin, Y., Kim, F., Yan, H., 2003. One-dimensional nanostructures: synthesis, characterization, and applications. Advanced Materials 15, 353–389.
- Xiao, K., Li, Y., Luo, J., Lee, J.S., Xiao, W., Gonik, A.M., Agarwal, R.G., Lam, K.S., 2011. The effect of surface charge on in vivo biodistribution of PEG-oligocholic acid based micellar nanoparticles. Biomaterials 32, 3435–3446.
- Xiao, Y., Cao, H., Liu, K., Zhang, S., Chernow, V., 2010. The synthesis of superhydrophobic Bi2S3 complex nanostructures. Nanotechnology 21, 145601.
- Yang, F., Li, Y., Yu, X., Wu, G., Yin, X., Yu, J., Ding, B., 2016. Hydrophobic polyvinylidene fluoride fibrous membranes with simultaneously water/windproof and breathable performance. RSC Advances 6, 87820-87827.
- Yuan, J., Xu, Y., Müller, A.H., 2011. One-dimensional magnetic inorganic—organic hybrid nanomaterials. Chemical Society Reviews 40, 640—655.
- Zach, M.P., Ng, K.H., Penner, R.M., 2000. Molybdenum nanowires by electrodeposition. Science 290, 2120–2123.
- Zeleny, J., 1914. The electrical discharge from liquid points, and a hydrostatic method of measuring the electric intensity at their surfaces. Physical Review 3, 69.
- Zeleny, J., 1917. Instability of electrified liquid surfaces. Physical Review 10, 1.
- Zhang, L., Fang, M., 2010. Nanomaterials in pollution trace detection and environmental improvement. Nano Today 5, 128–142.

- Zhang, Z., Li, X., Wang, C., Wei, L., Liu, Y., Shao, C., 2009. ZnO hollow nanofibers: fabrication from facile single capillary electrospinning and applications in gas sensors. The Journal of Physical Chemistry C 113, 19397–19403.
- Zhao, Y., Cao, X., Jiang, L., 2007. Bio-mimic multichannel microtubes by a facile method. Journal of the American Chemical Society 129, 764–765.
- Zhou, Y., Dong, Q., Yang, H., Liu, X., Yin, X., Tao, Y., Bai, Z., Xu, W., 2017. Photocrosslinked maleilated chitosan/methacrylated poly (vinyl alcohol) bicomponent nanofibrous scaffolds for use as potential wound dressings. Carbohydrate Polymers 168, 220–226.
- Zhu, X., Cui, W., Li, X., Jin, Y., 2008. Electrospun fibrous mats with high porosity as potential scaffolds for skin tissue engineering. Biomacromolecules 9, 1795–1801.
- Zilberman, M., Elsner, J.J., 2008. Antibiotic-eluting medical devices for various applications. Journal of Controlled Release 130, 202–215.