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**Nanofibers as New-Generation Materials:**  
**From Spinning and Nano-Spinning Fabrication Techniques to**  
**Emerging Applications**

Ahmed Barhoum<sup>1,2\*</sup>, Kaushik Pal<sup>3</sup>, Hubert Rahier<sup>4</sup>, Hasan Uludag<sup>5</sup>, Ick Soo Kim<sup>6</sup>, Mikhael Bechelany<sup>1\*</sup>

<sup>1</sup> *Institut Européen des Membranes, UMR 5635, ENSCM, UM, CNRS, Université Montpellier, Place Eugene Bataillon, F-34095 Montpellier cedex 5, France*

<sup>2</sup> *Chemistry Department, Faculty of Science, Helwan University, Cairo 11795, Helwan, Egypt*

<sup>3</sup> *Department of Nanotechnology, Bharath University, BIHER Research Park, 173 Agharam Road, Selaiyur, Chennai 600073, Tamil Nadu, India*

<sup>4</sup> *Vrije Universiteit Brussel (VUB), Department of Materials and Chemistry (MACH), B-1050 Brussels, Belgium*

<sup>5</sup> *Department of Chemical & Materials Engineering, and Department of Biomedical Engineering, University of Alberta, Edmonton, Alberta, Canada*

<sup>6</sup> *Department of Functional Machinery and Mechanics, Shinshu University, 3-15-1 Tokida, Ueda 386-8567, Japan*

*Corresponding authors:*

*Ahmed Barhoum ([ahmed.barhoum@umontpellier.fr](mailto:ahmed.barhoum@umontpellier.fr) and [ahmed.barhoum@science.helwan.edu.eg](mailto:ahmed.barhoum@science.helwan.edu.eg)); and Mikhael Bechelany ([mikhael.bechelany@umontpellier.fr](mailto:mikhael.bechelany@umontpellier.fr))*

## **Abstract**

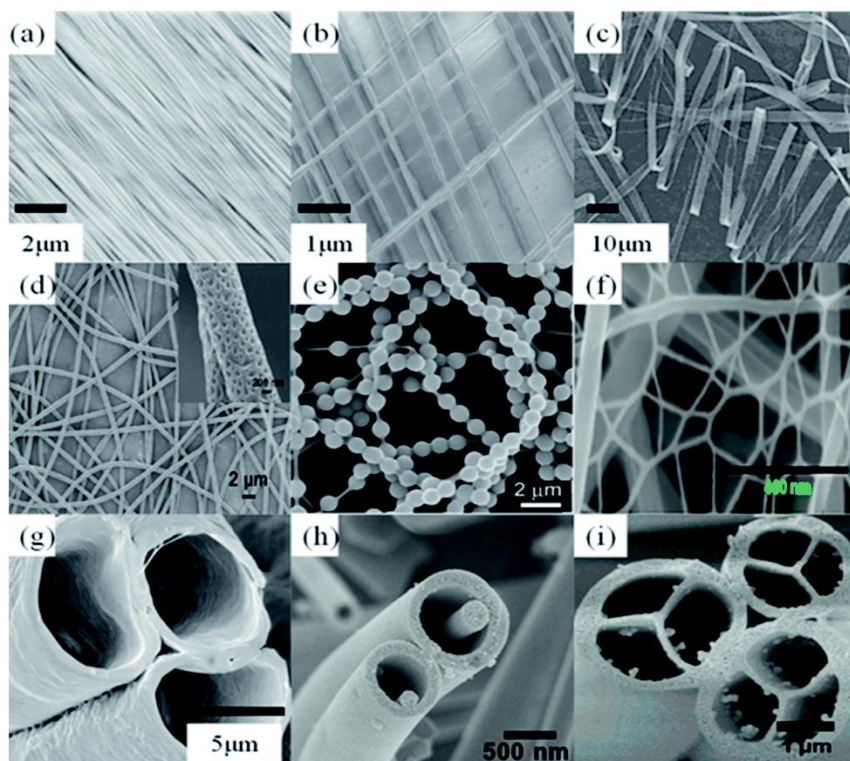
Nanofiber unique characteristics and potential applications offer innovative strategies and opportunities for sustainable energy production, and for creative solutions to biomedical, healthcare, and environmental problems. This review summarizes the history and development of nanofiber technology, their unique properties, fabrication techniques (using spinning and non-spinning approaches), and emerging applications in energy harvesting and storage, environmental protection and improvement, and biomedical technology and healthcare. Nanofibers are currently used as electrode and membrane materials for batteries, supercapacitors, fuel cells, and solar cells. Nanofiber membranes are also successfully used for ultra-high air filtration, wastewater treatment, water purification, and blood purification at low pressure. This review will describe the different types of nanostructured fibers (e.g., solid, mesoporous, hollow, core-shell nanofibers) fabricated from natural and synthetic polymers, metal and metal oxides, carbon-based, inorganic-organic hybrid nanofibers and their potential applications. Moreover, it will highlight the current and future research needs in nanofiber-based materials to improve and broaden their applications and commercialization.

**Keywords:** Nanofiber History, Fabrication Techniques, Energy Harvesting and Storage, Flexible Electronics, Environmental and Healthcare Applications, Biomedical Applications.

# 1. Introduction

Nanofibers have emerged as exciting one-dimensional (1D) nanomaterials for a wide range of research and commercial applications [1]. Nanofibers show several interesting features, such as a diameter 1000 times smaller than that of human hair, high surface area with tunable porosity, 3D topography, flexible surface functionalities, and better mechanical properties (i.e., stiffness and tensile strength) than any other commonly used base material [2]. The significant impact of nanofiber technology is due to the availability of a wide range of materials that can be used for nanofiber production, including natural and synthetic polymers, metals and metal oxides, carbon-based, and composite nanomaterials. Furthermore, the nanofiber surface and bulk features can be modified to carry various functionalities, leading to different physical properties and potential applications [3],[4].

A single, internationally accepted definition of nanomaterials does not exist. Indeed, they are often designed as nanoparticles (NPs), nanotubes, nanofibers, nanowires, or nanorods, in the function of their characteristics. According to the British Standards Institution, a nanomaterial is a material with any external dimension in the nanoscale (100 nm), or with an internal structure or surface structure at the nanoscale [5]. In NPs, all three external dimensions are in the nanoscale. Nanofibers possess two similar external dimensions (nanofiber diameter = X or Y) in the nanoscale, while the third dimension (nanofiber fiber length = Z) is significantly larger. There are many nanofiber types [6] and they are categorized on the basis of their nature (natural and man-made or engineered nanofibers), composition (organic-based, inorganic-based, carbon-based, and composite nanofibers), structure (solid, porous, nonporous, hollow, and core-shell), (**Figure 1**) and rigidity (flexible and stiff) [7].



**Figure 1.** Different nanofiber morphologies: (a) uniaxially aligned, (b) biaxially oriented, (c) ribbon, (d) porous fibers, (e) necklace-like, (f) nanoweb, (g) hollow, (h) nanowire-in-microtube, and (i) multichannel tubular [7]. Copyright 2014, Royal Society of Chemistry.

Due to their high aspect ratio and ability to form 3D-network structures, nanofibers are an excellent candidate for various biomedical applications, such as drug delivery, wound healing, and tissue engineering [1]. On the other hand, most NPs smaller than  $<100$  nm can penetrate the human cells (differently from nanofibers), and sometimes destroy the cell components and cause cell lysis [8]. Therefore, for safe use, NPs could be loaded onto nanofibers, if such fibers cannot easily penetrate into human cells. However, the nanofiber surface texture (porosity and surface roughness), composition (surface and bulk structure), network structure (random or aligned), and molecular orientation must be controlled to improve their bioactivity [9],[10].

The many different nanofiber fabrication techniques can be classified in two main types: top-down and bottom-up approaches. In top-down techniques, such as chemical and mechanical treatment of wood pulp, the bulk material is broken down into nanofibers. These techniques are commonly used for the preparation of cellulose nanofibers (CNF) [11]. Bottom-up techniques are commonly used for nanofiber fabrication from constituting molecules and include electrospinning [12], drawing [13], template synthesis, self-assembly and phase separation. Electrospinning is the most widely used method because of its simplicity, low-cost set-up, mass-production potential, and the possibility to control the nanofiber composition, diameter, and orientation in the function of the intended application [14].

The production of nanofibers has been already reviewed by many authors; however, a comprehensive overview on the nanofiber technology and development is still lacking. Therefore, here, we will briefly summarize the history and development of nanofiber fabrication techniques (spinning and non-spinning approaches). We will then describe the main categories of nanofiber fabrication techniques and the emerging applications in different fields, such as environmental remediation, healthcare, and biomedical engineering [15-17], energy production and storage [18-20], water treatment [21-28], air filtration, sensors [29-32] and electronics. In each section, we will mention selected studies to explain how nanofibers can be exploited to refine the operational performance of various inorganic, organic, carbon and composite membranes. Finally, we will discuss the challenges for the widespread application of nanofibers. By highlighting the advantages of the nanofiber technology, we hope that researchers and manufacturers will become more interested in these materials and will contribute to broadening their applications.

## 2. History of Micro and Nanofiber Technology

The first nanofibers were produced by electrospinning more than four centuries ago. The work by William Gilbert (in 1600) was considered as an early example of what would become the modern electrospinning technology [33]. Gilbert's study is the first record of the electrostatic attraction of a liquid [34]. In 1845, Louis Schwabe invented a number of methods for spinning silk and creating artificial fibers [35]. One of the first methods for the synthesis of carbon nanofibers was patented by Hughes and Chambers in 1889 [36]. In 1902, the American inventor John Francis Cooley patented the first electrospinning device: "Apparatus for electrically dispersing fluids" [37]. In 1912, Burton and Wiegand analyzed the effect of electricity on streams of water drops, and in 1914 John Zeleny studied the behavior of fluid droplets at the end of metal capillaries [38]. Between 1931 and 1944, Anton Formhals was granted at least 22 patents on electrospinning, including the first one (in 1934) on the experimental production of fibers [39]. In 1938, Rozenblum and Petryanov-Sokolov generated electrospun fibers that they used to produce filter materials, known as "Petryanov filters" [33]. In 1952, Radushkevich and Lukyanovich produced hollow graphitic carbon fibers [40], and Oberlin, Endo, and Koyama (1976) developed a chemical vapor deposition (CVD) process to fabricate nanoscale carbon fibers [41]. Between 1964 and 1969, Geoffrey Ingram Taylor established the theoretical foundation of electrospinning [42],[43],[44],[45]. In 1966, Harold L. Simons patented an instrument to produce fiber fabrics with various patterns [43]. The physicist Lord Rayleigh published several articles (1978-1979) on the influence of electricity on colliding water drops and the equilibrium of liquid conducting masses charged with electricity [46],[47]. In 1987, Charles Vernon Boys described the spinning process in an article on glass fiber manufacture

[48],[49]. The modern term 'electrospinning' was popularized by Doshi and Reneker (1995) [50] who produced fibers with a variety of cross-sectional shapes from different polymers from 50 nm to 5  $\mu\text{m}$  microns in size.

Since 1995, the number of publications on nanofibers has been increasing exponentially each year. In 2001, Wang used electrospinning to fabricate inorganic fibers [50]. In 2005, the first book on nanofibers (title: “An Introduction to Electrospinning and Nanofibers”) was published by Prof. Seeram Ramakrishna and co-authors [51]. In 2005, the Elmarco company developed Nanospider<sup>TM</sup>, the first technology in the world to enable the industrial scale production of nanofibers.

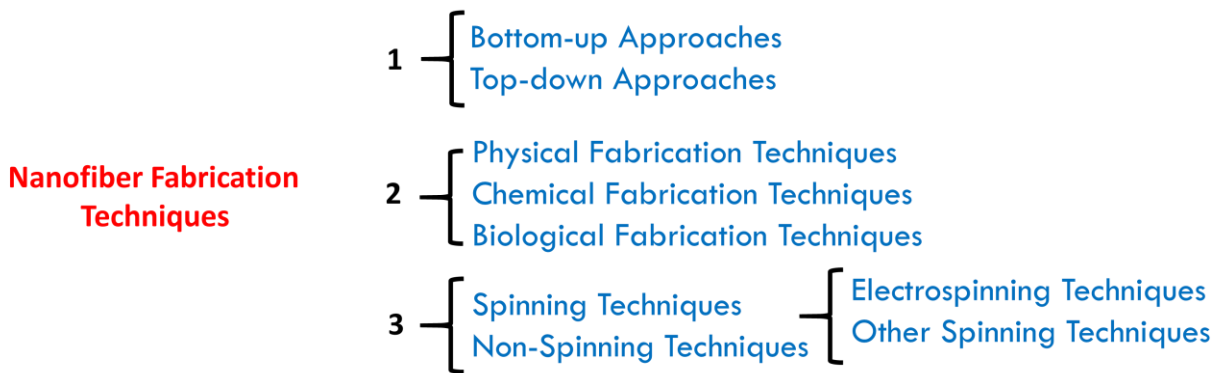
Currently, more than 200 universities and research institutes worldwide study various aspects of nanofiber production and their characteristics. More and more articles are published on new nanofiber fabrication techniques, and this trend does not seem to decline. Indeed, using the keywords nanofibers, nanofibres, nanofiber or nanofibre, the SciFinder database of chemical literature identified 23,728 articles up to October 2018. About 85% of these articles were published from 2006 to 2018.

### **3. Nanofiber fabrication techniques**

To date, various fabrication techniques to produce nanofibers have been reported in the literature under different names and classifications (Figure 2). For example, nanofiber fabrication techniques can be classified as bottom-up and top-down approaches. Bottom-up approaches to produce nanofibers, including mechanical grinding, physical vapor deposition (PVD), CVD, solution blowing [52], centrifugal spinning [53], drawing techniques [54], template synthesis [55], self-assembly [56], phase separation [57], freeze-drying synthesis [58], interfacial



polymerization [59], and electrospinning [60]. In top-down approaches, nanofibers are produced by grinding, refining, sequential cutting, or milling a larger bulk material. In bottom-up approaches, small units (atoms, ions, molecules or NPs) are used to fabricate nanofiber [61]. In this review, the nanofiber fabrication techniques can be classified in: (i) physical, chemical and biological fabrication techniques; and (ii) spinning and non-spinning techniques. Spinning techniques can then be subdivided in: (i) electrospinning approaches that use electric voltage to control the fiber morphology; and (ii) other spinning approaches that use other forces, such as pressurized air and centrifugal forces [62].



**Figure 2. Different classification for fabrication techniques to produce nanofibers.**

## 2.1. Physical, Chemical, and Biological Fabrication Techniques

Various physical approaches (grinding, milling, PVD, laser ablation, and spinning fabrication techniques), chemical approaches (electrochemical deposition, CVD, sol-gel, hydrothermal, template-assisted synthesis, sonochemical synthesis, and microwave synthesis), and biological approaches (bacterial cellulose synthesis, enzymatic hydrolysis of wood pulp) to produce nanofibers have been extensively investigated [63]. Physical methods usually apply mechanical pressure, high energy radiations, thermal or electrical energy to form nanofibers by melting, evaporating or condensing the starting material. Chemical fabrication techniques are typically

bottom-up approaches that need well control of reaction parameters to allow the reactants (atoms, ions, molecules) to combine and grow in long one-dimensional morphology rather than the formation of separate nanoparticles. Biological fabrication techniques have been reported for the synthesis of cellulose nanofibers as majorly accepted as alternative eco-friendly technology to overcome limits of physical and chemical methods. Cellulose nanofibers are extracted from cellulose obtained from various lignocellulosic fibers using bacteria cellulose and enzymatic treatment [64,65,66]. Table 1 shows a comparison between physical, chemical and biological techniques used to produce cellulose nanofibers with different size distribution [66]

Table 1. comparison between physical, chemical and biological techniques used to produce cellulose nanofibers with different size distribution [66].

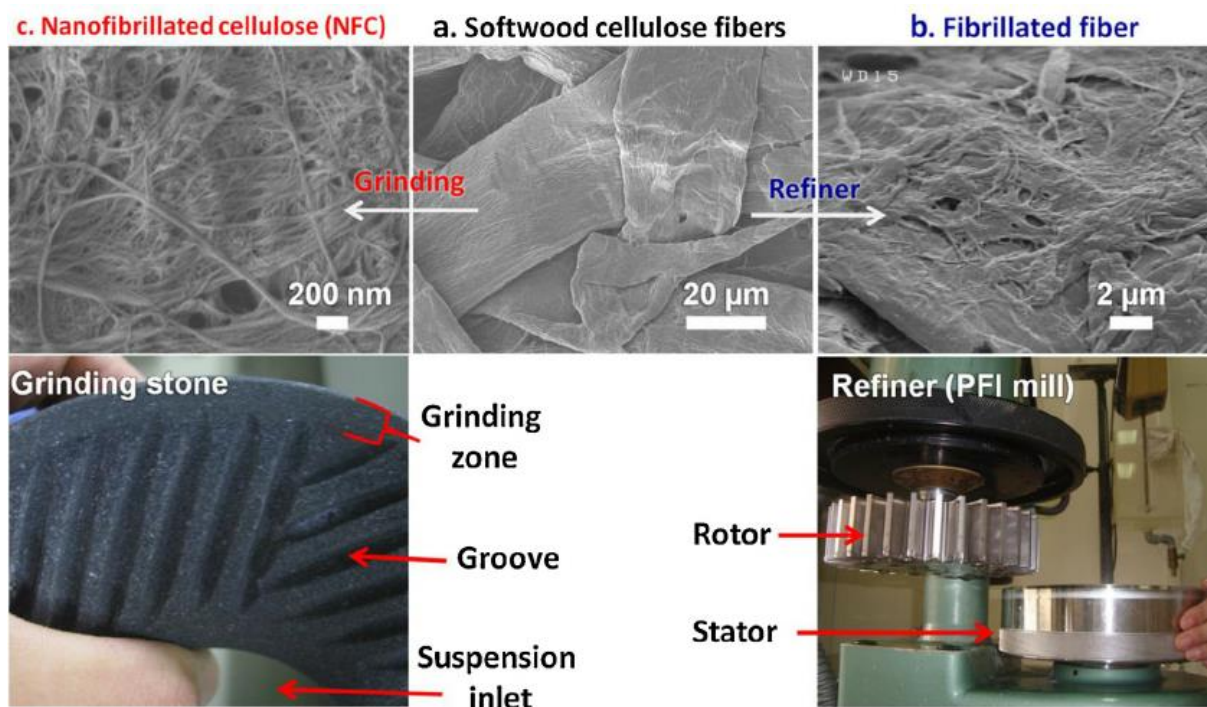
Techniques	Method	Dimension
Physical techniques	Mechanical treatment (refining) of cellulose-based materials such as wood or tunicates	Length: 50 nm–3 $\mu$ m Diameter: 5–50 nm
Chemical Techniques	Alkali treatment and acid hydrolysis of cellulose-based materials such as wood	Length: 50 nm–0.5 $\mu$ m Diameter: 3–15 nm
Biological Techniques	Biological treatment of cellulose-based materials with Gram-negative or Gram-positive bacteria	Length: 200 nm–3 $\mu$ m Diameter: 10–75 nm

### 2.1.1. Mechanical Fabrication Techniques

Grinding, ball milling, cryo-crushing, and high-pressure homogenization are physical fabrication methods (top-down approaches) that are frequently employed for CNF fabrication from natural materials, such as wood pulp [66], [67],[68]. The nanofiber size and morphology can be modulated by changing the grinding medium and speed, amount of materials, grinding condition (dry or wet) and duration, and amount of energy transferred between the grinding

medium and the material [69-71]. **Figure 3** summarizes CNF production from wood pulp using the ultrafine grinding and refining technique. The cellulose mud is put in a super-mass-collider device, in which it is squeezed between a static and a rotating grinding stone [72].

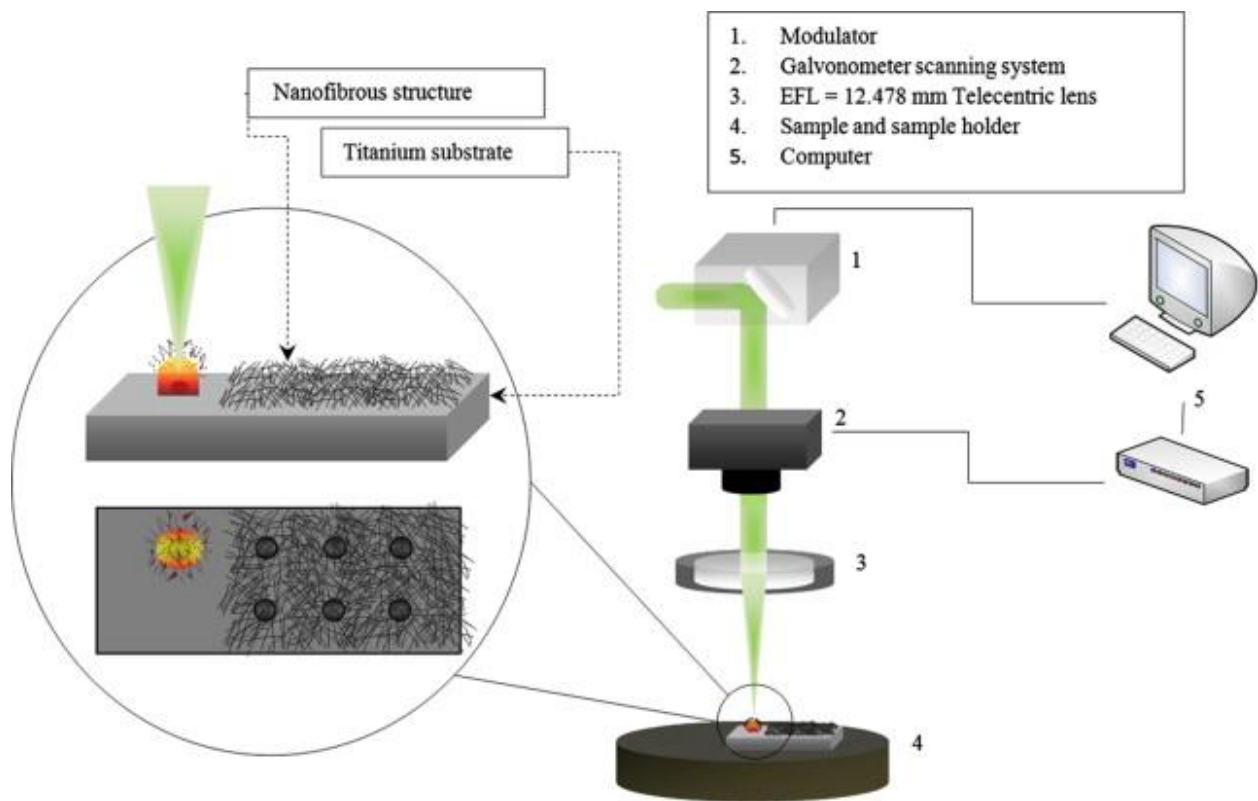
However, these physical methods usually lead to fiber shredding rather than elementary fibril delamination. Moreover, the produced CNFs are characterized by low polymerization degree, crystallinity and aspect ratio, and consequently relatively poor mechanical properties [73]. To overcome these drawbacks, chemical treatments, such as acid hydrolysis, alkaline–acid pretreatment and oxidation pretreatment, are used before the mechanical process. These treatments decrease the energy consumption, facilitates the bulk material disintegration, and increase the nanofibril yield [74], [75-77].



**Figure 3.** The finite element microscopy of the cork fiber is shown in three states: (a) as-received, (b) after refining, and (c) after grinding [72]. Copyright 2013, Elsevier.

### 2.1.2. Vapor Deposition Techniques

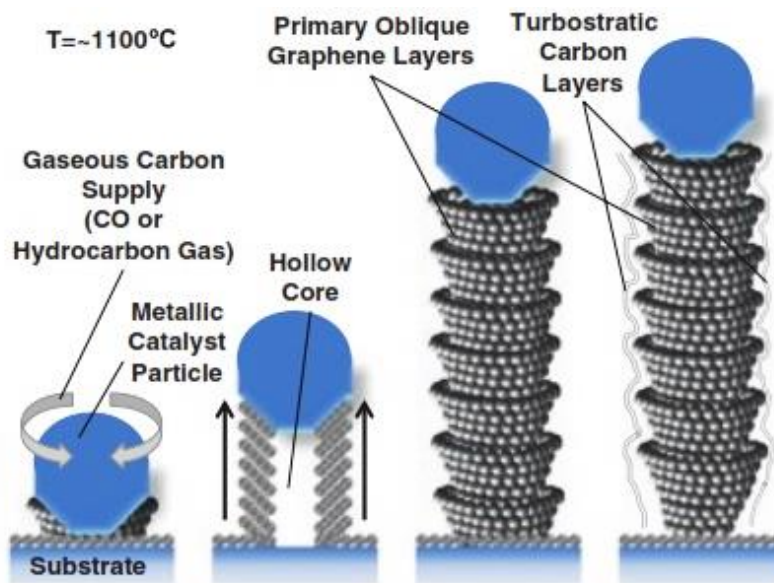
Gas-phase deposition techniques or vapor deposition techniques are widely used bottom-up techniques to produce a wide range of carbon and metal oxide nanoparticles. Gas-phase deposition techniques, such as PVD and CVD, that recently used to fabricate highly structured carbon and metal oxide nanofibers. The most common PVD methods are: (i) electron beam evaporation, in which the material is heated by electron bombardment under high vacuum and the produced vapor re-condensed to form nanofibers [78]; (ii) plasma sputtering, in which the material is bombarded by glow discharge to form a vapor for subsequent nanofiber deposition [79]; (iii) vacuum arc deposition, in which the targeted material is vaporized by the arc under vacuum and then redeposited to form nanofibers [80]; and (iv) pulsed laser deposition, in which the material is evaporated by a high-power laser ablation, and then nanofibers are deposited on a solid substrate (**Figure 4**) [81]. PVD has been recently tested for the fabrication of polymeric materials with fiber-like nanostructures [82].



**Figure 4:** Schematic representation for the synthesis of bio-functionalized titania nanofibrous structures on a titanium substrate using femtosecond laser ablation [81]. Copyright 2011, Elsevier.

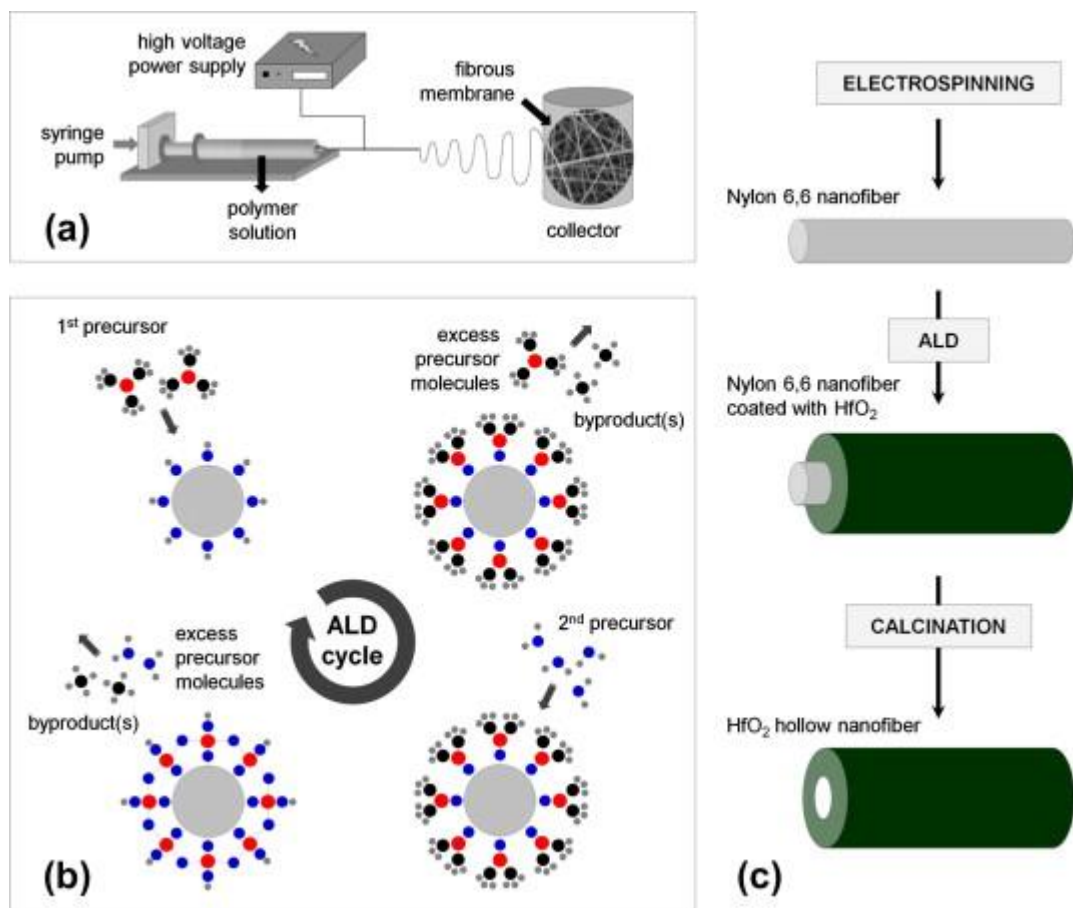
CVD is typically used to produce carbon nanofibers. Transition metal catalytic particles, such as Fe, Ni, Co, Pt, and Cu, are used with a carbon supply (e.g., CO, or a hydrocarbon gas) at temperatures between 500 and 1200°C to produce carbon nanofibers [83]. The size and shape of the catalyst particle (10-100 nm) determines the size of the carbon nanofiber graphitic structure (**Figure 5**) [84]. A faceted nanoparticle with catalytic activity may allow the production of angled layers in which graphitic platelets are deposited at an angle that promotes the carbon nanofiber growth [85]. CVD main drawbacks are the important amount of catalyst residue, the

relatively low production yield, and the expensive equipment [86]. Morphological changes of the catalyst NPs must be taken into account to explain the differences in yield.



**Figure 5.** Schematic representation showing cup-stacked graphene layers are folded to form a single carbon nanofiber formed during the CVD process and the formed stacked-cup carbon nanofiber helical structure with the inclined orientation of graphene planes along the side of the structure relative to the nanofiber axis [84]. Copyright 2016, Springer.

Nanofibers can also be fabricated using hard or soft templates and vapor deposition techniques. For instance, with atomic layer deposition (**Figure 6**), nanofibers are used as a template on which materials are deposited by vapor deposition, and then they are removed. However, it is difficult to completely remove the template without damaging the fibrous structure [62],[87]. Atomic layer deposition (ALD) can be considered as one of the most conformal deposition techniques at low temperatures. A wide selection of materials has been used as nanostructured templates for ALD growth. Among them, polymer nanofibers are the most widely reported template, which was in general used for the synthesis of oxide nanotubes [87].

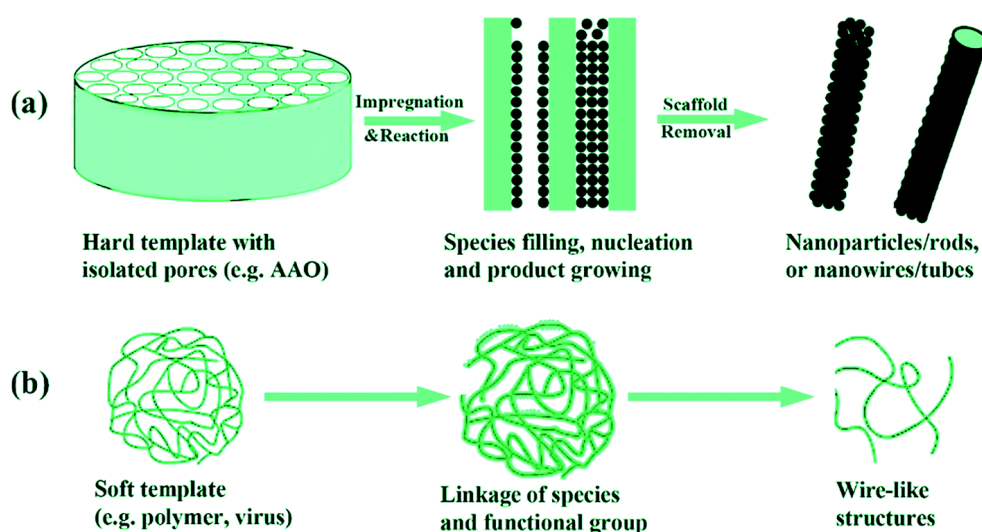


**Figure 6.** Fabrication of hafnia hollow nanofibers by atomic layer deposition using electrospun nanofiber templates [87]. Copyright @ 2013, Elsevier.

### 2.1.3. Wet Chemical Fabrication Techniques

Electrochemical deposition [88], polyol synthesis [89], phase-separation [90], microemulsion [91], sol-gel method [92], hydrothermal synthesis [93] are some of the most common wet chemical fabrication methods for nanofiber synthesis. Hard porous templates, such as polycarbonate and anodic aluminum oxide membranes, are often used in combination with electrochemical deposition to produce metallic nanofibers that are aligned after removal of the

template scaffold (**Figure 7**) [94]. Again, the need for completely removing the template without damaging the fiber structure is the major limitation. Hard templates might be dissolved or polished with a scalpel. Soft templates, such as surfactants and polymers, have been used in combination with electrodeposition techniques for nanofiber synthesis. For example, Nam *et al.* [95] prepared Sn nanofibers by cathodic electrodeposition from an aqueous solution of Triton X-100. Electrochemical techniques offer the possibility to grow nanotubes (100nm in diameter and several micrometers long) from a metal and metal oxide surface [96],[97].



**Figure 7.** Schematic description of (a) hard, and (b) soft template synthesis of nanofibrous structures [94]. Copyright 2008, American Chemical Society.

Hydrothermal synthesis of nanofibers involves chemical reactions in water at different (from room to very high) temperatures and pressures [98, 99]. Cao *et al.* [100] synthesized SrTiO<sub>3</sub>/TiO<sub>2</sub> nanofibers using a simple in-situ hydrothermal method. Simpraditpan *et al.* [101] produced titanate nanofibers using a hydrothermal method and a natural ilmenite mineral as the starting material. Cao *et al.* [102] described a one-step hydrothermal method for the successful synthesis of WO<sub>3</sub> nanofibers (~100 nm in diameter, and length up to tens of micrometers). The



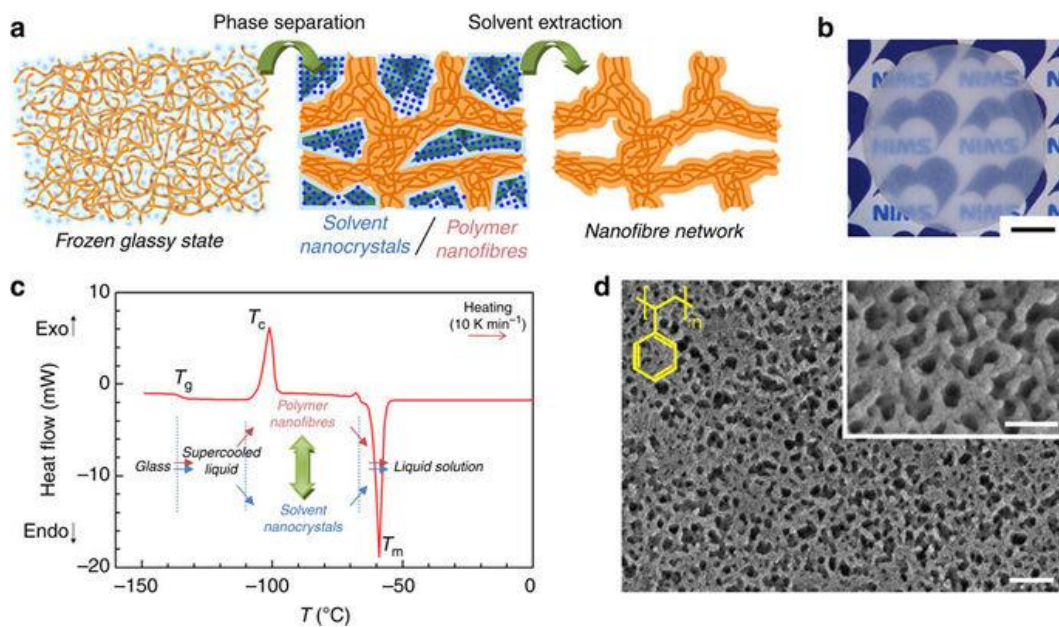
main advantages of hydrothermal methods are the mild reaction conditions and the good crystallization of the obtained materials.

The sol-gel process is a wet chemistry method often used to produce metal oxide NPs, nanofibers, and nanostructured thin films. This method involves the conversion of monomers into a sol (colloidal solution) that acts as the precursor for a gel (an integrated network) of discrete particles or network polymers [103]. Metal alkoxides are typical precursors. The sol-gel method includes two main reaction steps: (i) hydrolysis of the precursor, and then (ii) polycondensation and polymerization of the hydrolyzed products [103]. Polymer/metal oxide nanofibers have been produced by combining the sol-gel and electrospinning techniques [104]. Similarly, polyacrylonitrile (PAN)/silica [105], polyvinylpyrrolidone (PVP)/titanium (IV) oxide [106], PVP/zinc acetate [107], and PVP/aluminum isopropoxide fibers [108], among others, could be fabricated by combining controlled sol-gel synthesis with electrospinning. Calcination of these composite fibers at 500-900 °C in the air or inert atmosphere (N<sub>2</sub> or Ar) results in pure metal oxide or metal oxide/carbon nanofibers without contamination by other phases. Several groups assessed how the nature and concentration of the polymer and metal oxide precursor, calcination temperature, time, and heating rate influence the phase and size of the as-spun nanofibers.

Physical fabrication techniques such as ultrasound irradiation and microwave radiation have been recently employed for wet chemical synthesis of nanofibers [109],[110]. These two techniques accelerate the chemical reactions via completely different mechanisms. Ultrasound irradiation is useful to accelerate the reactant dissolution, to increase the reaction rates, and/or to renew the surface of a solid reactant in a variety of reaction systems. The ultrasound irradiation effect in liquids is explained by acoustic cavitation through the formation, growth, and implosive

collapse of bubbles [111]. On the other hand, microwave radiation provides heat energy to the reactants through molecular interactions with high-frequency electromagnetic radiation that is faster than the hydrothermal technique [112, 113]. For example, polyaniline (PANI) nanofibers were chemically prepared by ultrasonic irradiated polymerization using various ultrasonic power, frequency, and reaction temperatures [110]. CNFs [114] were isolated from bamboo by microwave liquefaction combined with chemical treatment and ultrasonic fibrillation.

The phase separation technique involves freezing to separate a solution (e.g., an emulsion or a hydrogel solution) [115-117] in the polymer-rich and solvent-rich phases, followed by freeze-drying to remove the moisture and solvent, to form a porous nanofiber structure (**Figure 8**) [118]. The main processing parameters are the concentration of polymer and solvent, the freeze/drying temperatures, and the presence of cross-linking additives.



**Figure 8.** Fabrication of mesoporous polymer nanofiber networks using the phase separation technique: (a) Formation of the polymer nanofiber network by flash freezing. (b) Micro-photograph of nanopaper made of polysulfone nanofibers. (c) Differential scanning calorimetry curve of a frozen solution of 20 wt % polystyrene (PS) in dimethylformamide (DMF). (d)

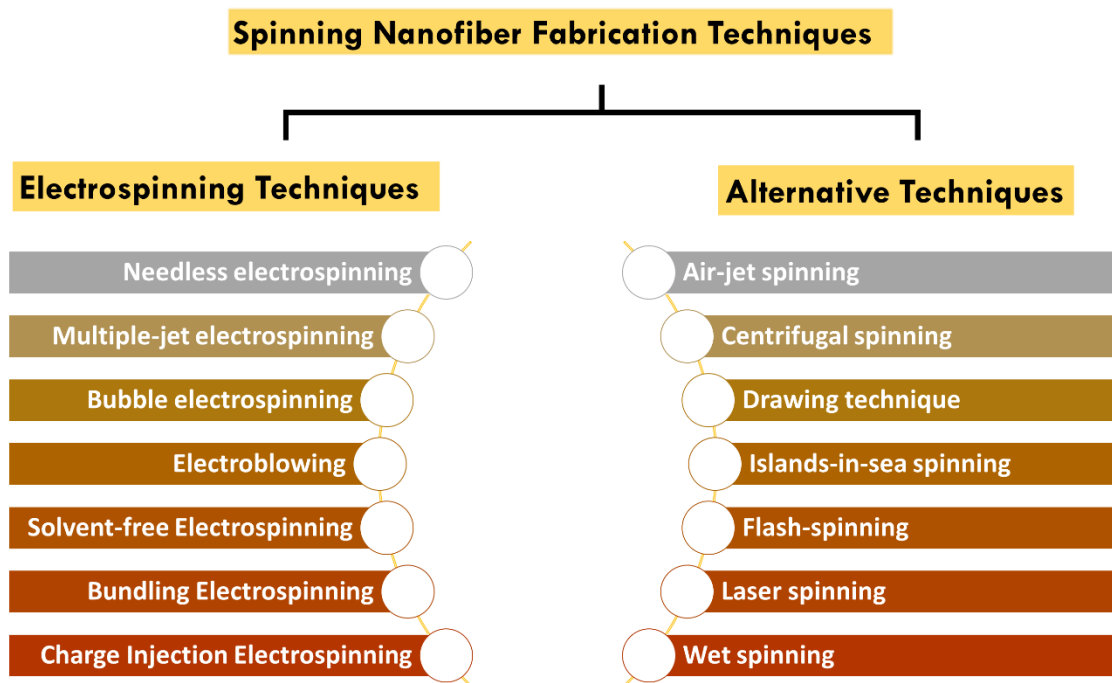
Scanning electron microscopy image of a porous PS nanofiber network formed after removal of the frozen DMF. Scale bar, 250 nm (inset: 100 nm) [118]. Copyright © 2017, American Chemical Society.

Other physical and chemical fabrication techniques have been described in the literature, such as the volatile diffusion method for the fabrication of C<sub>60</sub> fullerene nanofibers by using toluene as solvent and isopropyl alcohol as precipitation agent [119], and the template-free synthesis of polymer nanofibers. Moreover, Kaner and coworkers [120],[121],[122],[123] prepared PANIs by interfacial polymerization or direct mixing polymerization. Then, they produced nanofibers by inhibiting the secondary growth of the primary PANI nanofibers generated in the early reaction steps.

## **2.2. Fiber spinning: Electrospinning and Alternative techniques**

Spinning is a century-old technique used to produce textiles in which fibers of the plant, animal or synthetic origin are drawn out and twisted together to form yarn. Spinning can be classified as a physical fabrication technique, and can be combined with most of the previously described physical and chemical fabrication methods to produce nanofibers. Fiber spinning techniques can be classified in electrospinning and alternative spinning techniques (also called “non-electrospinning techniques”). Electrospinning employs electrostatic forces, whereas alternative spinning techniques use other forces (e.g., gravitational forces, centrifugal forces, pressurized air) to produce fibers with a diameter up to 100 nm by manipulating charged threads of polymer solutions or polymer melts. **Table 2 and Figure 9** summarizes some of the specific features of electrospinning and non-electrospinning techniques. In this section, we will briefly

describe the spinning techniques for nanofiber fabrication. We will discuss the spinning set-up and parameters (solution and processing) that significantly affect fiber morphology, and the advantages and limitations of the different electrospinning approaches.



**Figure 9.** List of the nanofiber spinning techniques (electrospinning and alternative spinning techniques).

**Table 2.** Comparison of nanofiber spinning techniques (electrospinning and alternative spinning techniques or non-electrospinning techniques) [62].

Methods	Electrospinning	Non-electrospinning techniques		
		Solution blowing /Air-jet spinning	Centrifugal spinning	Drawing technique
Nanofiber diameter	50 nm to 2 $\mu\text{m}$	50 nm to 3 $\mu\text{m}$	25 nm to 3 $\mu\text{m}$	100 nm to 3 $\mu\text{m}$
Production rate	10 $\mu\text{L min}^{-1}$	20 $\mu\text{L min}^{-1}$	Up to 1 ml $\text{min}^{-1}$ per nozzle	15–100 $\mu\text{L min}^{-1}$

Most influencing processing parameters	Viscosity Feeding rate Tip to collector distance Voltage	Viscosity Feeding rate Gas pressure Nozzle geometry	Viscosity Rotational speed Orifice diameter Evaporation rate	Polymer type Molecular weight Solvent properties Substrate speed
Larg-scale production	Scalable	Scalable	Scalable	Scalable
Producing aligned nanofibers	Possible	Possible	Possible	Possible
Possibility of spinning Polymer Melt	Possible	Possible	Possible	Not Possible
Voltage requirement	10–40 kV	Not required	Not required	Not required
Production of polymer/ceramic composite fiber	Possible	Possible	Possible	Not Possible
Production of core/shell nanofibers	Possible	Possible	Possible	Not Possible
Possibility of producing 3D nanofibrous structures	Possible	Possible	Possible	Possible

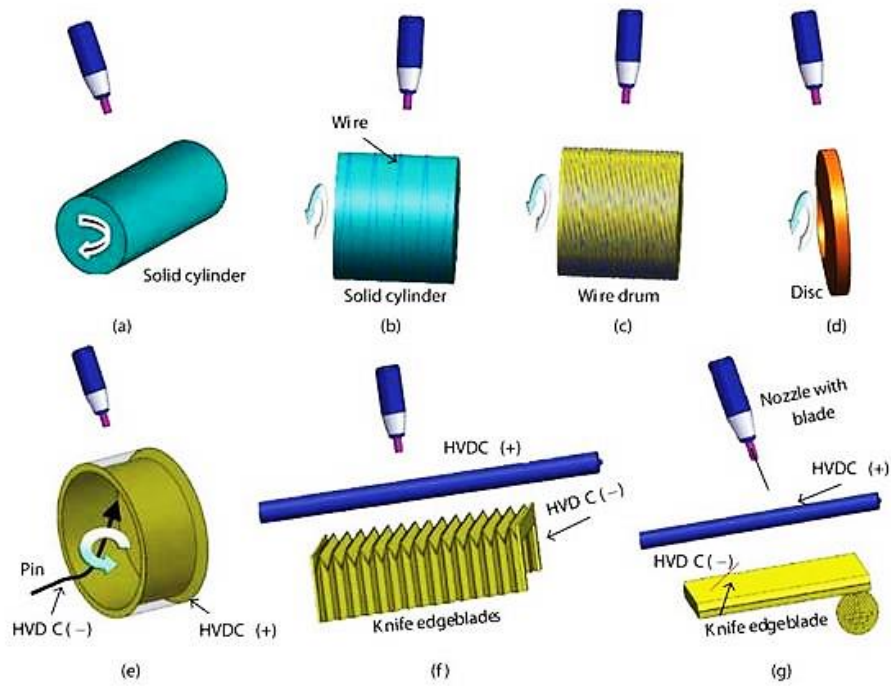
### 2.2.1. Electrospinning techniques

Electrospinning techniques work with polymer solutions [124]. Typically, the polymer is dissolved in a volatile solvent (5-30% polymer: solvent, w:w) and placed in a syringe or pipette. The polymer solution is then pushed at a specific rate through the syringe tip (spinneret) by external pumping using mechanical pistons. The quite high solvent concentration (up to 30%) gives sufficient viscoelastic properties. When the solution droplet is formed at the spinneret, an electric voltage bias (typically 10-40 kV, but up to 100 kV) is generated between the tip (metallic needle) and the collector that is placed at a distance of few cm to few tens of cm. Due to the progressive increase of the applied voltage, the electric forces becomes higher than the surface tension. Consequently, a jet is produced, and the droplet is deformed into an apex (Taylor cone) [125],[126]. When the solution feed rate is increased, the electric field strength also should be increased by applying a higher voltage or by decreasing the distance between the syringe tip and the collector [127]. The jet velocity and strain rates can reach values of few m/s and up to  $10^7 \text{ s}^{-1}$ , respectively.

Electrospinning has several advantages: (i) it can be used with all main material types (e.g., polymers, metal oxide, ceramics, carbon, composite) directly or indirectly (i.e., electrospinning of the basic material followed by thermal treatment). More than 200 different polymers have been electrospun for various applications, and the number is still increasing [128]; (ii) nanofibers can be functionalized before spinning (by blending the polymer solution), after spinning (surface functionalization), or by using core-shell electrospinning [3]; (iii) low starting cost, and commercial availability of set-ups for industrial production; (iv) nanofiber can be deposited onto a variety of substrates (metal, glass, microfibrinous mat, and water) with lower static charge; (v) different fibrous nanostructures can be constructed in ‘one-pot’; (vi) nanofiber fabrication by electrospinning is easier and cheaper than nanofiber extraction from natural sources (e.g., cellulosic nanofibers), or synthesis (e.g., carbon nanofibers) and with more versatile options.

Generally, the fiber diameter, morphology, alignment, and molecular orientation are influenced by the solvent, the collector, the applied voltage, the tip-to-collector distance, and the solution flow rate. Different collector types (e.g., flat piece of metal, rotating disk, rotating drum, or rotating frame collector) have been developed to control fiber orientation (**Table 3**). Rotating drum collectors are the most commonly used collectors for the continuous production of nanofibers (**Figure 10a-c**). Rotating disk collectors are used to produce uniaxially aligned fibers. Compared with a drum collector, a disk collector (**Figure 10d**) allows collecting a large number of fibers at the disk edge and making highly aligned nanofibers [129]. By increasing or lowering the applied voltage, the fiber length can be increased, and the fiber size decreased, respectively. The final fiber morphology can be modified from a circular to a flat shape by changing the nozzle-collector distance. Moreover, for aqueous polymer dispersion, a bigger distance is needed to dry the fibers [124].

When choosing an electrospinning approach to fabricate nanofibers from a polymer, the following features must be taken into account: (a) continuous single nanofibers must be collectible; (b) the fiber diameter must be uniform and controllable, and (c) the fiber surface must be defect-free or defect-controllable. The solution must have a minimum concentration and viscosity to produce fibers by electrospinning. At very low concentrations, the solution cannot be electrospun and is electrosprayed. By increasing the syringe flow rate, the fiber diameter is increased, and beads are formed. Beads are obtained also when using a polymer with very low molecular weight while keeping the solution concentration constant. Smooth fibers are produced by increasing the solution molecular weight, and fibers with high diameter are generated when using solutions with very high molecular weight [1]. The surface tension is influenced by the solvent used. A lower surface tension favors the generation of nanofibers without beads, but may not always offer ideal electrospinning conditions. The addition of salts to the electrospinning solution increases the solution conductivity and surface charge density [125], thus allowing better control of the fiber diameter and morphology. The applied voltage and the polymer flow rate in the syringe also are crucial factors. At higher voltages, the fiber diameter is more easily reduced, and in some cases, bead formation is more frequently observed. The influence of the tip-collector distance on the fiber morphology is less important compared with other parameters [125].



**Figure 10.** Different designs of rotating collectors for continuous nanofiber production by electrospinning: **(a)** solid cylindrical collector, **(b)** collector made of wire wound on an insulated cylinder, **(c)** wired drum collector, **(d)** disc collector, **(e)** rotating collector with a sharp pin inside, **(f)** knife-edged sharp pin with an electrode, and **(g)** knife-edged electrode and needle system [129]. Copyright 2011, Hindawi Publisher.

**Table 3.** Summary of the advantages and disadvantages of the different rotating collectors for continuous nanofiber production by electrospinning [6],[129].

Collector type	Advantage	Disadvantage
Rotating drum (Figure 8a)	(i) Simple set-up; and (ii) Possibility of fabricating large area of highly aligned fibers.	(i) Fiber breakage at high rotating speed; and (ii) Production of highly aligned fibers is difficult.

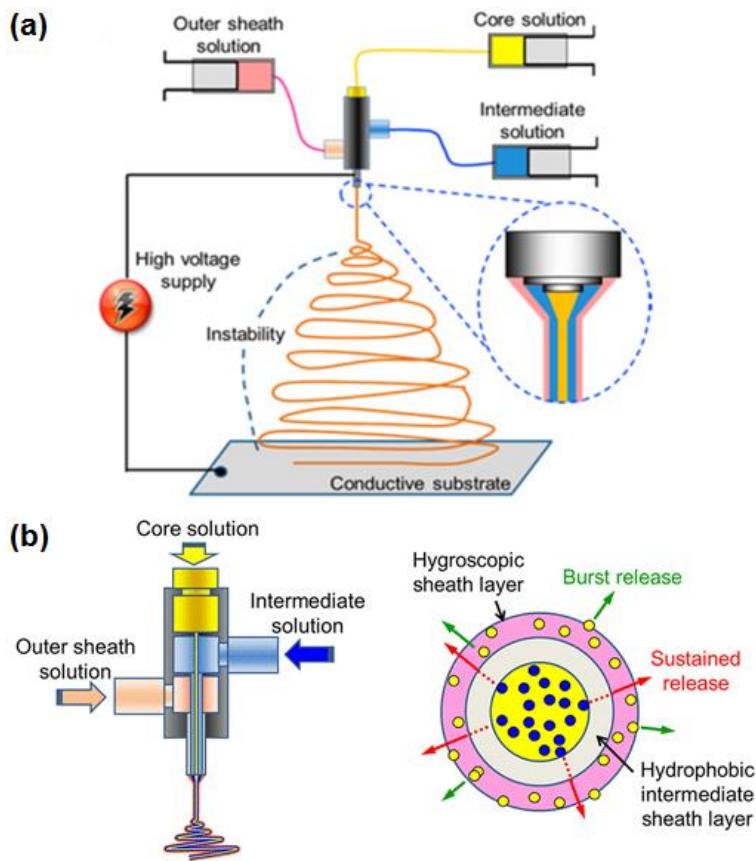


Rotating drum collector with wire wound on it (Figure 8b)	(i) Simple set-up; and (ii) Possibility of fabricating highly aligned fibers.	(i) Aligned fibers are concentrated on the wire, rather than on the whole drum.
Rotating wire drum collector (Figure 8c)	(i) Simple set-up; and (ii) Possibility of fabricating highly aligned fibers.	(i) A thicker layer of aligned fibers cannot be produced, and (ii) Fibers may not be aligned throughout the whole assembly.
Disc collector (Figure 8d)	(i) Simple set-up; (ii) Fabrication of arrayed fibers by attaching a rotatable table on the disc edge; and (iii) Possibility of fabricating highly aligned fibers.	(i) A small area of fiber alignment; and (ii) Cannot maintain high fiber alignment at the same rotating speed when the deposited fibers are thicker.
Rotating drum with a sharp pin inside (Figure 8e)	(i) Fabrication of a large area of arrayed fibers.	(i) Complex set-up; and (ii) Thicker area of arrayed fiber assembly may not be possible.
Rotating tube collector with knife-edge electrodes below (Figure 8g)	(i) Possibility of fabricating highly aligned fibers; (ii) Aligned fibers cover the whole tube; and (iii) Possible deposition of a thicker layer of aligned fiber.	(i) A negative electrode is required for an effective set-up; (ii) Only small diameter tubes can be used
Rotating tube collector with knife-	(i) Possibility of fabricating highly aligned fibers; (ii) Can	(i) A negative electrode is needed for an effective set-up; and (ii)

edged electrode and needle system (Figure 8f)	control the fiber alignment direction on the tube; and (iii) Possibility of depositing a thicker layer of aligned fibers.	Only small diameter tubes can be used.
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Various electrospinning techniques have been developed in the last 20 years, such as needlessly electrospinning, multiple-jet electrospinning, bubble electrospinning, cylindrical porous hollow tube electrospinning, electroblowing, melt electrospinning, coaxial electrospinning, self-bundling electrospinning, charge injection electrospinning, nanospider electrospinning [130], [131], [132], [133]. Coaxial and tri-axial electrospinning have allowed controlling the nanofiber composition and morphology to form core-shell nanofibers using a spinneret with two/three coaxial capillaries (**Figure 11**). Bi-component and multi-component electrospinning can be used for fabricating multi-component nanofibers. Specifically, multi-component fibers are made of two or more polymers with different chemical nature or physical properties, such as molecular weight. They are electrospun from the same spinneret and are contained within the same filament but separated by fine planes. Bi-component electrospinning can be used to produce nanofibers with different cross-sectional shapes, such as islands-in-the-sea [134], core-shell [7], side-by-side [6], split table pie [129], and eccentric sheath-core structures [7]. Magnetic-field-assisted electrospinning, near-field electrospinning, and hot-melt electrospinning allow good control of nanofiber deposition (i.e., alignment, drawing, and writing) onto different substrates. Magnetic-field-assisted electrospinning can be used to electrospin materials that respond to a magnetic field. This allows modulating the nanofiber deposition and alignment [135]. Nanofibers fabricated using this technique are more uniform and with less splitting than those produced

without magnetic field. Near-field electrospinning set-ups can be adapted to very small needle tip-collector (substrate) distances (from 500 nm to 3  $\mu\text{m}$ ) with voltages from 100V to 600V. This technique is suitable for direct writing on many different substrates.



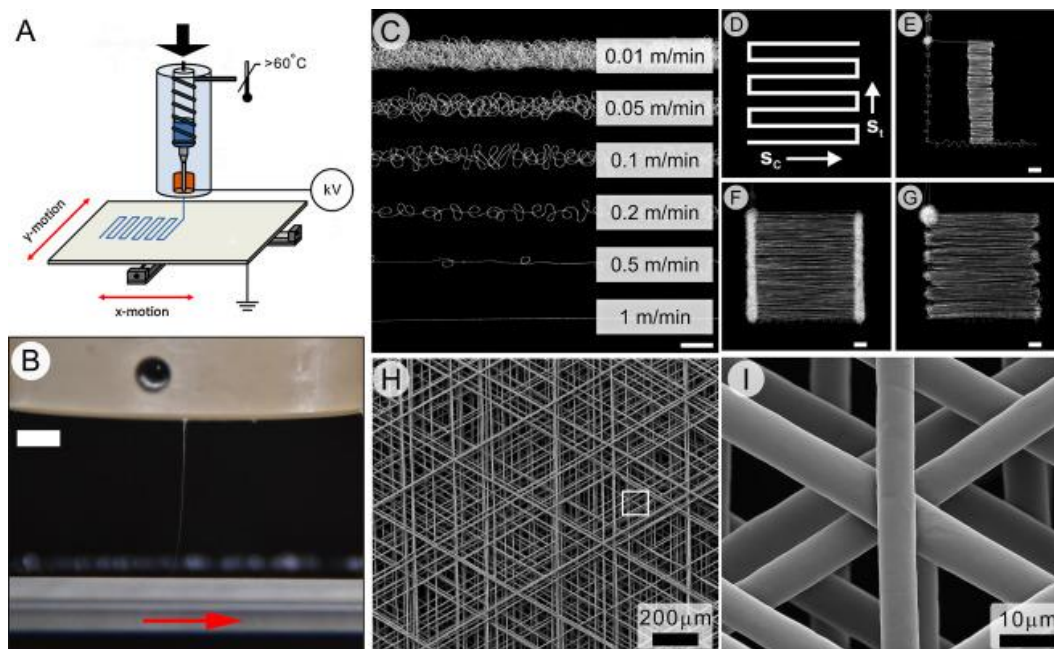
**Figure 11.** Schematic description of triaxial electrospinning: (a) triaxial setup; (b) cross-section of triaxial nanofibers loaded with dual drugs [136]. Copyright © 2013 American Chemical Society.

Despite the widespread use and low starting costs of electrospinning methods to fabricate nanofibers from polymer solutions, their mass production is still limited. Several techniques have been developed to overcome the low productivity and the need for using organic solvents of the standard electrospinning methods. These technologies also include new functions, such as

controlling the nanofiber morphology, compositing, electrospinning of low conductivity polymers and high molecular weight polymers [131-139]. The solvent evaporation in the electrospinning solution is still difficult to control, even after the introduction of many modifications to the collector. The large mass of the evaporating solvent (mainly organic solvents) is the major limitation for commercial use, due to its negative effect on the environment. To overcome this drawback, solvent-free electrospinning methods, such as hot melt electrospinning, supercritical CO<sub>2</sub>-assisted electrospinning, and UV-curing electrospinning and thermo-curing electrospinning, have been developed (**Table 4**) [132]. These techniques do not use conventional solvents, nearly all the precursor solution is spun, and only a few precursor fractions (<10%) enter the air via evaporation. Solvent-free electrospinning has been recognized as an eco-friendly process. However, it has not been widely used yet due to the specific set-up requirements due to the relatively higher precursor viscosity. Moreover, the diameter of nanofibers fabricated by solvent-free electrospinning is larger than that of nanofibers obtained by solution electrospinning [132].

Hot-melt electrospinning has a set-up with moving collectors to produce fibrous materials from polymer melts (**Figure 12**) [133]. However, melt electrospinning is not frequently used due to the difficulty to produce finer fibers, the higher viscosity of the molten polymer, and the electrical discharge associated with the high voltage applied to the polymeric melt. Supercritical CO<sub>2</sub>-assisted electrospinning uses supercritical CO<sub>2</sub> instead of liquid solvents and can be used to electrospin undissolved bulk polymer samples [132]. Compared with conventional solution electrospinning, supercritical CO<sub>2</sub>-assisted electrospinning produces very thick (~100 μm) and short (~4 mm) fibers. Thus, this method needs to be improved to produce thin and long fibers [132].

UV-curing electrospinning starts from UV-curable monomers (without any solvent) that are electrospun into nanofibers by UV irradiation in a  $N_2$  atmosphere [137]. However, the use of UV-curable materials, especially for high specific-surface-area fibers, is limited by oxygen inhibition [138]. A new solvent-free thermal assisted electrospinning process has been developed for the preparation of polyurethane (PU) fibers. Compared with the conventional PU synthesis, the synthesis of the PU precursor solution was improved for use in solvent-free electrospinning [139]. Anion-curing electrospinning is similar to UV-curing and thermal-curing electrospinning, but the monomer is polymerized via anionic initiators [132]. Polymers are typically added to the monomer solution to control the precursor viscosity. In these methods, almost all the precursor is used for nanofiber production, and less than 10% is lost via evaporation.



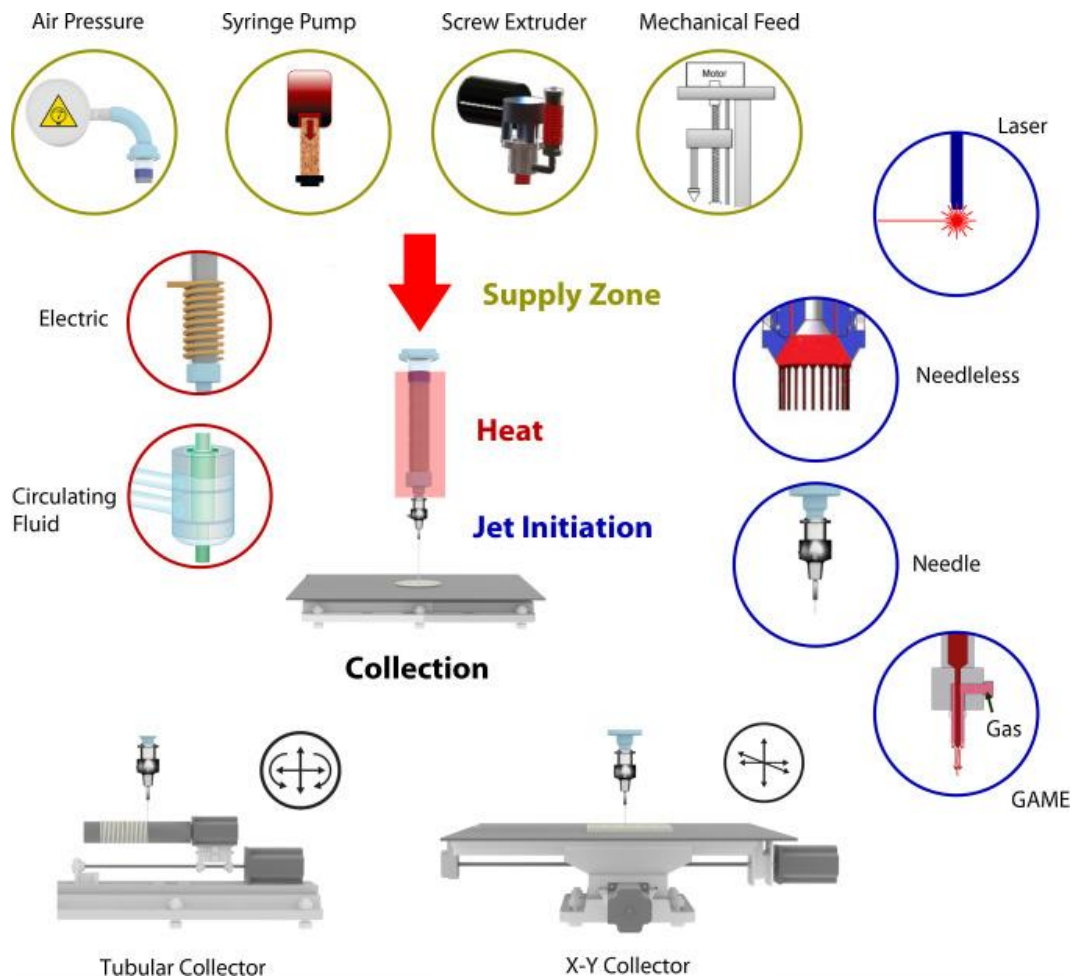


Figure 12. Hot-melt electrospinning with different configuration has been developed to produce fibrous materials from polymer melts. (A) Hot melt electrospinning direct writing with x-y moveable collector controlled by computer according to a preprogrammed pattern. (B) Image shows a stable PCL melt electrospinning jet in direct writing mode. (C) When the collector is translated at relatively slow speeds compared to the melt jet (0.01 m/min), the fibers coil due to viscous buckling of the depositing jet. (D) Schematic representing a programmed square wave pattern translated by the collector to direct write one layer of a TE scaffold. (E-G) PCL fibers wrote with constant straight line speed (SC matching the melt jet speed) while the turning speed (ST) is varied (E) above, (F) below and (G) to match the melt jet speed, causing different results

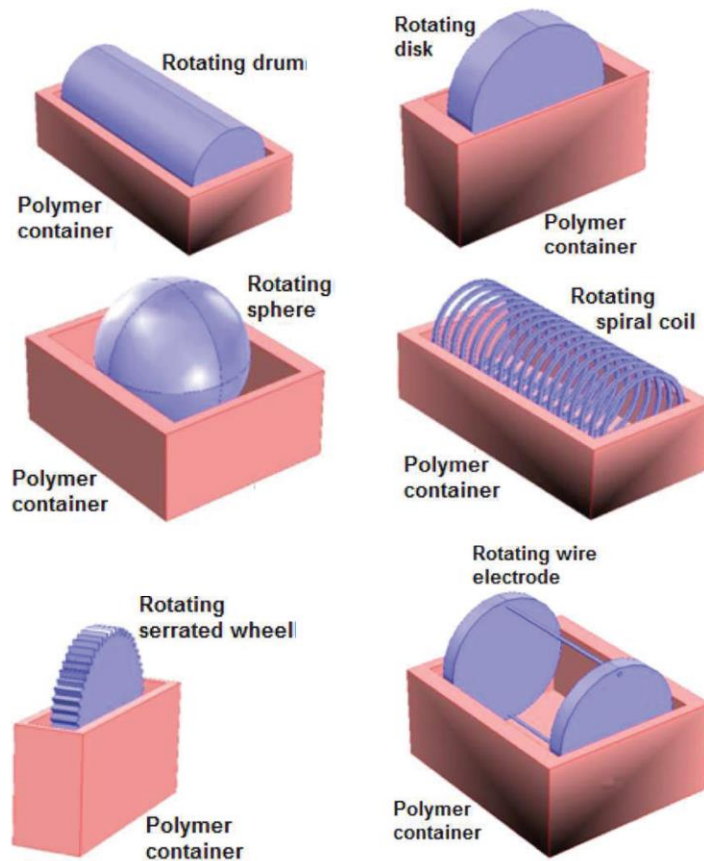
in fiber collection. (H, I) More complex collector translation patterns can be programmed to create TE scaffolds which are cell invasive, (k) Melt electrospinning configurations reported in the literature [133]. Copyright 2016, Elsevier

**Table 4.** Comparison of solution electrospinning and solvent-free spinning techniques [131], [132], [138], [139].

Technique	Solution electrospinning	Solvent-free spinning techniques				
		Melt electrospinning	Supercritical CO <sub>2</sub> -assisted electrospinning	Anion-curing electrospinning	UV-curing electrospinning	Thermocuring electrospinning
Electrospun materials	Polymer solution	Polymer melt	Supercritical CO <sub>2</sub> soluble polymer	Anion-curing monomers	UV-curing monomers	Thermocuring monomers
Precursor utilization	<20 wt%	>90 wt%	<20 wt%	>90 wt%	>90 wt%	>90 wt%
Solvent	Volatile organic solvent	No	Supercritical CO <sub>2</sub>	No	No	No
Solidification mechanism	Solvent evaporation	Heat transfer (cooling)	Solvent evaporation	Polymerization reaction	Polymerization reaction under UV radiation	Polymerization reaction under thermal radiation
Efficiency	Low	High	Low	Low	Low	Low
Set-up	Simple	Simple	Complex	Complex	Complex	Complex
Environmentally friendly	No	Yes	Yes	Yes	Yes	Yes
Modeling	Easy	Difficult	Difficult	Difficult	Difficult	Difficult
Fiber diameter	50 nm – 1000 nm	300 nm – 10 μm	100 μm	1-2 μm	10 – 20 μm	20 – 60 μm
Viscosity limitation	No	Yes	No	Yes	Yes	Yes

Multi-needle electrospinning was developed to increase the nanofiber production (g/h) compared with single-needle electrospinning [140-142]. For instance, in multi-jet electrospinning, the porous cylindrical tube is filled with a polymer solution and each hole inside the tube produces one jet, forming many fibers at the same time. Needleless electrospinning has been recently developed to overcome the limitations linked to the use of capillaries and needles (**Figure 13**) [142]. In this technique, waves of an electrically conductive polymer solution self-organize at the mesoscopic scale and form jets when the electric field intensity is higher than a critical value. Nanospider electrospinning, which is based on a roller electrospinning set-up (power supply, tank, rotating electrode, collector and supporting material), is used for continuous production of nanofiber layers. Specifically, the roller spinning electrode is partially immersed in a tank of the polymer solution and the collector is at the top of the spinner [142].



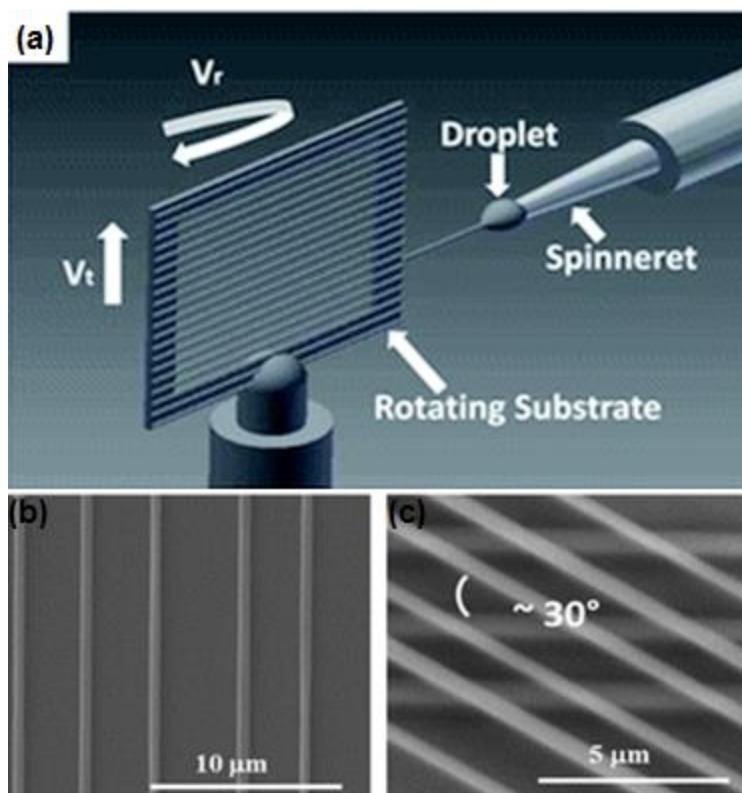


**Figure 13.** Different types of needleless electrospinning set-ups: **(a)** cylinder (the lower end is immersed in the polymer solution), **(b)** disk dipped in the polymer solution; **(c)** rotating spiral coil immersed in the polymer solution; and **(d)** rotating ball dipped in the polymer solution [142].

### 2.2.2. Alternative spinning approaches

Non-electrospinning (needleless spinning) techniques allow fabricating nanofibers starting from much higher precursor concentrations. These techniques require less solvent, increase productivity, and lower the production cost. Blowing bubble spinning (gas-jet spinning), centrifugal spinning, and fiber drawing are three of the most common non-electrospinning nanofiber production techniques.

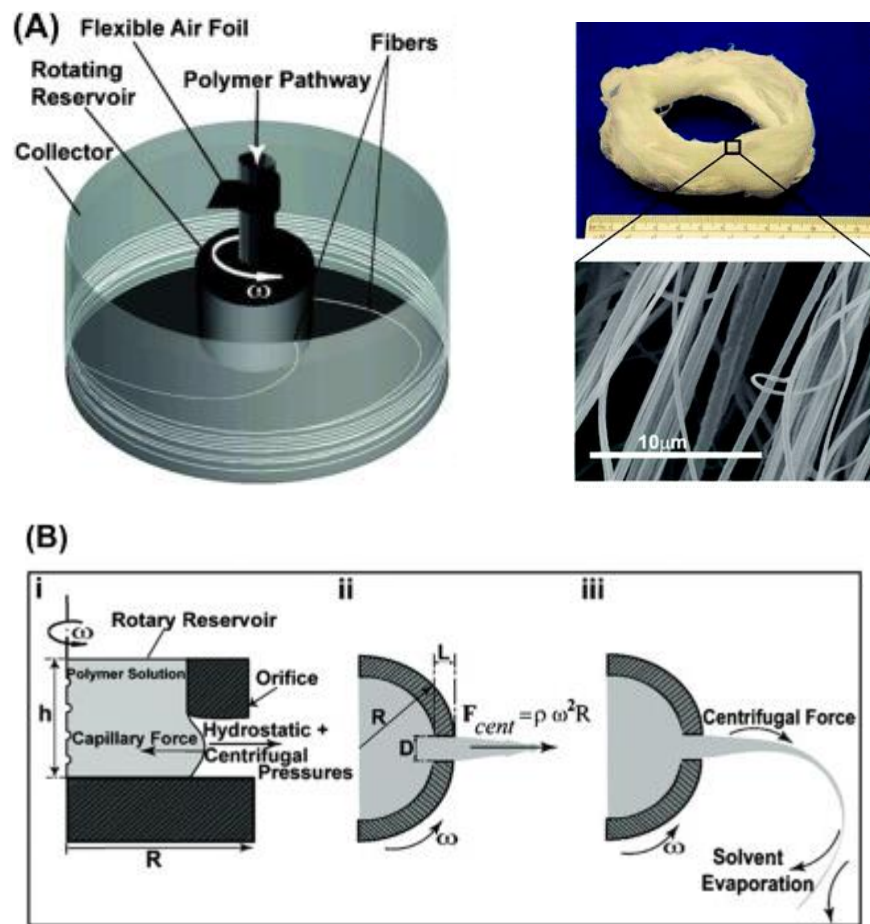
Differently from electrospinning, the drawing technique produces single nanofibers. This method uses a free rotating micropipette spinneret and a substrate for drawing polymer lines on flat substrates. As shown in **Figure 14**, a sharp probe tip is used to form polymer droplets. The single nanofibers can be drawn from polymer droplets at a specific rate, in the function of the polymer type [143]. The polymer solution extruded from the micropipette is deposited on the substrate and the movable micropipette spinneret contacts and pulls the solution to form a single nanofiber. The most critical processing parameters are the polymer type, the polymer solution concentration and viscosity, the micropipette spinneret configuration and rotation movements, and the substrate shape and micro-movements. The drawing technique major advantages are the possibility of studying individual nanofibers, and the minimal demands on the device. The major drawback is that the fibers can be drawn only for a specific amount of time. Indeed, due to solvent evaporation, the droplet viscosity progressively increases and the droplet volume decreases over time, thus modifying the fiber diameter [143]. To solve this problem, hollow glass micropipettes are used in which the polymer amount is maintained constant. This offers more flexibility in fiber drawing and in waiting time before drawing, as well as in drawing speed and viscosity. Consequently, fiber drawing can be repeated and the dimensions of the fabricated fibers can be better controlled [144].



**Figure 14.** Schematic representation of the drawing technique for the fabrication of micro/nanofibers: (a) drawing-spinning set-up and (b,c) SEM images showing single- and double-layer structures obtained using this method [143]. Copyright @ 2014, American Chemical Society.

In centrifugal spinning, nanofibers are fabricated by centrifugal forces, like cotton-candy production. Figure 15 shows a typical cylinder-shaped spinning head design. Centrifugal spinning can spin nanofibers directly from a polymer solution. Typically the nozzle diameter and length are the most important factor for controlling the fiber diameter and morphology. Compared with solution electrospinning, centrifugal spinning does not require high voltage, gives high production yields, has a simple structure, is environmentally friendly (no pollution), and can be used with high polymer materials. The polymer melts or solutions are fed from an extruder or a syringe pump into a rotating chamber, consisting of two or more orifices [145]. When the centrifugal force

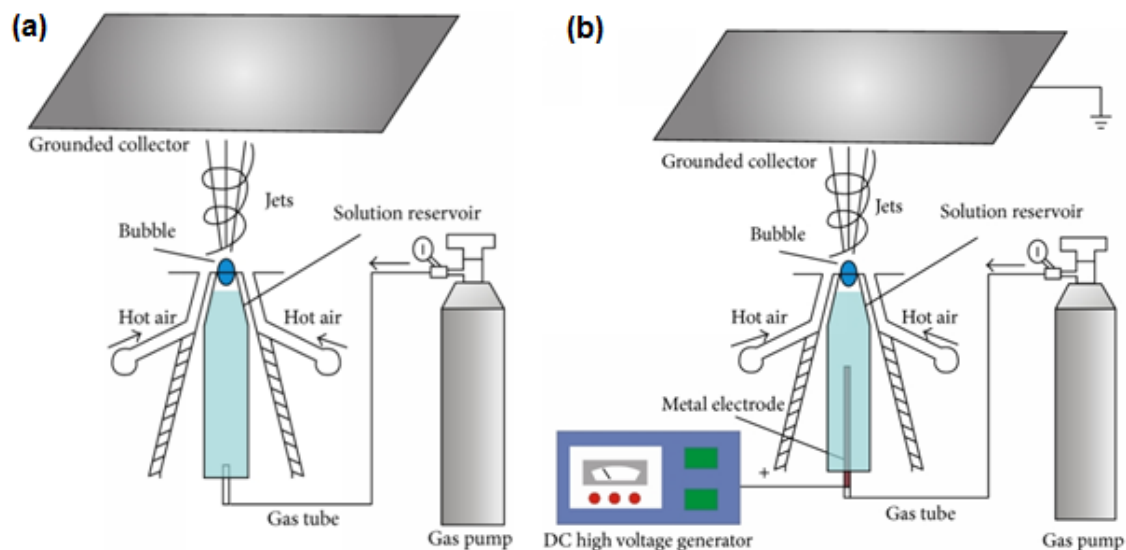
goes above a certain limit (the surface tension and the viscosity of the solution or melt), the polymer jets exit from the orifices, elongate, and the solvent evaporates until the nanofibers reach the collector plane. The main parameters are the chamber angular velocity, the orifice configuration and radius, the solution concentration and viscosity, the melt temperature and viscosity, the solvent evaporation rate, and particularly the orifice-collector distance [146]. If this distance is short, there will not be enough time to allow solvent evaporation. F



**Figure 15.** Cylinder-shaped centrifugal spinning technique: (A) Rotary jet spinner consisting of a perforated reservoir (internal volume of 700 mL and external diameter of 12.5 mm) with two sidewall orifices (orifice diameter of 340 μm and length-to-diameter ratio of 9) along with photoimage and

SEM image of the produced fibers. (B) Magnified view of the presumed formation mechanism of nanoscale fibers through the centrifugal spinning system: (i) jet initiation, (ii) jet extension, and (iii) solvent evaporation [146]. Copyright 2010, American Chemical Society.

Bubbfil spinning employs polymer solutions or polymer melts to produce discontinuous or smooth nanofibers by using blowing air, mechanical or electrostatic forces to overcome the surface tension. Blow bubble spinning, membrane-spinning, and bubble-electrospinning are the main bubbfil spinning techniques. With bubble spinning, the fiber production rate is much higher than that of electrospinning [52]. In blown bubble spinning, a compressed gas (e.g., air, N<sub>2</sub>) is used as the driving force for fiber formation through a concentric nozzle system, and also facilitates solvent evaporation (**Figure 16a**). The most critical processing parameters are the gas pressure, solution injection rate, nozzle-collector distance, and nozzle configuration and diameter [52]. Bubble electrospinning and air-jet assisted bubble electrospinning have been developed by adding a small electronic field that acts as an acting force for fiber deposition on the collector (**Figure 16b**)[147]. This technique is used for electrospinning high molecular weight polymers that cannot be fabricated with the standard electrospinning set-up because of the high surface tension of their Taylor cone. Melt-blowing is another gas-assisted spinning method that is used for spinning materials with low electrical conductivity or dielectric constant [52],[147].



**Figure 16.** Schematic representation of the air-assisted fiber-spinning system used for: (a) Blown bubble spinning (blowing air is the only acting force), and (b) Bubble electrospinning for tunable bubble size [147]. **Copyright Matéria**, 2014.

Flash-spinning is used to produce fibril strands [11]. It is suitable for difficult-to-dissolve polymers, such as polyolefins and high molecular weight polymers. Typically, a highly saturated solution of polymer/spin agent (solvent) is decompressed through a spin orifice at low temperature and substantially low pressure to generate plexi-filamentary film-fibril strands. The spin agent (solvent) evaporation splits the polymer into a fibril. The spin agent should exhibit specific characteristics: (i) non-solvent to the polymer below its normal boiling point; (ii) two-phase dispersion with the polymer at low pressure; (iii) formation of a solution with the polymer upon increase of the solution pressure; and (iv) vaporization when the flash is released into a low-pressure zone [11].

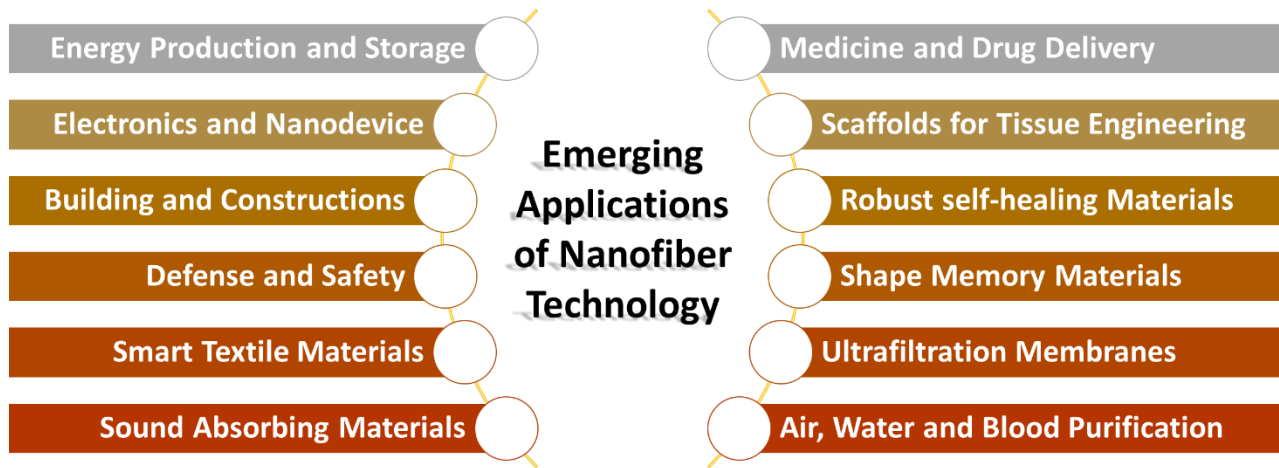
Many other non-electrospinning techniques have been described in the literature. For instance, laser spinning has been developed to produce ultra-long nanofibers with tailored chemical compositions [148, 149]. A high-power laser is used to melt a small volume of

precursor materials. Then, the injection of a supersonic gas jet leads to elongation of the molten precursor material and formation of amorphous nanofibers [150],[151]. Wet spinning is based on precipitation, whereby the polymer is drawn through a spinneret into a non-solvent [152, 153]. The prepared spinning material is extruded in the non-solvent and precipitation or coagulation occurs. This technique can be used to spin materials with low viscosity and that cannot be spun with the other available spinning methods [153]. The islands-in-sea spinning method involves melt spinning a ‘sea’ and an ‘island’ part of the polymer at a speed of 400 to 6,000 m/min [134]. Upon dissolution and removal of the ‘sea’ polymer from the composite fiber, a group of fine fibers is obtained with a thickness from 10 to 1,000 nm [134]. This technique offers some attractive advantages, such as high spinneret density and polymer choice flexibility. The cross-sectional area and the number of islands depend on the spinneret hole shape and diameter and the polymer distribution in the distribution plates [134].

#### **4. Emerging Applications of Nanofibers**

Nanofibers are used in several commercial products. The global market for nanofiber-based products was worth \$276.8 million in 2014, and should reach nearly \$2.0 billion in 2020 [154]. In this section, we will discuss the current and emerging applications of nanofibers for (i) building materials and constructions (i.e. reinforced polymers, self-healing materials) [155], (ii) energy production, conversion, and storage (i.e., batteries, supercapacitors, fuel cells and solar cells) [156],[157], (iii) environmental improvement and protection (i.e., ultrahigh air filtration, wastewater treatment, and water purification) [158], (iv) biomedical applications (i.e., drug delivery system, blood purification, tissue engineering, wound healing) [159], and v) other

applications, including defense and security [160]. Figure 17 summarizes the emerging application of nanofiber in different fields.



**Figure 17.** Emerging applications of nanofibers technology in different fields.

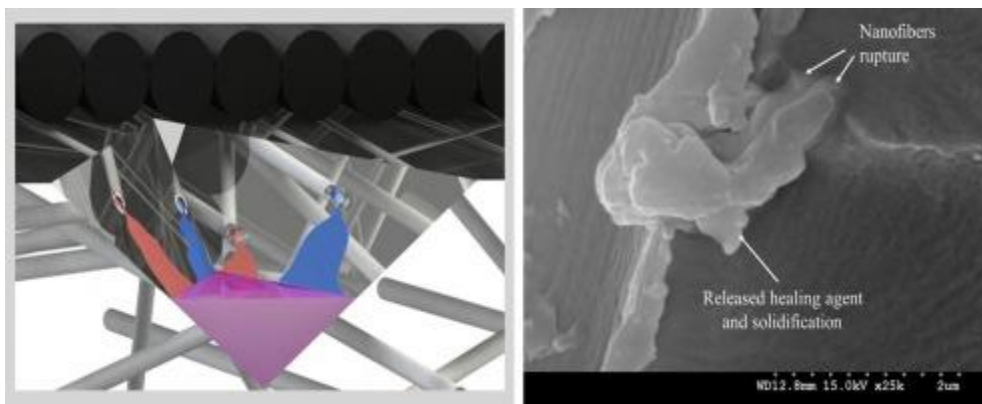
## 4.1. Reinforcing and Self-Healing Materials

The currently available polymeric materials do not meet all the requirements for specific commercial applications. Compared with macrocomposites, nanofiber/polymer nanocomposites display better features (e.g., mechanical strength) and minimal nanofiller loading [155]. The control of size, morphology, and dispersion of nanofiller materials is of crucial importance. Continuous nanofibers display a better interfacial adhesion than conventional fibers due to their large surface-to-volume ratio [161]. Many studies on nanofiber composites have focused on the use of carbon nanofibers for reinforcement material. However, the dispersion of carbon nanofibers into the polymer matrix increases with the increase of the matrix viscosity [162]. To overcome this limitation, new approaches have been developed in which carbon nanofiber sheets (nanosheets), made through the filtration of well-dispersed carbon nanofibers in controlled processing conditions, are integrated into composite laminates in an autoclave. CNFs have



replaced carbon nanofibers in several applications. Indeed, they show several advantages, including the abundance of raw material, easy preparation, and lower cost. Moreover, CNFs can be blended with a polymer at fiber contents up to 70 wt.%, while maintaining the polymer transparency (resin matrix) because they do not scatter visible light. The chemical compatibility between CNFs and polymer plays a major role in the particle dispersion in the matrix and in the adhesion between phases.

Self-healing materials, which can heal in response to damage, are one of the smartest nanofiber applications (**Figure 18**). Brittle polymers, such as epoxies (fiber-reinforced), are often used in the automotive, aircraft and aerospace industries [155, 163]. However, they are particularly susceptible to damage in the form of cracks (delamination between layers) deep within the structure, thus making their detection and repair nearly impossible. Typically, core-shell nanofibers are loaded into self-healing materials to store the monomer in the nanofiber core, while the curing agent (a trace quantity of a catalyst) is distributed in the matrix [164]. External stimuli (heat, light, or pressure damage volume) initiate the monomer polymerization upon contact with the catalyst. In the presence of cracks or delamination in the core-shell nanofibers, the released monomers will polymerize and heal the damage. The porous network structure of electrospun fibers allows the uniform coverage of the material with minimal changes in the bulk material properties. Fang *et al.* [165] described robust self-healing hydrogels in which a cross-linked nanofiber network containing redox agents acts as the healing layer. When the healing layer is embedded in the crack, it accelerates the self-healing process (50% reduction of the healing time) with 80% healing efficiency without compromising the mechanical properties [165].



**Figure 18.** Facile strategy toward fabrication of highly responsive self-healing carbon/epoxy composites via incorporation of healing agents encapsulated in poly(methylmethacrylate) nanofiber shell [163]. Copyright Elsevier, 2018.

## 4.2. Nanofibers for Energy Harvesting and Storage

Much effort has been focused on the development of renewable energy harvesting and storage devices, such as: (i) fourth-generation photovoltaic solar cells for more efficient and cost-effective use of solar energy [166], (ii) photoelectrochemical devices for water electrolysis to generate  $H_2$  and  $O_2$  that are used in fuel cells to generate electricity [167], and (iii) flexible batteries and supercapacitors for efficient energy storage by portable devices [168]. Electrospun nanofibers have been used as building blocks for optoelectronics and nanoelectronics (e.g., light emitting, photodetectors, transistors, piezo- and thermoelectric generators, and actuators) that display low weight, attractive mechanical properties and good potential for widespread implementation at low cost, and for application in human motion monitoring devices and robotics [169],[170]. The current challenges include improving the energy harvesting and conversion efficiency, energy/power density, charge and discharge rate, extending the device life with reversibility, and reducing the production and operation costs [171]. Nanofibers have a

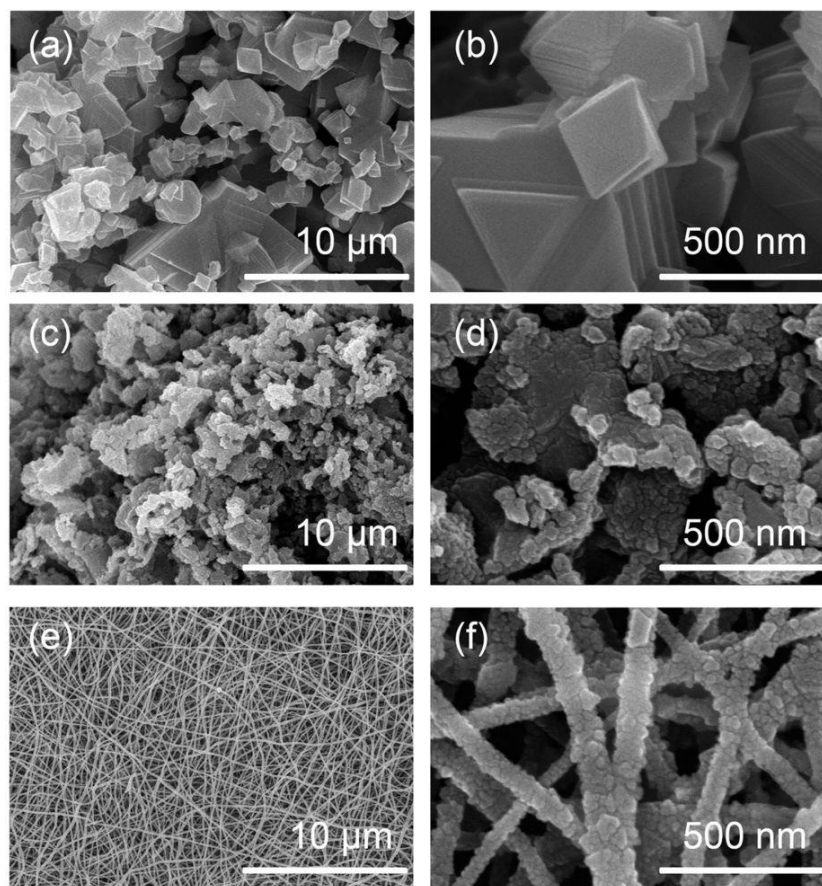
shorter diffusion path compared with the commonly employed nanopowder materials; however, they might display faster intercalation kinetics due to their high area/mass ratio. Several groups have investigated the use of nanofibers as electrode and membrane materials for flexible batteries, superconductors, solar cells, and fuel cells [131, 172]. Indeed, the nanofiber small diameter, high surface area, and porous network structure allow the rapid storage of electrolytes and support the long-term electron/ion transport. The nanofiber flexibility, electrical conductivity or isolation, and ionic permeability have improved the performance of new-generation energy storage and energy harvesting devices. By modulating the nanofiber properties (bulk content, surface texture, porosity, surface functionalization, fiber diameter, etc.), many active sites can be obtained and the large volume changes can be effectively buffered during electrochemical reactions [131].

#### **4.2.1. Electrode and Membrane Materials for Batteries**

An electric battery includes one or more cells in which chemical reactions create a flow of electrons in a circuit. All batteries are made of three basic components: one anode (the negative electrode), one cathode (the positive electrode), and one electrolyte that can chemically react with the two electrodes. Rechargeable lithium-ion (Li-ion) batteries (Li-S and Li-O<sub>2</sub> batteries) are among the most promising battery types. Although they are currently used in many portable and personal electronic devices, their widespread implementation is still hindered by several factors, particularly the limited capacity and efficiency of the electrode materials and their high cost. Therefore, new electrochemically active alternatives are needed with higher energy density and capacity, long life cycle, and reduced costs. Due to their excellent electrochemical performance and their high degree of scalability, carbon and metal oxide

nanofibers are ideal candidates for next-generation anodes, for example for electric vehicles [173].

Novel nanofiber technologies might allow the development of new cathode materials for advanced rechargeable Li-ion batteries. Li-based metal oxide nanofibers are cheap and environmentally friendly material for cathodes in Li-ion batteries [131, 174-176]. As metal oxide nanofibers offer a relatively large number of Li-insertion sites, the charge-transfer resistance at the interface between the electrolyte and active electrode materials is reduced. For example, Vu *et al.* [177] assessed three types of  $\text{Li}_{1.5}\text{MnTiO}_{4+\delta}$  (LMTO) electrodes (microparticles, nanoparticles, and nanofibers) for Li-ion batteries (**Figure 19**). LMTO nanofibers are constituted of uniformly arranged LMTO NPs that are held together in long fibers (30  $\mu\text{m}$  in length and 80 nm in diameter) by the removable polymer network. The morphology of LMTO nanofiber gives a good contact with the electrolyte, longitudinal electron transport, effective  $\text{Li}^+$  exchange with excellent connectivity between the electronic and ionic components, and shorter diffusion pathways due to the particle nanoscale dimension. PAN and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  can be used to produce  $\text{Co}_3\text{O}_4$ /carbon nanofibers by electrospinning. When  $\text{Co}_3\text{O}_4$ /carbon nanofibers are used as  $\text{O}_2$  electrode in Li- $\text{O}_2$  batteries, they exhibit a higher initial discharge limit of 760 mAh/g.



**Figure 19.** Different types of LMTO cathode materials for Li-ion batteries. SEM images of (a,b) LMTO microparticles, (c, d) NPs, and (e, f) ultra-long nanofibers [177]. Copyright Nature, 2017.

The anode materials of Li-ion batteries are typically carbon-based (e.g., carbon nanobeads, nanospheres, nanotubes, or nanofibers, and their composites, and graphene) due to its good electrical conductivity and excellent chemical stability (**Figure 20**) [178]. Hollow carbon nanofibers are particularly attractive because of their high dimensional flexibility, the high energy density per unit weight, large capacity, high charge/discharge rate, and extended cycle life. Li *et al.* [179] developed hollow carbon nanofibers with good and durable lithium-storage capability. The anode made of these carbon tubes shows a very good reversible capacity

(1635 mA.h.g<sup>-1</sup> at 100 mA.g<sup>-1</sup> after 300 cycles, and 1103 mA.h.g<sup>-1</sup> at 500 mA.g<sup>-1</sup> after 500 cycles). Due to their excellent electrochemical performance, nitrogen-doped hollow carbon nanofibers are a potential anode material for next-generation Li-ion batteries. The hollow structure offers a large electrode/electrolyte interface and a short Li-ion diffusion path [179].

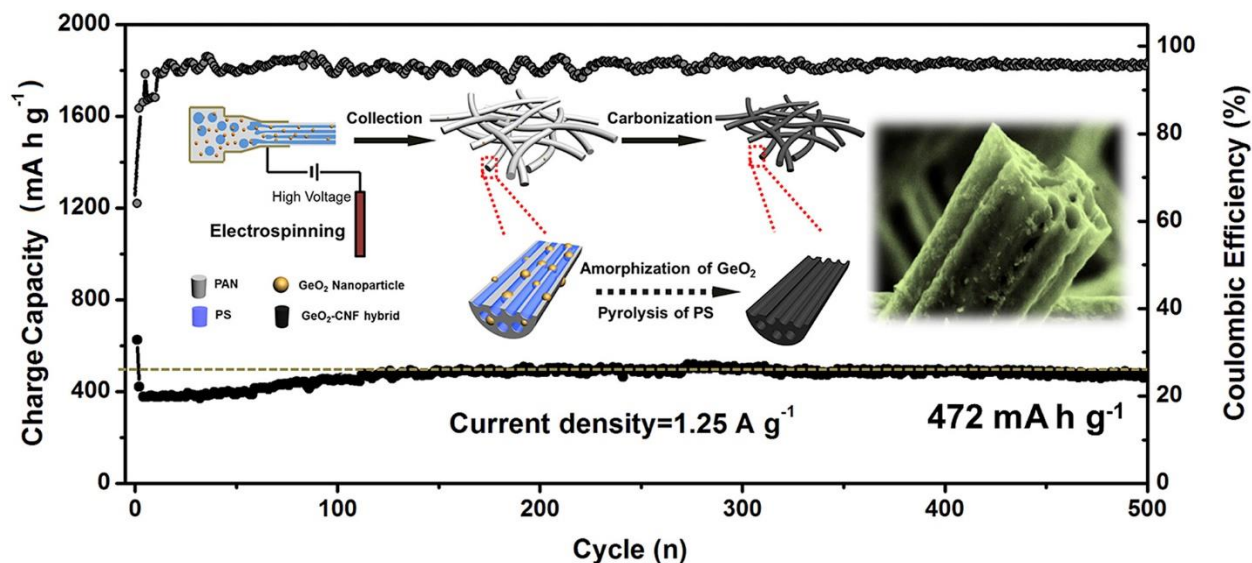
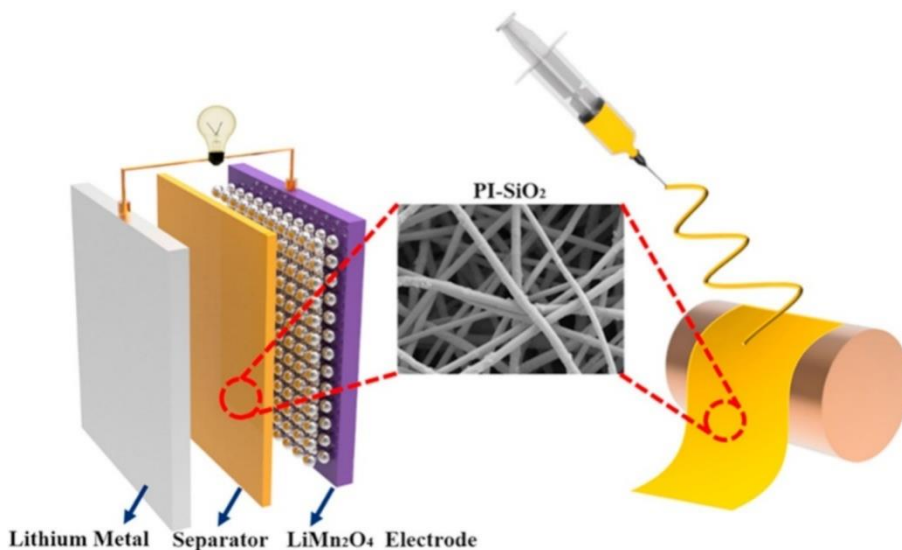


Figure 20. Channelized carbon nanofiber with uniform-dispersed GeO<sub>2</sub> as anode for long-lifespan lithium-ion batteries [178]. Copyright 2017, Elsevier.

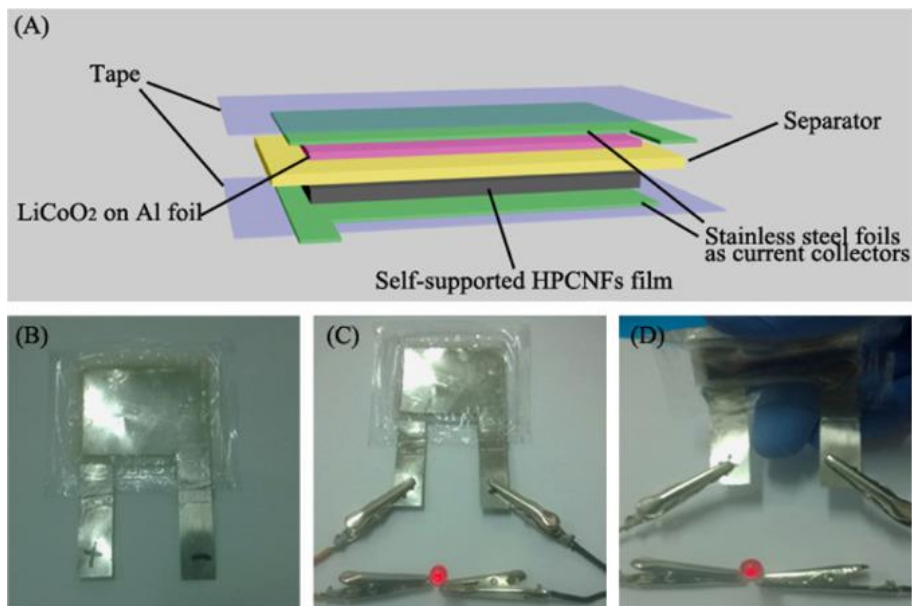
The separator (membrane) in the electrochemical cells plays an important role in regulating cell kinetics, preventing electronic contact between electrodes, and maintaining the liquid electrolyte in cells. Consequently, the Li-ion battery performance can be influenced by the choice of the separator. During charging, Li-ions de-intercalate from the Li-based metal oxide cathode, pass through the conductive electrolyte and then intercalate in the carbon-based anode [1, 179]. A porous permeable membrane can prevent short circuits resulting from the direct contact between electrodes, and regulate the transfer of Li ions from the cathode to the anode. Electrons travel through the external electrical circuit and interact with Li<sup>+</sup> in the electrode. The

commercial separators (e.g., polyolefin membranes) have good chemical stability, suitable thickness, and reasonable mechanical strength. However, their major limitations (low porosity, poor thermal stability, and poor wettability) lead to high cell resistance, reduced energy density, and low rechargeability of Li-ion batteries. It was recently reported that polymer nanofiber mats [e.g., polyvinylidene fluoride [180], poly(methyl methacrylate) [181], polyoxyethylene [182] and polyimide (PI) [183]] can be used as separator in Li-ion batteries due to their low electrolyte leakage, high dimensional flexibility, and extended cycle life [184]. For example, Wang *et al.* [92] prepared a PI/silica nanofiber membrane by electrospinning (**Figure 21**) that showed excellent electrolyte wettability (electrolyte uptake of about 2400%), improved conductivity and thermal stability, and good mechanical flexibility when used as a separator for Li-ion batteries [185].



**Figure 21.** Polyimide/silica nanofiber membrane (separator) with improved flexibility, thermal stability, and excellent wetting properties for high safety Li-ion batteries [92]. Copyright Elsevier, 2017.

The increasing demand for portable and flexible electronic devices has led to the development of flexible batteries. The nanofiber technology offers new architectural design opportunities for the development of the next-generation, highly flexible energy storage devices. Recently Hu's group [186] produced a new class of highly flexible batteries, called "h-nanomat cells", based on the unitized separator/electrode assembly architecture. The "h-nanomat cell" includes (i) a binder-free electrode based on netted carbon nanotubes (CNT) and (ii) a cellulose nanofiber separator membrane. H-nanomat electrochemical execution, shape flexibility and safety tolerance are much superior compared with those that can be obtained with conventional batteries. Li *et al.* [187] developed highly flexible Li-ion batteries in which the anode is made of flexible highly porous carbon nanofibers and the cathode of commercial LiCoO<sub>2</sub> loaded on Al foil (**Figure 22**). Thanks to the highly porous carbon nanofibers, these batteries have a high reversible capacity (1780 mAh g<sup>-1</sup> after 40 cycles at 50 mA g<sup>-1</sup>) and very long cycle life (1550 mAh g<sup>-1</sup> after 600 cycles at 500 mA g<sup>-1</sup>).



**Figure 22.** Highly porous carbon nanofibers (HPCNFs) for flexible Li-ion batteries: (A) Flexible Li-ion battery in which an HPCNF film is used as anode, and commercial LiCoO<sub>2</sub> loaded on Al



foil as cathode; (B–D) Photographs of the flexible battery (B) and of a red LED powered by the flexible battery in the flat (C) and bent (D) state [187]. Copyright Elsevier, 2015.

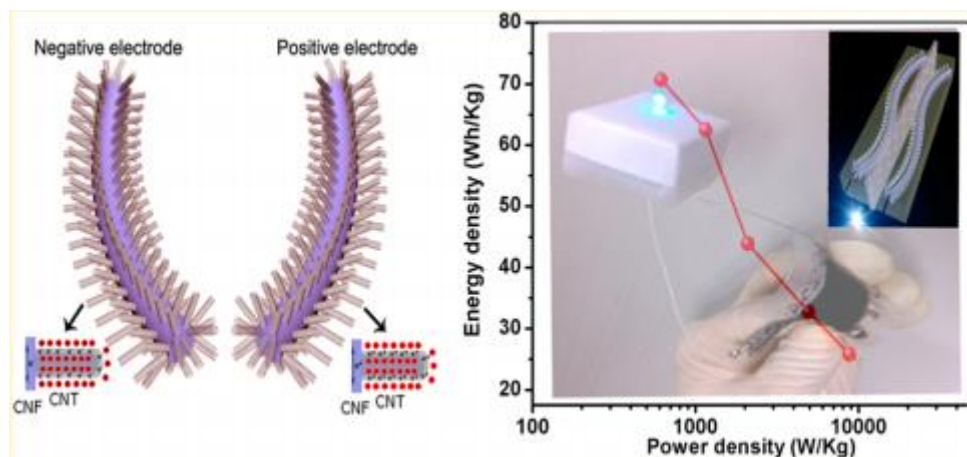
#### **4.2.2. Electrode and Membrane Materials for Supercapacitors**

Supercapacitors are energy storage devices with short charging time, good temperature characteristics, long lifetime, and low energy consumption. Based on the type of electrode material, supercapacitors are divided into three main categories: (i) Electric double layer capacitors that store energy by adsorption and desorption of ions at the interface between the electrode material and the electrolyte; (ii) Pseudocapacitors in which the electrode material actively stores a large amount of charge through rapidly reversible redox reactions (chemical adsorption/desorption); and (iii) Hybrid capacitors in which one of the electrodes displays mainly electrochemical capacitance and the other mostly electrostatic capacitance.

Although supercapacitors show excellent cyclability, their low energy density compared with batteries limit their application. Nanofiber electrodes are interesting because their energy density is higher than that of the electrodes used in conventional capacitors. Moreover, they show excellent cycling stability due to their non-faradic and highly reversible energy storage mechanism. The operational voltage is another crucial factor that influences the supercapacitor performance. Therefore, much effort has been put on increasing the energy density by developing nanofiber materials with high surface areas. Carbon nanofibers are particularly suitable because of their homogeneous high surface area, good electrical conductivity, and non-requirement of conductive additives. Carbon fibers have been widely used in flexible and binder-free electrodes with various electrochemically active materials (e.g., noble metals) that display good capacitance performance [188-190]. The performance of carbon nanofiber electrodes has

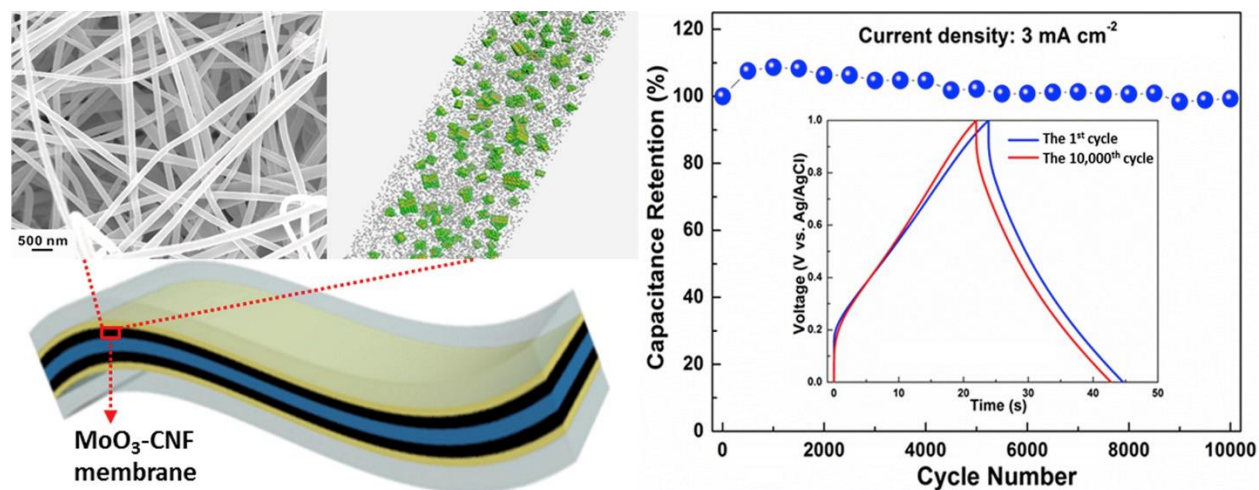
been greatly increased by controlling the nanofiber porosity through the addition of pore-forming agents during their preparation. Fan *et al.* [191] used carbon nanofibers as cathodes and MnO<sub>2</sub>/graphene as anodes to produce high energy density supercapacitors with superior electrochemical performance (energy density of 51 Wh.kg<sup>-1</sup>, voltage range of 0–1.8 V, and 97% of specific capacitance retained after 1000 cycles).

Flexible supercapacitors could be used in wearable, miniaturized, portable, large-scale transparent and flexible electronic devices. Electrospinning opens new opportunities for the development of highly flexible supercapacitors. Zhang *et al.*[192] used electrospinning followed by carbonation in an inert atmosphere to prepare a hierarchical 3D-structure of aligned CNTs that were perpendicularly grown on carbon nanofibers. These highly structured CNTs are very good candidate electrode material for flexible supercapacitors (**Figure 23**). When using an ionic liquid electrolyte, the flexible CNT/carbon nanofiber-based supercapacitors deliver high specific energy of 70.7 Wh/kg at a current density of 0.5 A/g at 30°C, and retain 97% of the initial capacitance even after 20,000 cycles. Huang *et al.*[193] developed high-performance wearable supercapacitor fabrics, based on flexible nickel–cotton fabrics on which CNT-containing nanofiber webs were directly electrospun without any post-treatment. These wearable supercapacitor fabrics are characterized by the high areal capacitance (973.5 mF cm<sup>-2</sup>; 2.5 mA cm<sup>-2</sup>) and very high stability in the bend test with a very small bending radius (2 mm).



**Figure 23:** Schematic representation of flexible supercapacitors: (left) 3D-structure of vertically aligned CNTs directly grown on carbon nanofibers (right) and a photograph of a flexible CNT/carbon nanofiber-based supercapacitor [192]. Copyright American Chemical Society, 2014.

Near-field electrospinning techniques can be used to integrate micro-energy storage devices, such as micro-supercapacitors, in other flexible and miniaturized systems. For instance, Shen *et al.* [194] integrated a polypyrrole nanofiber-based micro-supercapacitor in an energy harvester and other circuits. During the deposition of polypyrrole nanofibers onto the electrodes by near-field electrospinning, the substrate was fixed on a computer-controlled X–Y motion stage. The prototype shows high capacitance (up to  $0.48 \text{ mF cm}^{-2}$ ) and its performance is not modified during the bend test [194]. Tian *et al.* developed flexible binder free, self-supported membranes of carbon nanofibers with embedded  $\alpha\text{-MoO}_3$  nanoparticles by using electrospinning followed by thermal carbonation. The developed electrodes showed fast intercalation pseudocapacitance, high specific capacitance ( $544 \text{ mF cm}^{-2}$  at  $1 \text{ mA cm}^{-2}$ ) and an excellent cycling stability (106.7% retention after 20,000 cycles) [131].



**Figure 24.** Flexible, free-standing and binder-free membranes of carbon nanofibers with embedded  $\alpha$ -MoO<sub>3</sub> nanoparticles (MoO<sub>3</sub>-CNF) were fabricated by electrospinning. Copyright 2017, Elsevier [131].

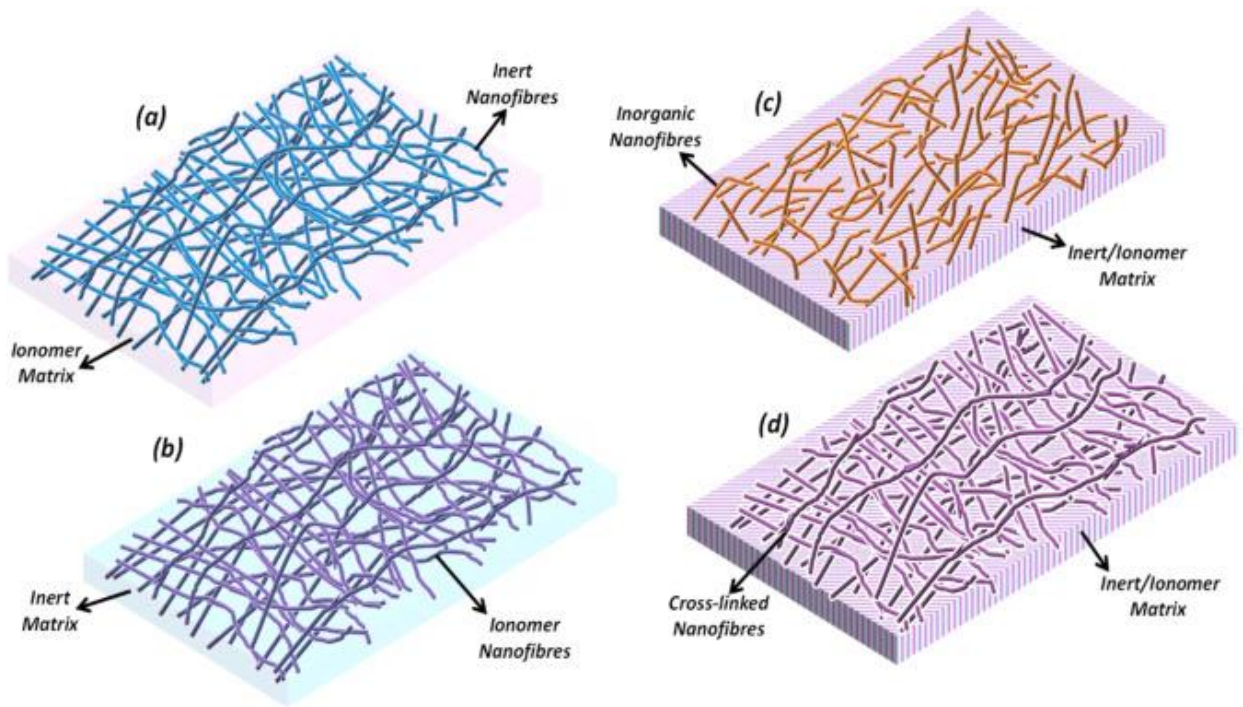
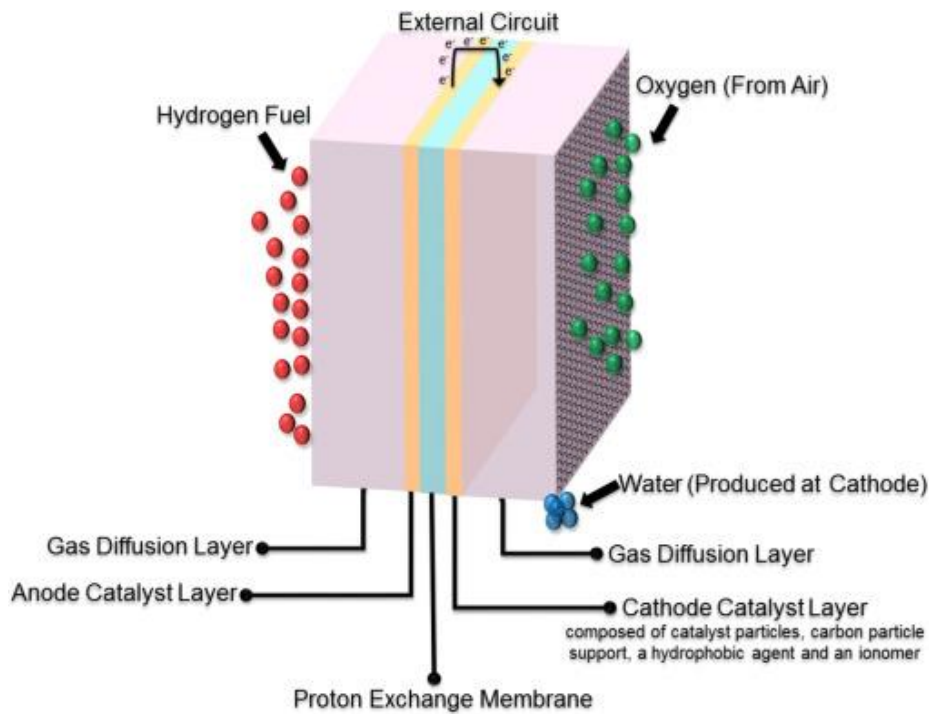
#### 4.2.3. Membrane and Electrode Materials for Fuel Cells

A fuel cell is an electrochemical device that converts chemical energy from fuel (e.g., O<sub>2</sub> and H<sub>2</sub>) into electricity through the electrochemical reaction of H<sub>2</sub> with O<sub>2</sub> or another oxidizing agent. There are several types of fuel cells with different characteristics and configurations: proton exchange membrane fuel cells (PEMFCs), direct methanol fuel cells, solid oxide fuel cells, molten carbonate fuel cells, phosphoric acid fuel cells, and microbial fuel cells (MFCs). Like a battery, in a fuel cell, the anode and cathode are separated by a cation-specific membrane [172]. Figure 25 shows different types of electrospun nanofibre membranes used electrochemical cell, for example, fuel cell.

PEMFCs consumes H<sub>2</sub> and O<sub>2</sub> to produce electricity [195]. The oxidation reaction occurs at the anode. H<sub>2</sub> loses its electrons, and atoms become ionized to form H<sup>+</sup>. The electrons travel through wires to provide a current to reduce O<sub>2</sub> (usually from the air) at the cathode. The oxygen

and hydrogen ions produced in the electrolyte combine and form water (H<sub>2</sub>O) as a by-product that exits the fuel cell. H<sub>2</sub> and O<sub>2</sub> are separated by a proton exchange membrane to prevent their direct contact in the fuel cell. The electrodes used in PEMFCs are made of a thin film of catalyst particles (Pt or Pd on carbon powder) bound to a polymer and with a porous charge collector for charge transfer [1]. As the Pt-carbon catalyst is the most expensive component of the fuel cells, electrospun carbon nanofibers have been used as an alternative catalyst due to their high catalytic efficiency and durability, and larger catalyst surface area for H<sub>2</sub> and O<sub>2</sub> reactions. The pores between nanofibers in the mat electrode facilitate water removal [1].

Implantable glucose fuel cells are a new generation of fuel cells used as an autonomous energy supply for medical implants. They work by oxidizing glucose at the anode, and by reducing the oxidant at the cathode. Due to the ubiquity of glucose and oxygen in the extracellular fluid, they can operate indefinitely [196]. The glucose fuel cells rely on the electrochemical reaction between oxygen and glucose at two separated Pt NP electrodes as a catalyst. As Pt NPs can catalyze glucose oxidation and also oxygen reduction, a membrane is used to avoid the concomitant presence of glucose and oxygen at the two electrodes. Liu *et al.* [197] recently developed a glucose fuel cell in which a Pt NP/multi-walled carbon nanotube (MWCNT)/bacterial cellulose (BC) nanofiber membrane was the anode and a platinum sheet was the cathode. The combination of BC nanofibers and Pt NP/CNTs in the conductive anode membrane allows glucose oxidation. The electrochemical performance of this glucose fuel cell ( $2.24 \pm 0.20 \mu\text{W cm}^{-2}$ ) is close to that of the commercial glucose fuel cell “RANEY®-type”. This system is a step forward to the development of an implantable glucose sensor targeted to patients with diabetes [198] for accurate automated insulin delivery in response to the local glucose concentration.



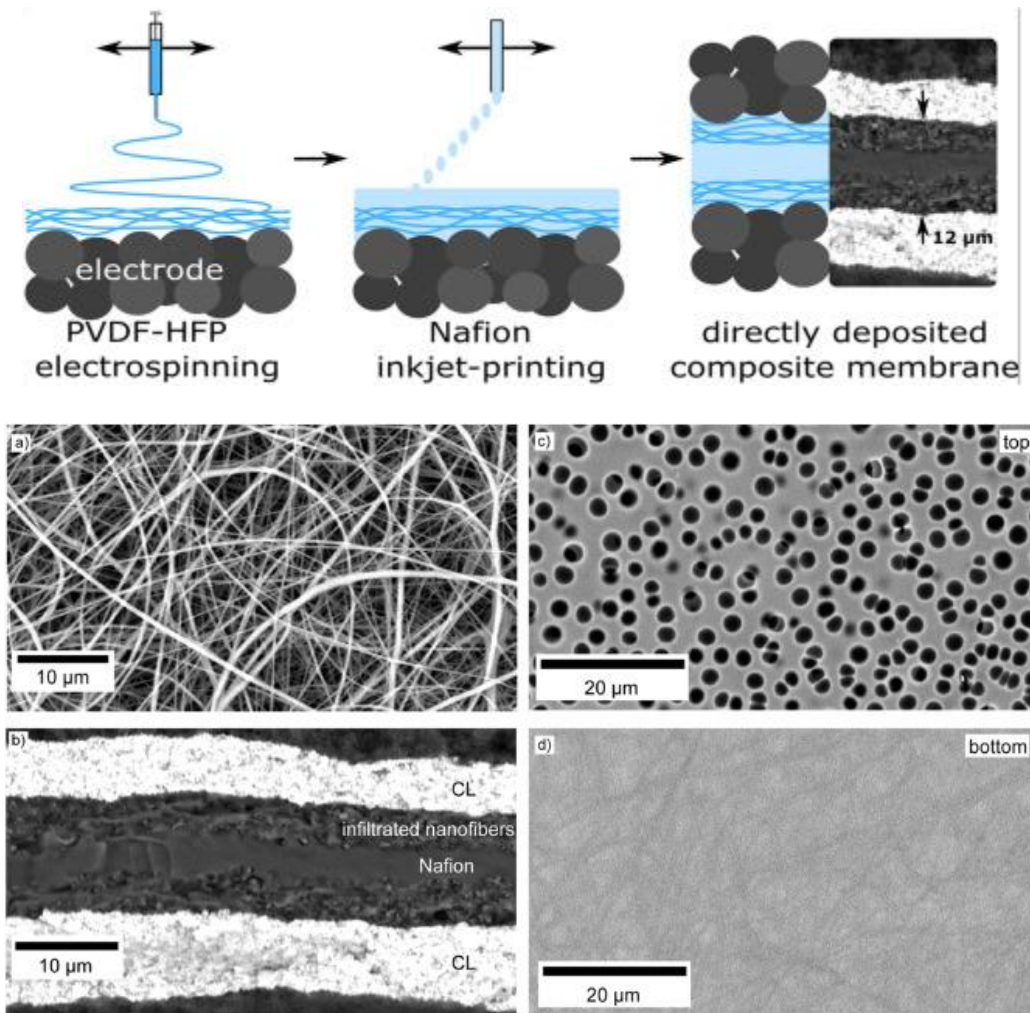
**Figure 25.** Schematic representation of a membrane electrode assembly in fuel cells and different morphologies of electrospun nanofibre membranes (a). a proton conducting polymer surrounding

an electrospun mat of nanofibres of an inert reinforcing material, (b). an inert material surrounding a 3D interconnected mat of nanofibres of a proton conducting polymer, (c). an electrospun (proton conducting or non-conducting) inorganic mat embedded into a (proton conducting or non-conducting) polymer matrix, (d). a cross-linked electrospun polymer mat embedded in a polymer/inert matrix [198]. Copyright @ 2016, Elsevier.

Several groups have assessed the value of polymer nanofiber membranes as electrolyte membranes in PEMFCs. The key property of electrolyte membranes is their high proton conductivity and inhibition of electron transport. Protons are transmitted through the electrolyte membrane that contains distilled water, while electrons are transmitted externally. As distilled water is required for proton conductivity, water maintenance in the membrane is crucial. Nanofibers significantly improve the dimensional stability, mechanical properties, and lifetime of proton exchange membranes. Electrospun N-doped Fe/carbon nanofibers are an attractive low-cost catalyst for Pt and are more efficient than traditional carbon-supported catalysts [199]. With this catalyst, the membrane electrode shows volumetric current densities of 0.25, 3.3 and 60  $\text{A}\cdot\text{cm}^{-3}$  at 0.95, 0.9 and 0.8  $V_{\text{iR-free}}$ , respectively [199]. A proton exchange membrane has been developed also for direct methanol fuel cells [200].

MFC are bio-electrochemical devices that transform organic waste and microbes into electric current. They are cheap, self-sustaining, and adaptable catalysts that could use agricultural residues, urban waste, and industrial wastewater as carbon and energy sources [201]. Research has focused on strategies to increase MFC power output using more electrochemically active microbes. However, most MFCs are not suitable for high electricity production [202]. Recently, carbon nanofibers have been used as an efficient MFC anode due to their high

conductivity, stability, and biocompatibility. For instance, Jung and Roh reported that CNT/carbon nanofiber nanostructures in MFCs increase the power density by 1.8-fold compared with commercial graphite felt. Breitwieser *et al.* [203] fabricated 12  $\mu\text{m}$  thin nanocomposite fuel cell membranes by inkjet-printing Nafion ionomer dispersion into the pore space of poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) nanofiber mats (**Figure 26**). The fabricated fuel cell high power ( $0.19 \text{ W cm}^{-2}$ ), was about 1.7 times higher than that of the reference fuel cell ( $0.11 \text{ W cm}^{-2}$ ) at a lower ionic resistance [203].



**Figure 26.** Nanocomposite fuel cell membranes fabricated by inkjet-printing Nafion ionomer dispersion into the pore space of poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP)



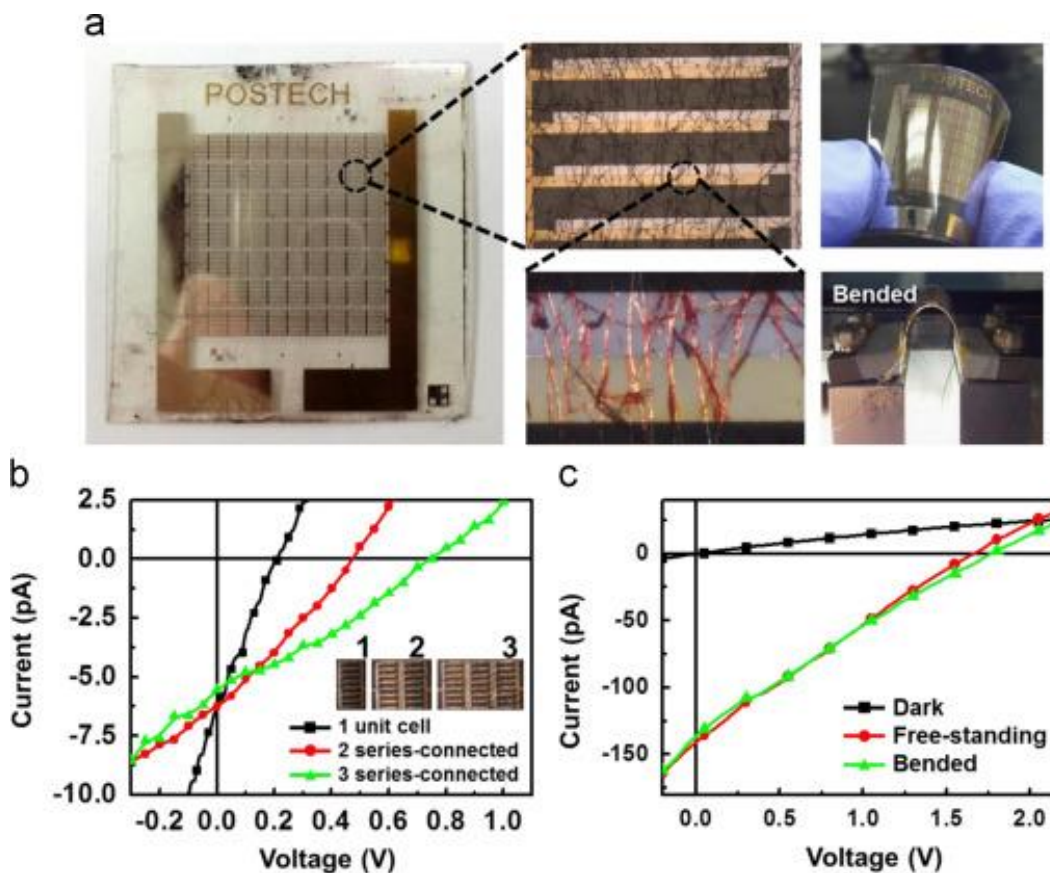
nanofiber mats: (a) SEM image of PVDF-HFP fiber mat on the gas diffusion electrode prior to Nafion infiltration, (b) Cryo-fractured cross-section of the MEA, showing the catalyst layers (CL) and the composite structure of the PEM: A pure Nafion layer is sandwiched between two Nafion-infiltrated layers of PVDF-HFP nanofibers resulting in a thin composite membrane of about 12  $\mu\text{m}$  total thickness. (c) Top view on the Nafion infiltrated PVDF-HFP fiber pore space on the GDE is shown and (d) Bottom view on the composite membrane is shown [203]. Copyright 2017, Elsevier.

#### **4.2.4. Membrane and Electrode Materials for Solar Cells**

A solar (photovoltaic) cell converts photons from the sun (solar light) into electricity (photovoltaic effect) through different steps: (i) light absorption and generation of electron-hole pairs or excitons; (ii) separation of charge carriers (electron-hole pairs); and (iii) separate extraction of such carriers to an external circuit. Currently, several solar cell types with different configurations and operating voltages are produced, including amorphous-silicon solar cells, crystalline silicon solar cells, polycrystalline Si solar cells, Cu-In-Ga-Se solar cells, dye-sensitized solar cells (DSSCs), perovskite solar cells, organic solar cells, luminescent solar concentrator cells, multi-junction solar cells, and monocrystalline solar cells.

Recent studies have shown that effective polymer solar cells can be developed using polymer nanofibers as light absorbing materials. A typical polymer solar cell contains three parts: (i) an anode made of indium tin oxide modified with PEDOT/polystyrene sulfonate; (ii) a cathode (Al electrode); and (iii) a light active layer inserted between the electrodes. Compared with silicon-based solar cells, polymer solar cells are lighter, cheaper, more flexible and can be directly fabricated into many flexible devices. Conjugated polymer nanofibers are the most

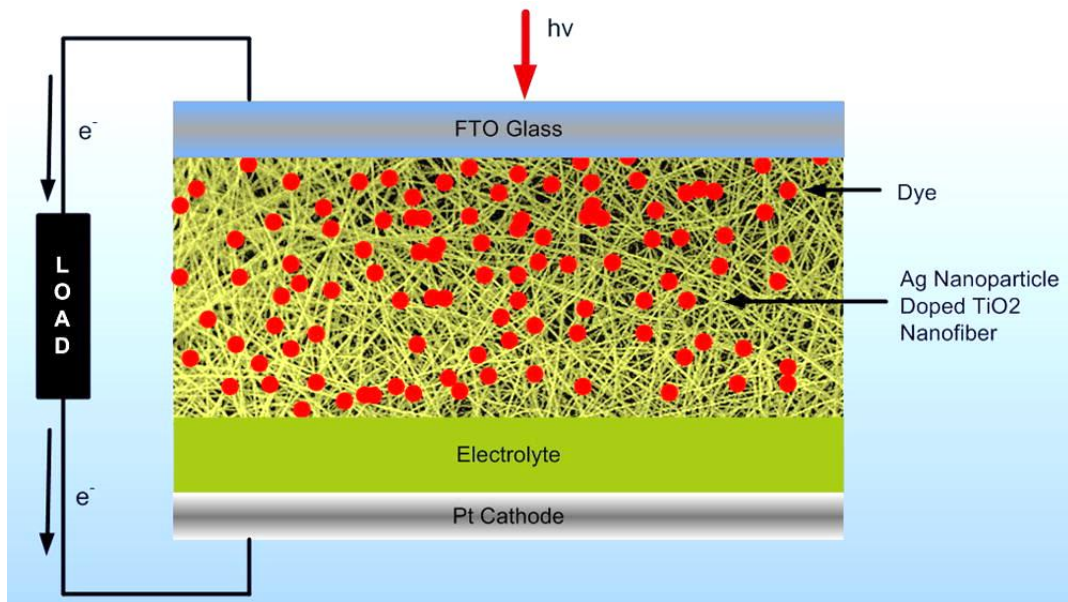
promising p-type material for producing flexible polymer solar cells [204]. Sundararajan and his coworkers [205] employed the coaxial electrospinning technique to produce organic semiconductor fibers made of poly(3-hexylthiophene-2,5-diyl)/phenyl C<sub>61</sub>-butyric acid methyl ester (core) and PVP (shell) that can be used for solar cells (**Figure 27**) [205].



**Figure 27.** Coaxial electrospinning technique to produce organic semiconductor fibers: (a) Photograph of the poly(3-hexylthiophene): phenyl-C<sub>61</sub>-butyric acid methyl ester nanofiber module device (25 mm<sup>2</sup>), and optical images of the interdigitated electrodes and crossed fibers that connect the electrodes, and images of the flexible module device under mechanical bending; (b) Current-voltage characteristics of the series-connected devices under illumination as a function of the number of series connections, and (c) Current-voltage characteristics of the

flexible module device (with 10 series-connections) constructed on the flexible plastic substrate and operated under mechanical bending (radius 5 mm) [205]. Copyright Elsevier, 2015.

DSSCs are an effective and cheaper substitute for the current p–n junction photovoltaic devices. In a typical DSSC, a porous layer of TiO<sub>2</sub> NPs covered with a molecular dye that absorbs sunlight is used as the light absorbing material. As TiO<sub>2</sub> NPs have photovoltaic properties but absorb only UV light, dyes are added to increase their efficiency. Spin coating, screen-printing, doctor blading, and CVD have been used to produce porous dye-TiO<sub>2</sub> nanofilms on fluorine-doped tin dioxide (FTO) or indium tin oxide as photoanode for DSSCs. The photoanode (dye-TiO<sub>2</sub>-FTO) is immersed in an electrolyte solution (I<sup>-</sup>/I<sub>3</sub><sup>-</sup>), above which is the cathode (glass plate with a thin Pt film as a catalyst) (**Figure 28**) [206]. The charge conduction can be increased by replacing the porous TiO<sub>2</sub> NPs with porous TiO<sub>2</sub> nanofiber mats because the nanofibers have reduced particle boundaries and higher specific surface area that can absorb more sensitizing dyes [207]. Recently, the surface of TiO<sub>2</sub> nanofibers has been modified with noble metal NPs (e.g., Ag, Au, Pt) to increase DSSC efficiency by plasmon enhanced optical absorption of such NPs. Jin *et al.* [208] showed that photoanodes made of TiO<sub>2</sub> nanofibers doped with Ag NPs significantly increase DSSC photocurrent density, leading to a conversion efficiency improvement of 25% compared with non-doped TiO<sub>2</sub> nanofibers.



**Figure 28.** A schematic representation of a dye-sensitized solar cell with dye-covered Ag-doped TiO<sub>2</sub> nanofibers [206]. Copyright 2011, Elsevier.

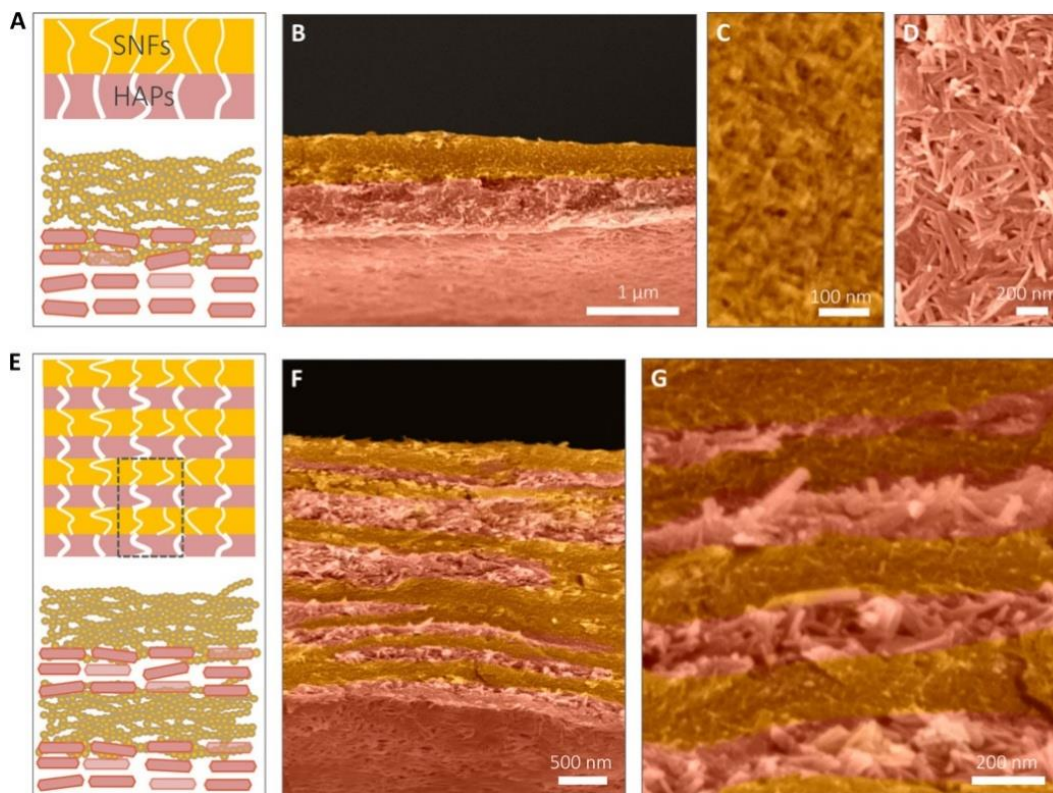
### 4.3. Environmental Improvement and Protection

Many groups have investigated the environmental applications of functional nanofibers, for instance for filtration [209], self-cleaning [210], adsorbents [211], oil-spill cleanup [212] and electromagnetic shielding [213]. Currently, nanofibers are used in air and water filters and blood purification membranes to minimize the pressure drop and improve efficiency compared with conventional fiber mats. The nanofiber large surface area-to-volume ratio increases the area available for contaminant adsorption and the filter lifetime.

#### 4.3.1. Membrane Materials for Wastewater Treatment

Water pollution is a major issue worldwide. It is estimated that more than 50% of countries will experience freshwater stress or shortages by 2025, and 75% by 2075 [214].

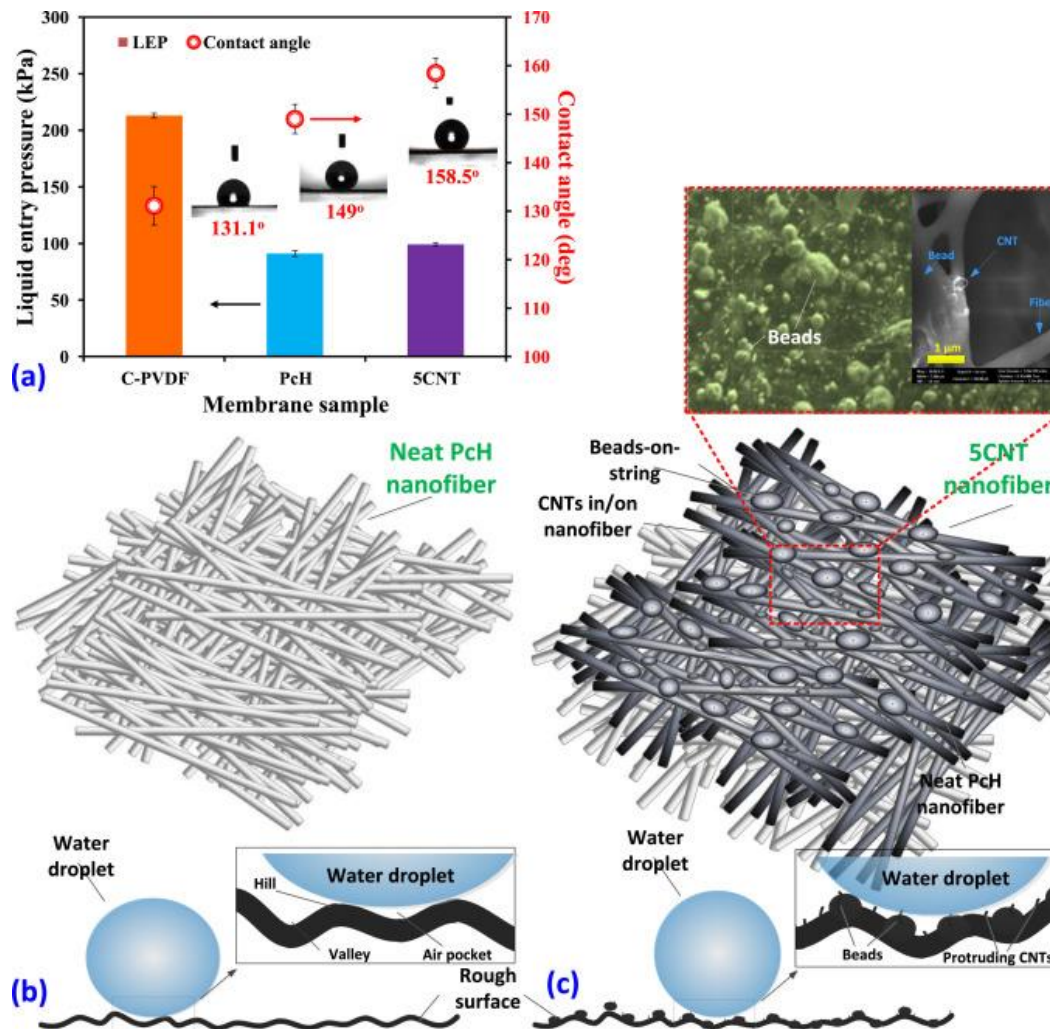
Conventional water purification and wastewater treatment membranes include a selective (active) layer supported by a thick non-selective and highly permeable substrate. By controlling the pore size of the active layer, nanofiltration, ultrafiltration, reverse osmosis, and microfiltration membranes can be produced.[215] The traditionally used membranes have intrinsic limitations, such as low flux, susceptibility to fouling, and formation of pinholes during the preparation steps. Nanofiber membranes could replace such membranes in smaller treatment systems that operate at low pressures [216]. The major advantage of nanofiber membranes in wastewater are their ultra-high filtration efficiency [216]. Nanofiber membrane could remove submicron particles (e.g., bacteria, and dust particles) by size exclusion. Conversely, much smaller pores are required for efficient nanoparticle removal (e.g., virus), but this would significantly limit the water flux. This problem can be solved by using multi-layer nanofiber membranes that allow high filter efficiency and increased water throughput. However, it is still challenging to fabricate membranes with well-organized multilayer structures, starting from the nanoscale, to maximize filtration efficiency [217]. Recently, Ling and coworkers [217] designed biomimetic multilayer nanofiber membranes (see **Figure 29** for an example) for the efficient removal and even reuse of many different contaminants (e.g., heavy metal ions, dyes, and proteins in water).



**Figure 29.** Silk nanofiber (SNF)/Hydroxyapatite (HAP) self-assembled multilayer membrane for water treatment. **(A)** Double-layer structure in which the top SNF-rich layer has small-size pores and the bottom HAP layer has larger-size pores. **(B)** Cross-sectional SEM image. **(C)** SEM image of the SNF-rich layer (top view) **(D)** SEM image of the HAP-rich layer (top view). **(E to G)** The multilayer structure of the SNF/HAP membrane: **(E)** Schematic representation and **(F,G)** Cross-sectional SEM images of the multilayer membrane [217]. Copyright American Association for the Advancement of Science, 2017.

Besides particle exclusion, nanofiber membranes are efficient adsorption media for catalysis and removal of heavy metals, low molecular weight organics, and oils from wastewater. The nanofiber membrane features could be modulated to obtain high porosity, suitable pore sizes, narrow pore size distribution, and thin thickness coupled with super-hydrophobicity in

order to use then for high-performance wastewater treatment. Some environmental contaminants (e.g., heavy metals) are difficult to eliminate using conventional water purification strategies [208]. On the other hand, nanofiber membranes can efficiently adsorb heavy metals [218], volatile organic compounds [219], and low viscous oils [220] from wastewater. Hassan *et al.* [221] used never-dried BC and cross-linked CNF to remove oil from oil-in-water emulsions with droplet sizes  $<1 \mu\text{m}$ . Tijing *et al.* [222] produced super-hydrophobic polyvinylidene fluoride-co-hexafluoropropylene nanofiber membranes that contain CNTs (1–5 wt%) for high-performance direct contact membrane distillation (**Figure 30**). They found that the flux of the membrane that contains 5 wt% CNTs (24–29.5 L/m<sup>2</sup> h) is reproducibly higher than that of commercial super-hydrophobic PVDF membranes (18–18.5 L/m<sup>2</sup> h).



**Figure 30.** Super-hydrophobic nanofiber membrane for high-performance direct contact membrane distillation. CNTs were added as nanofillers for additional mechanical and hydrophobic properties. **(a)** Liquid entry pressure and contact angle of different super-hydrophobic membrane upon the incorporation of 5 wt% CNTs, and **(b)** Structure of the neat and CNT-incorporated nanofibers, **(c)** SEM images showing the beads and CNTs on the fiber, and **(d)** SEM image of the pristine CNTs used in this study [222]. Copyright 2016, Elsevier.

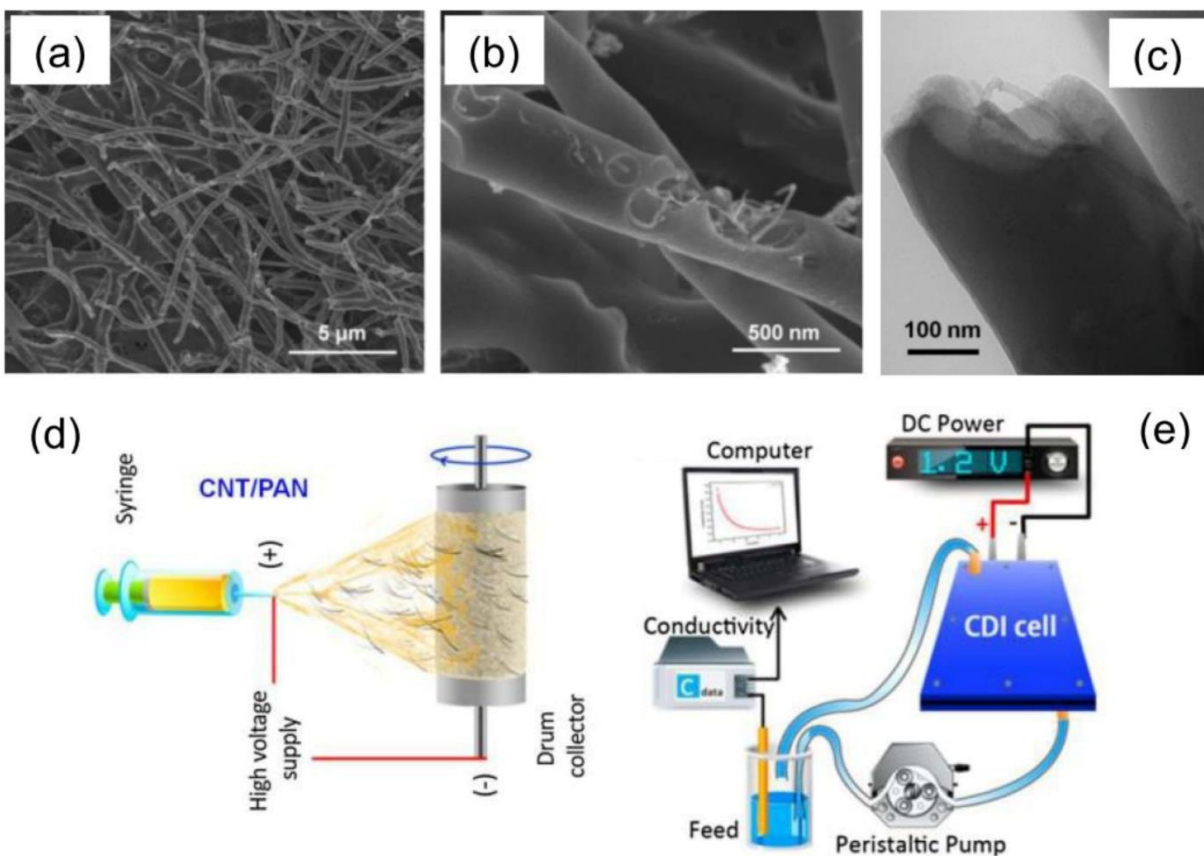
Hybrid nanofiber membranes with both photocatalysis and filtration functions can improve water treatment.[223] The membrane photocatalytic activity can solve problems related to the



formation of toxic condensates and membrane fouling, and to the presence of very small and harmful organic pollutants in the permeate effluent. Ceramic nanofiber or hybrid polymer/metal oxide nanofiber membranes modified with thin photocatalytic layers are typically used for these purposes [224],[225],[226]. Singh *et al.* [227] fabricated mesoporous hollow TiO<sub>2</sub> nanofibers by coaxial electrospinning for the photocatalytic degradation of organic compounds. These nanofibers were modified by deposition of cadmium sulfide NPs (co-catalyst) on their surface to enhance the light absorption in the visible region. The resulting nanofibers have excellent photocatalytic activity in an aqueous medium, are reusable, and their nanostructures do not change after repetitive usage [227].

Capacitive deionization (CDI) is an electrochemical approach to deionize water by applying an electrical potential difference over two electrodes, mainly made of porous carbon, immersed in water [141, 228-230]. Anionic species are removed from the water and then stored (adsorbed/absorbed) into the anode, whereas cations are stored in the cathode. CDI units are now mainly used for water desalination and deionization, electrodialysis, and reverse osmosis. Mesoporous and hollow carbon nanofibers are excellent candidates for making the electrodes used in CDI units [231]. Metal oxide/carbon nanofibers also have been investigated as electrode material. For instance, Yasin and coworkers [232] showed that ZrO<sub>2</sub> nanofiber/activated carbon composites are suitable electrode material for increasing CDI (**Figure 31**). Specifically, water desalination was much improved by the addition of ZrO<sub>2</sub> nanofiber/activated carbon composites (best performance obtained with 10 wt% zirconia nanofibers relative to the activated carbon). Indeed, electrosorption and salt removal increased from 5.4 mg g<sup>-1</sup> and 16.4% with the pristine electrode to 16.4 mg g<sup>-1</sup> and 53.3% with the composite electrode, respectively [232]. Dong *et al.* [229] have utilized electrospinning followed by CO<sub>2</sub> activation to prepare a hybrid nanomaterial

consisting of CNTs embedded in carbon fibers (Figure 25a–c). The prepared composite nanofibers have led to a desalination capacity of 6.4 mg/g at an initial NaCl concentration of 400 mg/L and a working potential of 1.2 V. The great improvement (39%) with respect to the modification of the CNF with CNTs, high specific surface area (651 m<sup>2</sup>/g), and mesopore ratio (64%) of the composite fibers due to the CO<sub>2</sub>-mediated activation [229].



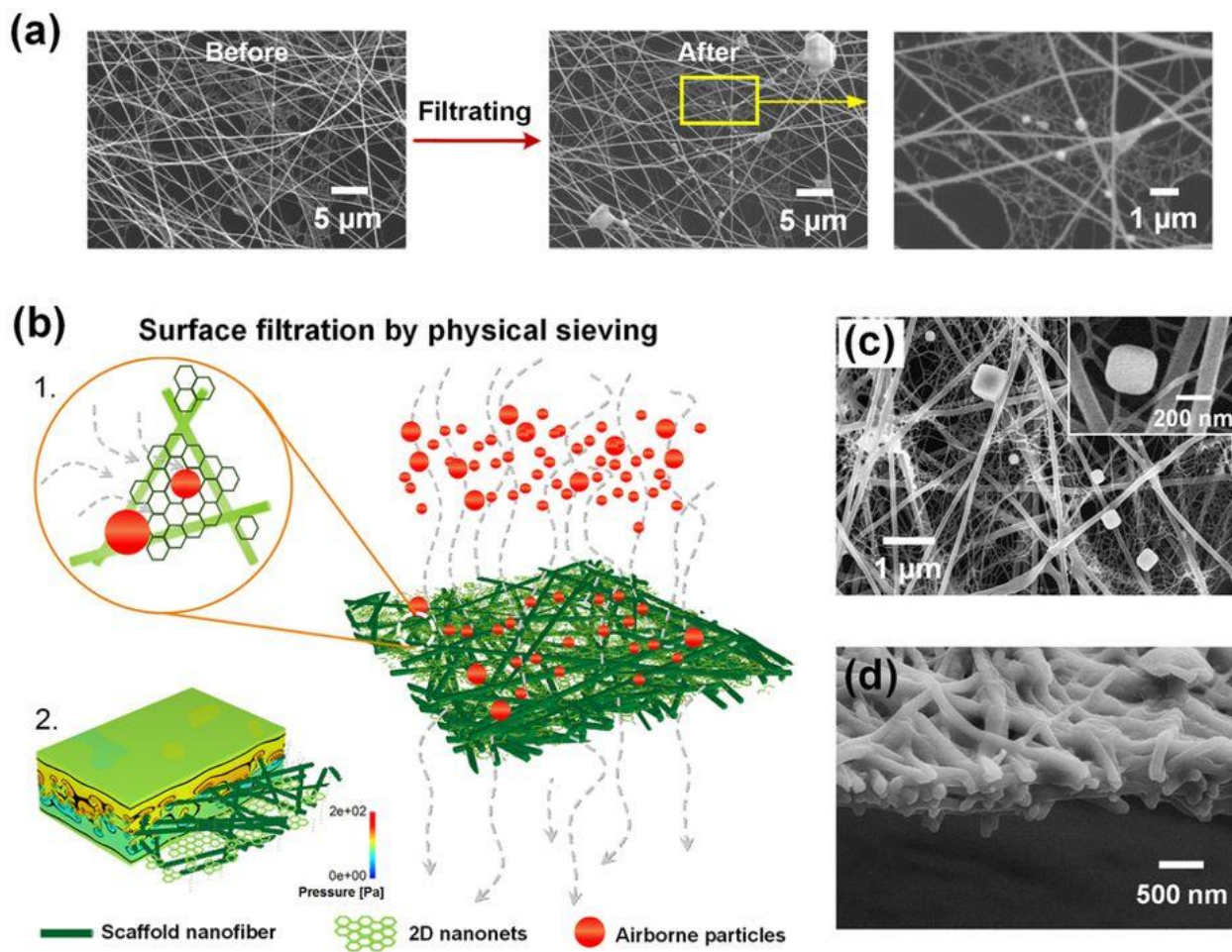
**Figure 31.** Enhancing capacitive deionization performance of electrospun activated carbon nanofibers by coupling with carbon nanotubes (a,b) SEM and (c) TEM images of the composite CNT/CNF material, consisting of CNTs embedded in carbon nanofibers (CF), (d) electrospinning setup used to produce the composite nanofibers and (d) the CDI setup that used to test the prepared samples [229]. Copyright Elsevier, 2015.

## 4.2. Membranes for Air Filtration

Air filters are used in disposable respirators, indoor air purification, industrial gas cleaning, and automotive engine intake filters for the removal of dust particles, viruses, bacteria and volatile organic compounds [233]. In the function of the particle size, the particulate matter (PM) can be classified as PM<sub>10</sub> ( $\leq 10 \mu\text{m}$ ) and PM<sub>2.5</sub> ( $\leq 2.5 \mu\text{m}$ ). PM<sub>2.5</sub> particles are considered more harmful because they can penetrate in the human respiratory system, causing lung disease, heart disease, and premature death [234]. Nanofiber-based filters can be used in hospitals to remove fine dust, bacteria, and viruses from the air. Different polymer and ceramic nanofiber membrane types, such as poly(vinyl alcohol), polyethylene terephthalate, PAN, silica, and alumina, have been developed for airborne particle filtration [234]. The major advantages of nanofiber membranes in air cleaning are their high filtration efficiency and low air resistance [216].

As the nanofiber diameter and morphology can significantly affect the membrane filtering efficiency, electrospinning is suitable for air-filter applications because the morphology and diameter (from 40 to 2000 nm) of the electrospun fibers can be tuned by using specific electrospinning parameters [235]. The fine fiber diameters and high packing densities of nanofibrous membranes lead to compact structures with high airflow resistance. This shortens the filter service life and increases energy consumption [236]. To overcome this problem, Gao *et al.* [234] fabricated a low-resistance 3D nanofibrous composite membrane by free surface electrospinning for effective capture of PM<sub>2.5</sub> particles. This composite nanofiber membrane has a ternary PAN structure composed of scaffold nanofibers, thin nanofibers, and microspheres. The microspheres enlarge the inter-fiber voids, thus significantly reducing the pressure drop [234]. Zhang *et al.* fabricated an efficient poly(m-phenylene isophthalamide) nanofiber/nets (PMIA

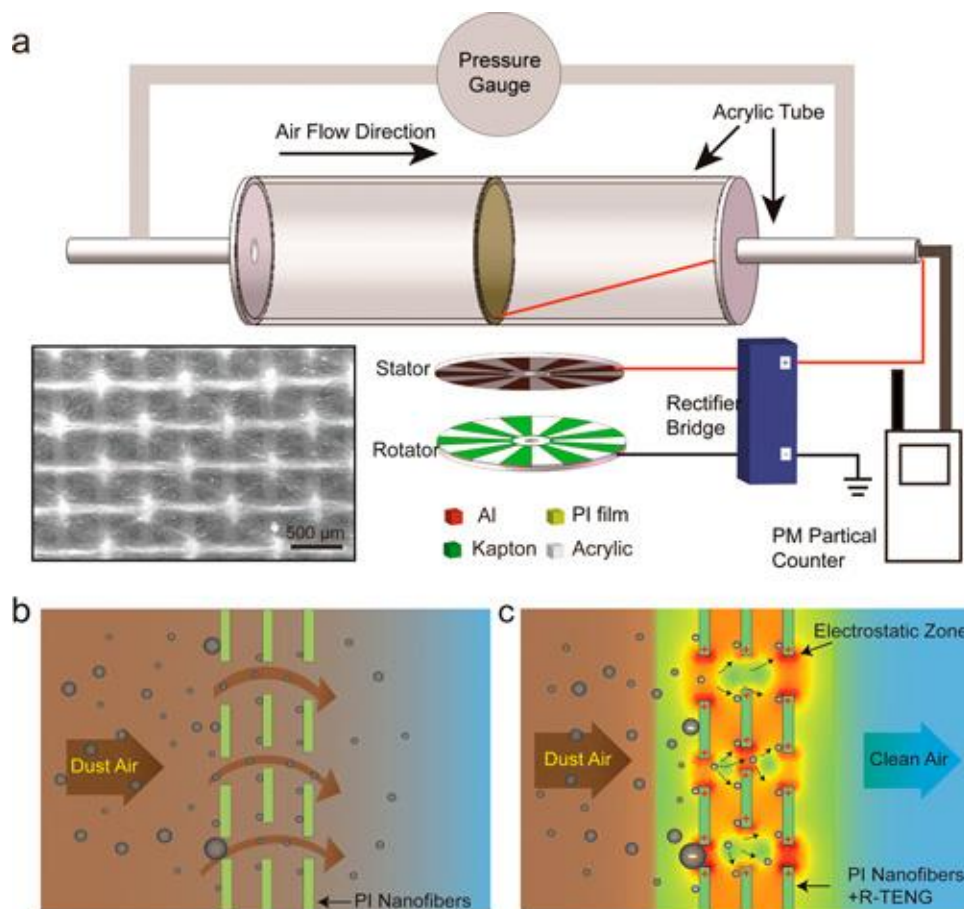
NF/N) air filter via electrospinning/netting. The prepared filter exhibits the superior properties including ultralight weight ( $0.365 \text{ g m}^{-2}$ ), ultrathin thickness ( $\sim 0.5 \mu\text{m}$ ), and high tensile strength ( $72.8 \text{ MPa}$ ) for effective air filtration of about 99.9% and low-pressure drop of 92 Pa for 300–500 nm particles (**Figure 32**).



**Figure 32.** 3D nanofibrous composite membrane with low filtration resistance fabricated by electrospinning for effective capture of PM<sub>2.5</sub> particles. (a) In situ study of NaCl aerosol particle capture by poly(*m*-phenylene isophthalamide) nanofiber/nets ( $\sim 0.1 \text{ g m}^{-2}$ ) characterized by SEM showing morphologies before and after the filtration process. (b) 3D model illustrating the filtration process of the membrane for 300–500 nm particles by surface filtration and physical sieving mechanism: (1) absolute removal manner and (2) robust air permeability. FE-SEM

images of (c) the top surface and (d) cross-section of the membrane with a basis weight of  $0.365 \text{ g m}^{-2}$  after filtration (air flow of  $32 \text{ L min}^{-1}$ , testing for just 1 min) [233]. Copyright 217, Nature.

Carbon nanofibers combined with other non-woven products have been used to produce aerosol filters and face masks. Electrospun nylon nanofibers are incorporated in gas filters for turbines, compressors and generators [237, 238]. PI nanofibers are suitable high-temperature air filter material due to their excellent thermal stability, chemical resistance, and strong mechanical properties [239]. Gu *et al.* [240] recently described a rotating triboelectric nanogenerator (R-TENG)-enhanced PI nanofiber filter that efficiently removes airborne PM ( $>0.5 \mu\text{m}$ ) (**Figure 33**). They showed that the filter removal efficiency is increased, particularly for particles smaller than 100 nm, from 27.1% without R-TENG to 83.6% with the R-TENG, with the highest removal efficiency (90.6%) for nanofiber with a diameter of 33.4 nm [240].



**Figure 33.** R-TENG-enhanced nanofiber air filters for efficient PM removal: (a) Set-up for PM removal efficiency measurement, with SEM image of the PI nanofiber membrane (left), (b-c) Filtration mechanism of the nanofiber filter without R-TENG (b), and with R-TENG (d) [240]. Copyright American Chemical Society, 2017.

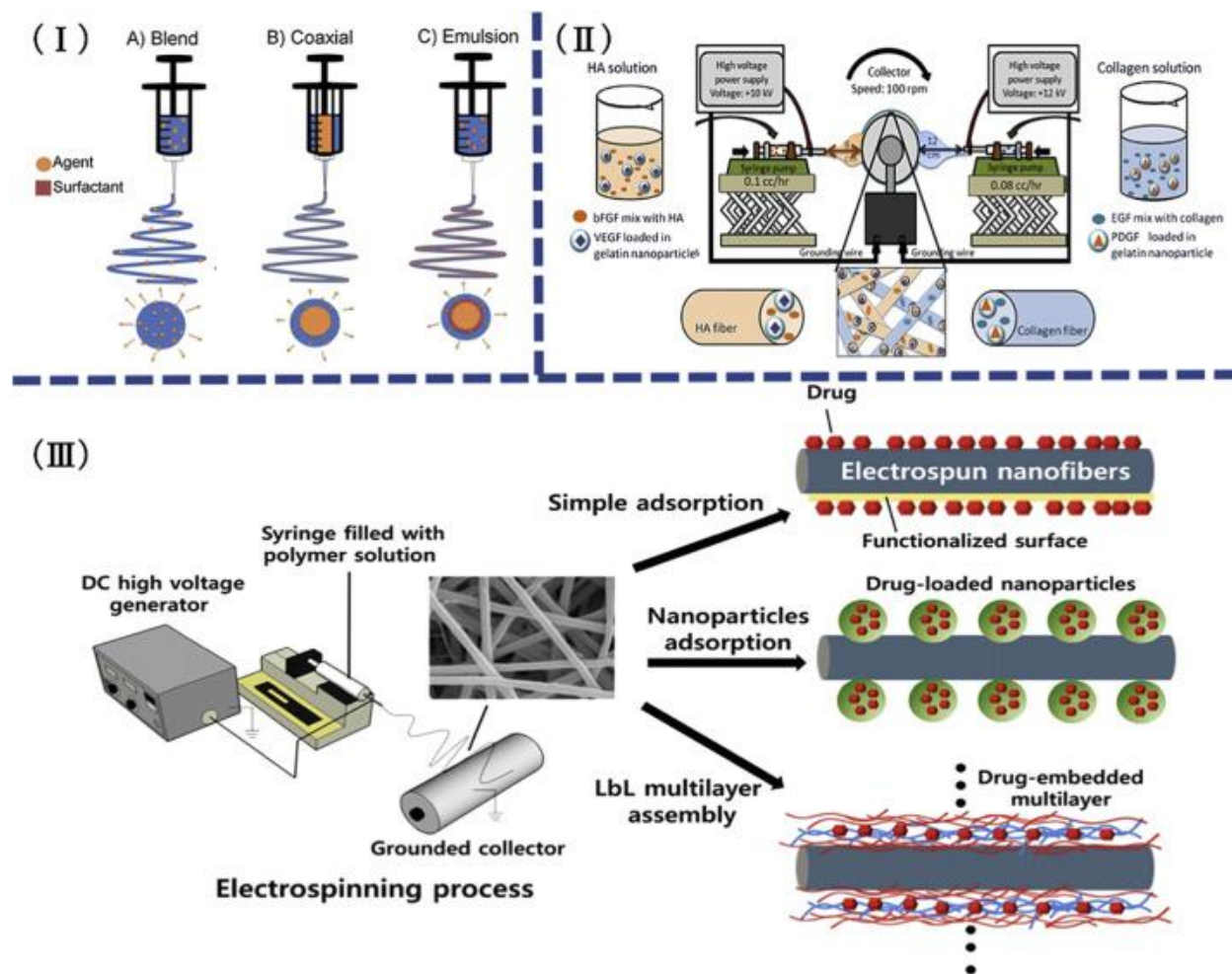
## 5. Nanofibers for Biomedical Applications

Nanofibers are particularly attractive for applications in drug delivery, burn and wound care, tissue engineering, blood purification, and treatment of various diseases. The nanofiber high surface area increases the adhesion of cells, proteins, and drugs while providing lightweight devices with

significant cost savings [241]. Here, we will describe some of the most popular biomedical applications of nanofibers and the key parameters that influence their performance.

## 5.1. Drug Delivery

Nanofiber potential for drug delivery has been investigated using small organic drugs and macromolecules, such as proteins and nucleic acids (DNA and RNA). Nevertheless, before clinical validation and marketing approval, *in vivo* pre-clinical studies must be carried out to evaluate the safety and toxicity of these systems [242]. Bioactive molecules can be incorporated in the bulk phase of electrospun nanofibers or on their surfaces by nanofiber post-treatment, immobilization of drug-loaded nanocarriers on nanofibers, co-electrospinning of drug-polymer compounds, and coaxial/emulsion electrospinning (**Figure 34**) [243]. Co-electrospinning is the most used drug incorporation strategy due to its simplicity (no need for post-fabrication processing), and relatively low-cost. The first studies focused mainly on encapsulating various antibacterial and anti-tumor agents in electrospun nanofibers to develop a slow-release drug delivery system [243].



**Figure 34.** Schematic outline of various techniques to produce drug-loaded nanofibers. (I) Schematic illustration of blend electrospinning, coaxial electrospinning, and emulsion electrospinning. (II) The synergistic combination of nanocontainers and nanofibers. (III) Surface-functionalization of electrospun nanofibers. Copyright 2017, Elsevier [243].

## 5.2 Scaffolds for Tissue Engineering

Tissue engineering approaches typically require scaffolds, cells and biochemical cues (e.g., growth factors) and mechanical stimuli to create functional tissues. Compared to traditional implant/biomaterial surfaces, nanofiber scaffolds with a nanofibril framework are an exceptional

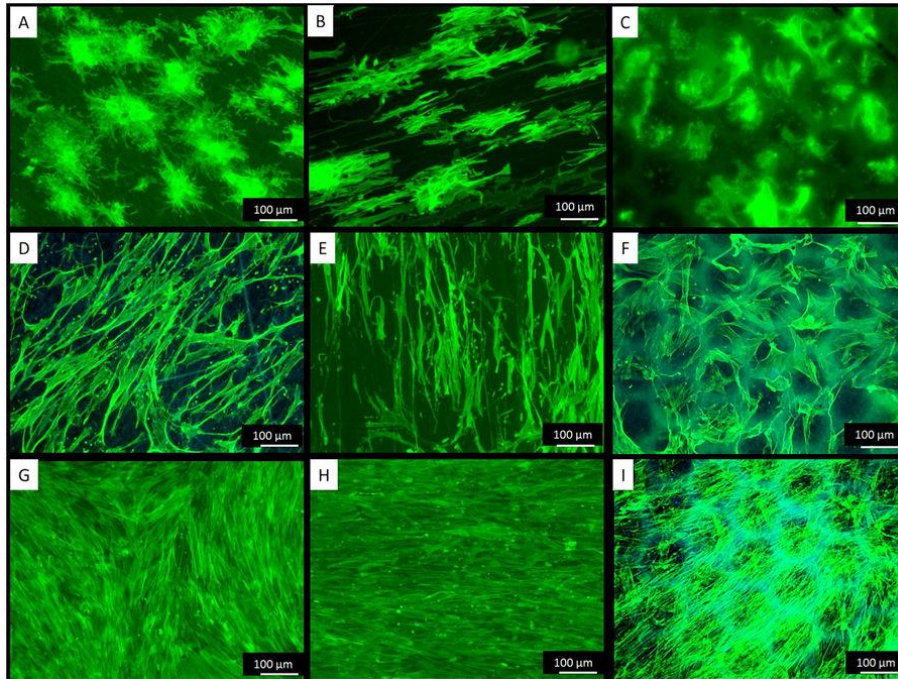


system that can mimic the natural human tissue design at the nanometer scale [244]. The nanofiber small diameter closely matches that of natural extracellular matrix fibers, and its relatively large surface area favors cell attachment and bioactive factor loading [245]. Similar to extracellular matrices, nanofibers could be loaded with various bioactive agents to control their local concentration and diffusion. In restorative surgery, nanofibers are used as scaffolds for skin, and musculoskeletal (bone, cartilage, ligaments, and skeletal muscle) and neural tissues [246]. They are commonly used for the fabrication of artificial blood vessels and organs, biocompatible and biodegradable medical implants, medical diagnostic tools, fabrics for protection against environmental and infectious agents in hospitals, and cosmetic and dental material.

In scaffold fabrication, the pore structure must be finely controlled because it directly affects cell infiltration and nutrient supply. Nanofiber scaffolds with high fiber alignment display the desired mechanical properties and promote cell migration, orientation, and differentiation, compared with randomly-distributed nanofibers [247],[248]. Recently, Nedjari *et al.* [249] developed a novel 3D honeycomb architecture scaffold based on electrospun hybrid nanofibers that include hydrolytically degradable poly (L-lactide- $\epsilon$ -caprolactone) and extracellular matrix protein fibrinogen (PLCL/FBG) and strongly supports osteogenic differentiation of human adipose-derived mesenchymal stem cells (ADMSCs) (**Figure 35**). This has important clinical implications because it can pave the way to the development of bioinspired scaffolds for bone regeneration by mimicking the osteogenic conditions in the stem cell niche [249].

Shape memory polymers (SMPs) have been investigated for various academic and industrial biomedical applications in drug release, scaffold design, and cell growth templates.

Ongoing research suggests that “nanofibers offer new microscopic structures with the potential of enhanced SMP performance” [250-252].



**Figure 35.** 3D honeycomb architecture PLCL/FBG nanofiber scaffolds strongly support osteogenic differentiation of human ADMSCs. ADMSCs grown on random (A,D,G), aligned (B,E, and H), or honeycomb-arranged (C,F,I) nanofibers were stained with phalloidin (green) to mark the actin cytoskeleton at day 1 (A–C), day 2 (D–F) and day 6 (G–I) [249]. Copyright Nature, 2017.

Nanofibrous scaffolds are used as drug delivery vehicles to induce a specific cell or tissue response [3]. They can be loaded with drugs using several methods [253],[254],[253]; however, with most of these techniques, the drug ‘burst release’ will lead to an initial high delivery rate, followed by a lower release rate. This may reduce the time during which the drug is released at effective doses. Coating the nanofiber surface with a polymer and altering the polymer composition may reduce the initial burst and extend the release time course [255]. Although

some small compounds could be easily mixed with polymers in organic or aqueous solvents, highly charged (nucleic acids) and large (proteins) molecules do not homogeneously dissolve in the organic solvents that are typically used in electrospinning, and others cannot be electrospun. On the other hand, by using coaxial electrospinning, the drug is restricted to the central core of the fibers, creating a reservoir for drug release. Surface modification techniques (e.g., plasma or wet chemical treatment) can be used to treat the nanofibers before the drug adsorption/immobilization on such surfaces. This will create surface conditions suitable for drug binding/adsorption, although it does not limit the burst release.

Engineering living tissues for reconstructive surgery requires an appropriate cell source, optimal culture conditions, and a biodegradable scaffold. A variety of natural (e.g., gelatin [256], collagen [257] and elastin [258]) and synthetic (poly( $\epsilon$ -caprolactone) (PCL) [259], poly(l-lactic acid) [248], PU [260], poly(ethylene glycol) and PCL copolymers, poly(l-lactic acid-co- $\epsilon$ -caprolactone) (PLCL) [261] and poly(d,l-lactic-co-glycolic acid) [262]) bridgeable polymers have been electrospun into nanofibers for tissue engineering applications. The choice of the most suitable drug/polymers combination for surface modification and the control of the nanofiber diameter and alignment can provide a blueprint for engineering specific tissues [263].

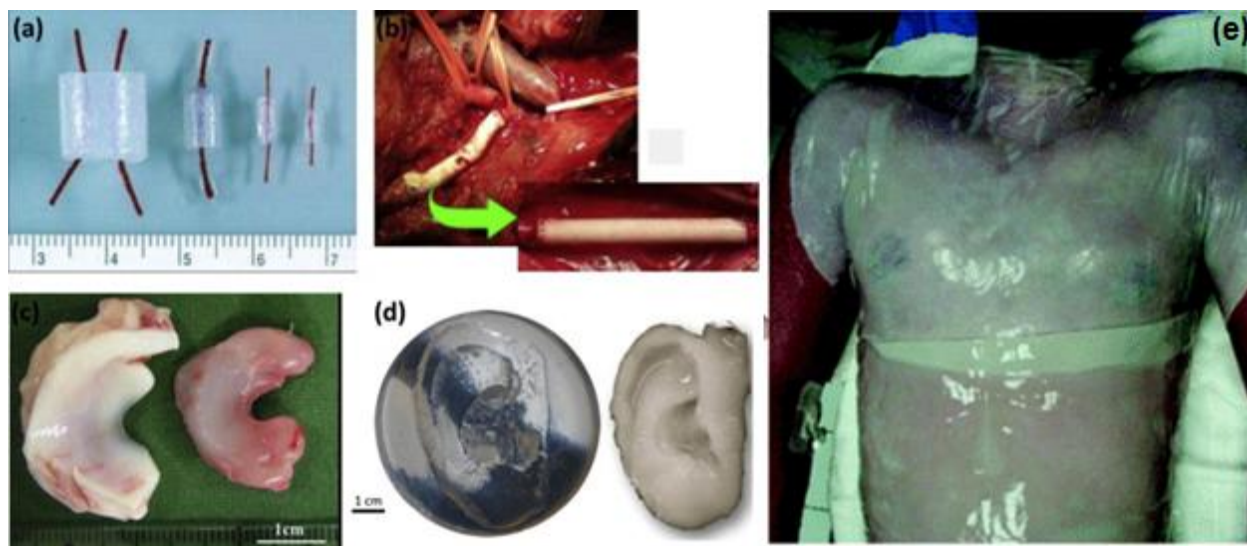
### **5.3. Wound Dressing and Substitute Biomaterials**

Skin is the largest organ of the human body, is at the interface with the external environment, and protects the body against pathogens and water loss [264]. Wound dressings are used to protect the wound from the external environment, maintain a moist environment, and facilitate healing. Therefore, their performance is influenced by their fluid uptake capacity (moisture retention) and water evaporation rate. Micro and nanofibrous materials have been used

for wound dressings [265]. Indeed, the nanofiber morphology and dimensions are similar to those of the local (insoluble) extracellular matrix structure. Nanofibrous wound dressings promote hemostasis, efficiently absorb exudates, and also facilitates cell respiration (due to their porosity), and the skin 3D re-organization (due to the nanofiber flexibility). Moreover, they can be loaded with antimicrobials drugs, growth factors, vitamins, and compounds that promote skin regeneration and prevent contamination [265],[266]. Nanofibers can function in moist environments and do not need to be frequently changed, thus reducing pain and scarring, which is very important for the management of burn victims.

Natural polymers, such as collagen [267], elastin [258] and chitosan [268], are particularly good candidates for wound dressing. They are inherently biocompatible with the invading cells and can be remodeled and degraded through natural mechanisms. They may also display inherent hemostatic and anti-microbial activities that ultimately accelerate wound-healing [269]. Electrospinning versatility allows the production of nanofibers from type I and III collagens, which represent 80–85% and 8–11% of the dermal matrix, respectively [270]. Chitosan contains amino and hydroxyl groups that offer unique cationic, chelating, and film-forming properties. Chitosan-PCL nanofibers associate chitosan biological features with PCL mechanical features. Chitosan-PCL nanofiber scaffolds represent a biomimetic approach to skin repair by functioning as a provisional matrix that favor wound closure [271]. Recent studies on the use of BC tubes as blood vessel replacement showed that BC biomaterials promote coagulation [272], endothelial cell attachment, proliferation, viability and invasion [273],[274].

**Figure 36** shows some examples of CNF-based substitute biomaterials.



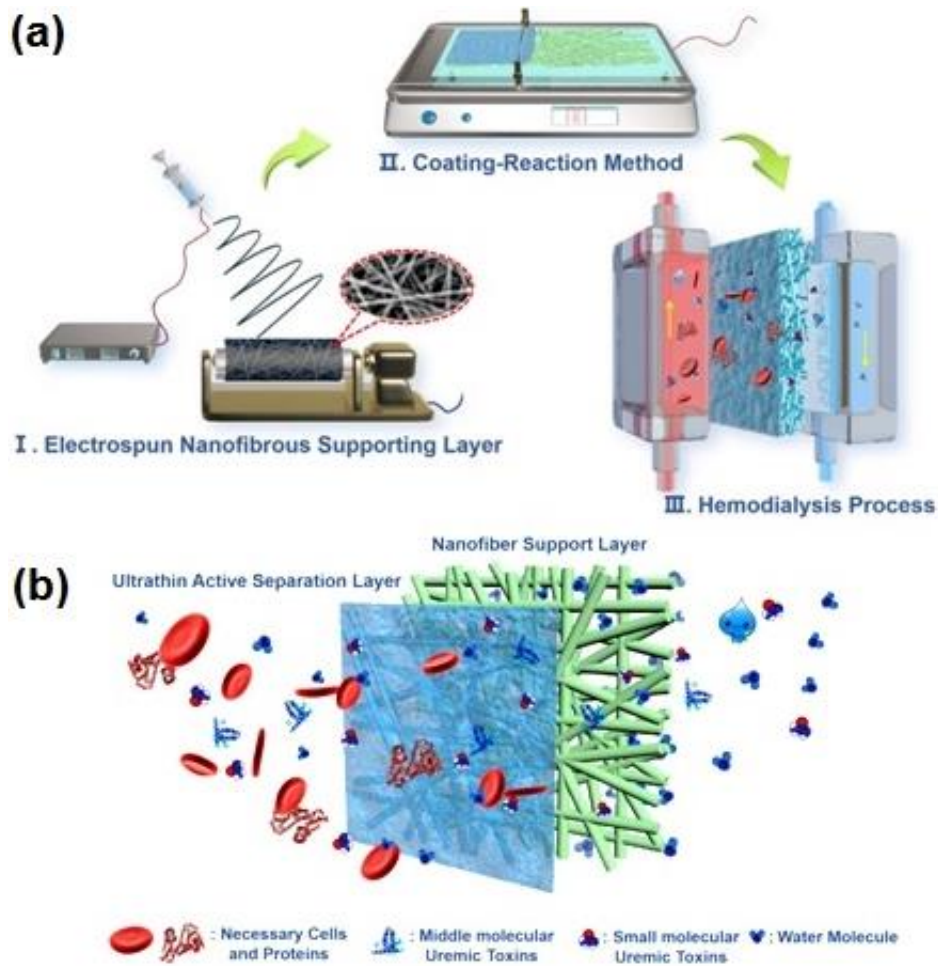
**Figure 36.** Substitute biomaterials made of CNFs: **(a)** Tubes with different dimensions made of BC nanofibers, **(b)** Vascular prostheses made of CNFs-polyurethane placed between the brachiocephalic trunk and the right common carotid artery in a patient, **(c)** Comparison between a pig meniscus (left) and a BC hydrogel meniscus implant (right), **(d)** Negative silicone mold used to guide bacteria during the bacterial culture to reproduce the large-scale features of the outer ear (left), and 3D BC nanofiber-based outer ear implant prototype (1% effective cellulose content) produced using the 3T MRI scanning technique (right) and **(e)** Wound dressing membrane [275]. Copyright Elsevier, 2014.

#### 5.4. Membranes for Blood Filtration

Hemodialysis is a treatment for patients with kidney failure that can be performed at home or in the hospital. However, the machines used to filter blood (i.e., to replace the kidney function) are often very large, expensive, and require intensive maintenance. Recently, researchers have developed a wearable nanofiber mesh that could be a cheaper alternative to hemodialysis [276]. The blood-contacting membrane is made of an electrospun polyethylene-co-

vinyl alcohol polymer and zeolites, which are aluminosilicates with microporous structures that can absorb waste products/toxins from the blood. The ratio of silicon to aluminum within zeolites could be used to control the number of adsorbed toxins [276].

Due to their high porosity, interconnectivity, micro-scale interstitial space, and large surface-to-volume, non-woven electrospun nanofiber meshes are an ideal material for blood filtration, protein purification and toxin removal from biological fluids, and also for removal of inorganic waste and heavy metals in water treatment devices [277]. In such meshes, affinity layers can be fabricated to selectively capture specific molecules by immobilizing the relevant ligand onto the surfaces [160, 236]. **Figure 37** shows high-performance composite hemodialysis membranes that include a two-tier composite structure with an ultrathin hydrophilic separation layer of chemically cross-linked polyvinyl acetate (PVA) and an electrospun PAN nanofibrous supporting layer. The optimized PVA/PAN membrane shows high permeability ( $\sim 290.5$  L/m<sup>2</sup>h at 0.1 MPa) and excellent selectivity. In hemodialysis simulation experiments, 82.6% of urea and 45.8% of lysozyme were cleaned and 98.8% of bovine serum albumin was retained by optimized PVA/PAN membranes [160].



**Figure 37.** High-performance thin-film nanofibrous composite hemodialysis membranes that efficiently remove middle-molecule uremic toxins: **(a)** fabrication of two-tier membranes based on a PAN electrospun nanofibrous scaffold support and PVA hydrogel coating for hemodialysis; and **(b)** ideal hemodialysis membrane that efficiently removes excess water and toxic metabolites, while limiting protein loss, with an active separation layer and a scaffold-like nanofiber support layer. Permeability and selectivity are improved by the ultrathin and hydrophilic top active layer and its narrow pore-size distribution, respectively. The nanofiber support layer has a highly interconnected pore structure with direct paths for water and toxic metabolite excretion [160]. Copyright 2006, Elsevier.

## **6. Other Applications**

We are still in the early days of the commercial exploitation of nanofibers, but some interesting applications in textiles, papermaking, composite toughening, sound absorbing materials and shape memory materials are currently explored.

### **6.1. Defense and Safety**

Militaries, firefighters, as well as law implementation and medical staff may require high-level protection against [160] biological (e.g., bacterial spores, viruses) and chemical threats (e.g., nerve agents, mustard gas, and cyanides) [278]. Such protection should be effective in various environments (urban, agricultural, and industrial settings). Governments are putting extra resources to strengthen soldiers' safety on the battlefield [279-281]. Nanofibers can improve: (i) the detection (sensitivity and specificity) of chemical and biological warfare agents at very small concentrations (parts per billion); and (ii) the protection against threats through filtration and destruction by decomposition of dangerous toxins (e.g., aerosols, toxic volatile compounds, viruses, bacteria). Different strategies to design nanofiber surfaces to capture and decontaminate warfare agents are currently under investigation [282, 283]. Metal NPs (Ag, MgO, Ni, Ti, etc.) that can decompose warfare agents also can be embedded in nanofibers [284].

### **6.2. Functional Materials for Smart Textile**

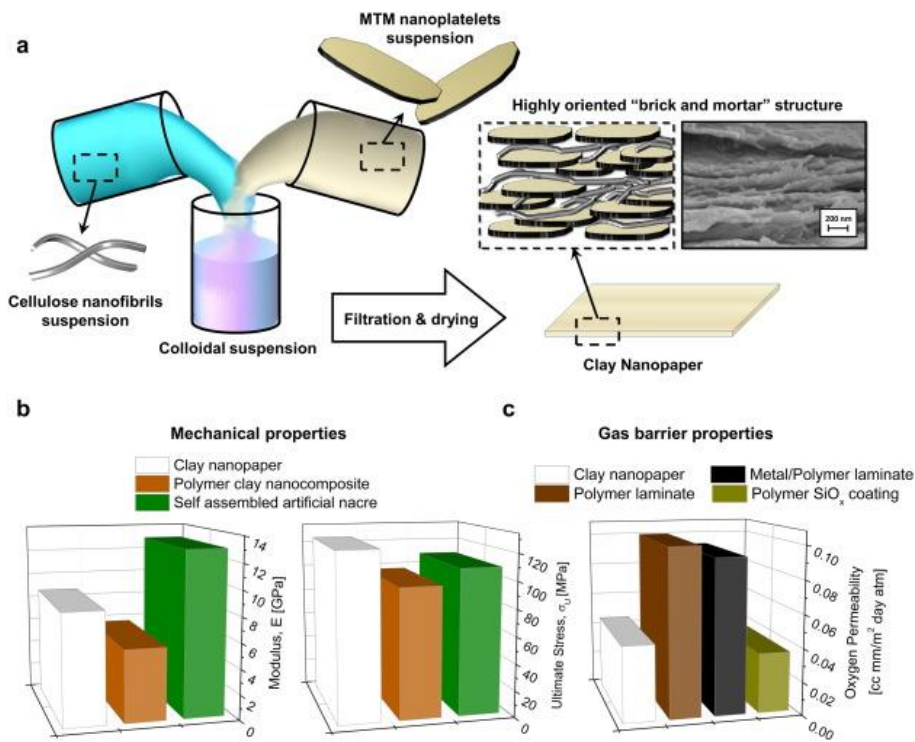
Nanofiber-based textiles and fabrics can have multifunctional properties and applications as warming and cooling materials, conductive textiles, communicating textiles, sensors and actuators, digital fashion, chromatic textiles [285, 286]. The high porosity and small pores of nanofiber mats offer good resistance to harmful chemical aerosols. Nanofiber technology can be



used to improve the fabric performance (e.g., anti-bacterial properties, detoxification capability, waterproofing, and breathability) . For clothing, it also is important to be able to add different colors to the fabric. Colored solution electrospinning has been used to fabricate colorful and visually appealing nanofiber fabrics with various functionalities. In this method, powdered dyes can be dissolved or dispersed in the electrospinning solution or in the pre-formed polymer to produce stained nanofibers by electrospinning [287]. The as-spun colored fabrics and membranes have excellent level-dyeing properties and color stability. For instance, polyvinyl butyral/cationic dye membranes show good color uniformity and high hydrophobicity with potential applications in color printing and anticorrosive coating/painting [288]. However, this technique is laborious and inefficient, particularly in the case of nanofibers with high surface area and high light scattering ability [289],[290].

### **6.3. Additives for Papermaking**

Addition of silicate, carbo, and CNFs in papermaking may improve the process and product sustainability [291]. For example, they allow obtaining a stronger paper with unique functionalities and lower base paper weight [73]. CNFs and clay nanosheets, such as montmorillonite, are often used in papermaking and polymer industry to increase the mechanical properties and barrier resistance of papers and polymers (**Figure 38**). Replacing pigment fillers with silicate-based nanofibers can increase the opacity of some base sheets [292]. Conductive carbon nanofiber paper can be fabricated using carbon nanofibers, solvents, and dispersants [293].



**Figure 38.** (a) Description of the fabrication of clay-cellulose nanopaper and of its oriented structure; (b-c) Comparison of the mechanical properties (b) and of the oxygen barrier properties (measured in humid conditions: 23°C 50% R.H.) of clay-cellulose nanopaper containing 50% montmorillonite and of other clay nanocomposites [294]. Copyright © 2016 Elsevier.

## 6.4. Sound Absorbing and Shape Memory Materials

Sound absorption materials (e.g., paper, cotton, cork, foams, fibers, membranes and perforated panels) can efficiently reduce high-frequency sounds, but display poor absorption properties for the low- and medium-frequency components (250-2000 Hz) to which the human ear is sensitive. Nanofiber-based materials are promising alternatives for noise reduction, and some studies have investigated the acoustic applications of nanofibril membranes. Aircraft manufacturers are assessing new methods and materials to decrease the amount of noise in the fuselage. Electrospun nanocomposite fibers may be the ideal solution, and may offer several

advantages compared with conventional materials, such as fiberglass, mineral fiber wool and wood fibers [295],[296], particularly (i) larger surface area (100-10,000 times bigger than that of conventional fibers); (ii) theoretically higher noise absorption rate because of the interaction of air molecules of sound waves with the nanofiber surfaces; (iii) lower overall weight; (iii) higher porosity; and (iv) possibility to electrospin nanofibers on composite, metal surfaces, polymeric materials, including flame-resistant polymers.

## **7. Opportunities and Future Challenges**

Nanofiber technology advances allow now the fabrication of nanofibers starting from a very broad range of materials, such as synthetic and natural polymers, and also metals, ceramics, and organic/inorganic, inorganic/inorganic composite system [297-306]. Combining different materials into a device might offer unique properties (e.g., the polymer flexibility with the conductivity of metallic dopants). It also represents a fabrication challenge because the most suitable manufacturing conditions and solution phases need to be identified. The incorporation or utilization of functional nanofibers will open new opportunities for nanofiber-based materials.

Currently, many efforts are focused on up-scaling the production and improving the nanofiber properties. Among the different fabrication techniques, electrospinning has the unique ability to produce nanofibers using different materials in various fibrous assemblies. Due to the relative simple set-up and high production rate, electrospinning is highly attractive for both academic and industrial applications. Several electrospinning methods have been developed to overcome the main limitations of the standard electrospinning method: low productivity (e.g., needleless electrospinning) and the requirement of organic solvents (e.g., hot melt electrospinning). These new methods also add new functions, such as controlling nanofiber

morphology, compositing, electrospinning of low conductivity polymers and high molecular weight polymers [131].

Nevertheless, the production of nanofiber materials must overcome many challenges:

- (i) Despite the development of new nanofiber fabrication techniques, the commercial production of high-quality nanofibers is still limited. Particularly, industrial fabrication techniques should be able to reproduce the specific positions and orientation of nanofibers at a larger scale. From an environmental perspective, it is also important to consider the biocompatibility and number of used materials and the amount of energy required for the manufacturing process.
- (ii) Spinning of new materials might be required to facilitate continuous operations at larger scales. Moreover, ‘green’ materials (e.g., degradable and recyclable materials derived from biological sources) might be needed to minimize the impact of electrospun nanofibers on the environment and human health. More attention should be given to eco-friendly polymers. More research on needleless and solvent-free electrospinning is needed to produce ultrafine fibers of sub-micrometer size and high efficiency. Solvent-free electrospinning is a promising candidate for a wide range of advanced applications.
- (iii) Future research should focus on improving the properties (e.g., composition, diameter, morphology, pore size) of nanofibers used for healthcare and biomedical applications. Most of the current applications of nanofibers are at the early proof-of-concept stage, and most studies are still performed only *in vitro*.

## **8. Conclusions and Remarks**

Although, currently, nanofibers are mainly used for environmental protection, many other applications such as energy production and storage, drug delivery, healthcare, constructions, and building materials, are rapidly emerging. By selecting the suitable fabrication techniques, the nanofiber bulk and surface properties can be readily engineered to obtain the desired optical, biological, chemical, mechanical, magnetic or electrical properties. Nanofibers incorporating NPs have an interesting and promising future. In this review, we described many devices and applications that use functional and flexible nanofiber electrodes and membranes. Due to their small diameter, high surface area, controlled mechanical properties, and porous network structure, nanofibers can be used as: (i) electrode and membrane materials in fuel cells, batteries, and supercapacitors; (ii) ultrafiltration membranes for air purification, and wastewater treatment; (iii) bioactive materials and scaffolds for tissue engineering, drug delivery, wound dressing. Nanofiber devices and components should bring major changes, particularly in the medical and healthcare sectors thanks to their superior performances, due to the bigger surface areas that maximize interactions with biological systems, and the possibility to incorporate different features in a singular device. However, before their widespread medical application, major issues linked to the nanofiber biocompatibility and chemical integrity must be solved. For instance, the disintegration and/or leaching of nanoparticulates in bodily fluids cannot be tolerated because their retrieval is nearly impossible.

Despite the many studies on the nanofiber properties and applications in the last decade, the technologies for reproducible, large-scale production of nanofibers have emerged very slowly, and this limits their widespread applications. Nevertheless, research on nanofiber functionality will eventually lead to the development of low-cost, energy-efficient and

biocompatible functional products, some of which might possess unique functionalities that are not available yet.

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## **Conflict of interest**

All authors have declared that there are no conflicts of interests regarding the contributions in this publication.

## **References**

1. Gugulothu, D., et al., *Fabrication of Nanofibers: Electrospinning and Non-Electrospinning Techniques*, in *Handbook of Nanofibers*, A. Barhoum, M. Bechelany, and A. Makhoulouf, Editors. 2018, Springer International Publishing: Cham. p. 1-34.
2. Huang, Z.-M., et al., *A review on polymer nanofibers by electrospinning and their applications in nanocomposites*. *Composites science and technology*, 2003. 63(15): p. 2223-2253.
3. Yoo, H.S., T.G. Kim, and T.G. Park, *Surface-functionalized electrospun nanofibers for tissue engineering and drug delivery*. *Advanced Drug Delivery Reviews*, 2009. 61(12): p. 1033-1042.
4. Li, D., J.T. McCann, and Y. Xia, *Use of electrospinning to directly fabricate hollow nanofibers with functionalized inner and outer surfaces*. *Small*, 2005. 1(1): p. 83-86.
5. Jeevanandam, J., et al., *Review on nanoparticles and nanostructured materials: history, sources, toxicity and regulations*. *Beilstein journal of nanotechnology*, 2018. 9: p. 1050.
6. Teo, W.E. and S. Ramakrishna, *A review on electrospinning design and nanofibre assemblies*. *Nanotechnology*, 2006. 17(14): p. R89.
7. Su, Z., J. Ding, and G. Wei, *Electrospinning: A facile technique for fabricating polymeric nanofibers doped with carbon nanotubes and metallic nanoparticles for sensor applications*. *RSC Advances*, 2014. 4(94): p. 52598-52610.
8. Elsaesser, A. and C.V. Howard, *Toxicology of nanoparticles*. *Advanced Drug Delivery Reviews*, 2012. 64(2): p. 129-137.
9. Horváth, L., et al. *Toxicity Study of Nanofibers*. 2011. Dordrecht: Springer Netherlands.

10. Lee, H., et al., *Enhancement of mechanical properties of polymeric nanofibers by controlling crystallization behavior using a simple freezing/thawing process*. RSC Advances, 2017. 7(69): p. 43994-44000.
11. Nayak, R., et al., *Recent advances in nanofibre fabrication techniques*. Textile Research Journal, 2012. 82(2): p. 129-147.
12. Lee, H., et al., *Control of the morphology of cellulose acetate nanofibers via electrospinning*. Cellulose, 2018. 25(5): p. 2829-2837.
13. Lee, H., et al., *Handspinning enabled highly concentrated carbon nanotubes with controlled orientation in nanofibers*. Scientific Reports, 2016. 6: p. 37590.
14. Lee, H., et al., *The chemical deposition method for the decoration of palladium particles on carbon nanofibers with rapid conductivity changes*. Nanomaterials, 2016. 6(12): p. 226.
15. Nagarajan, S., et al., *Design of Boron Nitride/Gelatin Electrospun Nanofibers for Bone Tissue Engineering*. ACS applied materials & interfaces, 2017. 9(39): p. 33695-33706.
16. Nagarajan, S., et al., *Electrospun fibers in regenerative tissue engineering and drug delivery*. Pure and Applied Chemistry, 2017. 89(12): p. 1799-1808.
17. Nagarajan, S., et al., *Novel biocompatible electrospun gelatin fiber mats with antibiotic drug delivery properties*. Journal of Materials Chemistry B, 2016. 4(6): p. 1134-1141.
18. Engel, A.B., et al., *Control of Spatial Organization of Electrospun Fibers in a Carbon Felt for Enhanced Bioelectrode Performance*. Chempluschem, 2015. 80(3): p. 494-502.
19. Schlicht, S., et al., *An electrochemically functional layer of hydrogenase extract on an electrode of large and tunable specific surface area*. Journal of Materials Chemistry A, 2016. 4(17): p. 6487-6494.
20. Selloum, D., et al., *A highly efficient gold/electrospun PAN fiber material for improved laccase biocathodes for biofuel cell applications*. Journal of Materials Chemistry A, 2014. 2(8): p. 2794-2800.
21. Weber, M., et al., *Novel and Facile Route for the Synthesis of Tunable Boron Nitride Nanotubes Combining Atomic Layer Deposition and Annealing Processes for Water Purification*. Advanced Materials Interfaces, 2018. 5(16).
22. Nada, A.A., et al., *Mesoporous ZnFe<sub>2</sub>O<sub>4</sub>@TiO<sub>2</sub> Nanofibers Prepared by Electrospinning Coupled to PECVD as Highly Performing Photocatalytic Materials*. Journal of Physical Chemistry C, 2017. 121(44): p. 24669-24677.
23. Nasr, M., et al., *Enhanced Visible-Light Photocatalytic Performance of Electrospun rGO/TiO<sub>2</sub> Composite Nanofibers*. Journal of Physical Chemistry C, 2017. 121(1): p. 261-269.
24. Nasr, M., et al., *Enhanced photocatalytic performance of novel electrospun BN/TiO<sub>2</sub> composite nanofibers*. New Journal of Chemistry, 2017. 41(1): p. 81-89.
25. Nasr, M., et al., *Optical and structural properties of Al<sub>2</sub>O<sub>3</sub> doped ZnO nanotubes prepared by ALD and their photocatalytic application*. Surface & Coatings Technology, 2018. 343: p. 24-29.
26. Nasr, M., et al., *Photoluminescence: A very sensitive tool to detect the presence of anatase in rutile phase electrospun TiO<sub>2</sub> nanofibers*. Superlattices and Microstructures, 2015. 77: p. 18-24.
27. Nasr, M., et al., *Synthesis of novel ZnO/ZnAl<sub>2</sub>O<sub>4</sub> multi co-centric nanotubes and their long-term stability in photocatalytic application*. RSC Advances, 2016. 6(105): p. 103692-103699.
28. Nasr, M., et al., *Recent Progress on Titanium Dioxide Nanomaterials for Photocatalytic Applications*. Chemsuschem, 2018. 11(18): p. 3023-3047.
29. Iatsunskyi, I., et al., *Tailoring of the electronic properties of ZnO-polyacrylonitrile nanofibers: Experiment and theory*. Applied Surface Science, 2017. 411: p. 494-501.
30. Viter, R., et al., *Tuning of ZnO 1D nanostructures by atomic layer deposition and electrospinning for optical gas sensor applications*. Nanotechnology, 2015. 26(10).

31. Viter, R., et al., *Enhancement of Electronic and Optical Properties of ZnO/Al<sub>2</sub>O<sub>3</sub> Nanolaminate Coated Electrospun Nanofibers*. Journal of Physical Chemistry C, 2016. 120(9): p. 5124-5132.
32. Abou Chaaya, A., et al., *ZnO 1D nanostructures designed by combining atomic layer deposition and electrospinning for UV sensor applications*. Journal of Materials Chemistry A, 2014. 2(48): p. 20650-20658.
33. Tucker, N., et al., *The history of the science and technology of electrospinning from 1600 to 1995*. Journal of engineered fibers and fabrics, 2012. 7: p. 63-73.
34. Gilbert, W. and E. Wright, *De magnete, magneticisque corporibus, et de magno magnete tellure: physiologia noua, plurimis & argumentis, & experimentis demonstrata* 1677: excudebat Short.
35. Kauffman, G.B., *Rayon: the first semi-synthetic fiber product*. Journal of chemical education, 1993. 70(11): p. 887.
36. Hughes, T. and C. Chambers, *US Patent 405, 480*. Manufacture of carbon filaments, 1889.
37. Cooley, J.F., *Apparatus for electrically dispersing fluids*, 1902, Google Patents.
38. Arinstein, A. and E. Zussman, *Electrospun polymer nanofibers: mechanical and thermodynamic perspectives*. Journal of Polymer Science Part B: Polymer Physics, 2011. 49(10): p. 691-707.
39. Anton, F., *Process and apparatus for preparing artificial threads*, 1934, Google Patents.
40. Radushkevich, L. and V. Lukyanovich, *Carbon structure formed under thermal decomposition of carbon monoxide on iron*. Zh. Fiz. Khim, 1952. 26(1): p. 88-95.
41. Oberlin, A., M. Endo, and T. Koyama, *Filamentous growth of carbon through benzene decomposition*. Journal of crystal growth, 1976. 32(3): p. 335-349.
42. Taylor, G.I., *Disintegration of water drops in an electric field*. Proc. R. Soc. Lond. A, 1964. 280(1382): p. 383-397.
43. Simons, H.L., *Process and apparatus for producing patterned non-woven fabrics*, 1966, Google Patents.
44. Taylor, G.I., *Electrically driven jets*. Proc. R. Soc. Lond. A, 1969. 313(1515): p. 453-475.
45. Melcher, J. and G. Taylor, *Electrohydrodynamics: a review of the role of interfacial shear stresses*. Annual review of fluid mechanics, 1969. 1(1): p. 111-146.
46. Rayleigh, L., *On the instability of jets*. Proceedings of the London mathematical society, 1878. 1(1): p. 4-13.
47. Rayleigh, L., *On the capillary phenomena of jets*. Proc. R. Soc. London, 1879. 29(196-199): p. 71-97.
48. Boys, C.V., *On the production, properties, and some suggested uses of the finest threads*. Proceedings of the Physical Society of London, 1887. 9(1): p. 8.
49. Doshi, J. and D.H. Reneker, *Electrospinning process and applications of electrospun fibers*. Journal of Electrostatics, 1995. 35(2): p. 151-160.
50. Wang, Y., S. Serrano, and J.J. Santiago-Aviles, *Electrostatic synthesis and characterization of Pb (Zr x Ti 1-x) O 3 micro/nano-fibers*. MRS Online Proceedings Library Archive, 2001. 702.
51. Ramakrishna, S., *An introduction to electrospinning and nanofibers* 2005: World Scientific.
52. Medeiros, E.S., et al., *Solution blow spinning: A new method to produce micro-and nanofibers from polymer solutions*. Journal of applied polymer science, 2009. 113(4): p. 2322-2330.
53. Weitz, R., et al., *Polymer nanofibers via nozzle-free centrifugal spinning*. Nano Letters, 2008. 8(4): p. 1187-1191.
54. Xing, X., Y. Wang, and B. Li, *Nanofiber drawing and nanodevice assembly in poly (trimethylene terephthalate)*. Optics express, 2008. 16(14): p. 10815-10822.
55. Tao, S.L. and T.A. Desai, *Aligned arrays of biodegradable poly ( $\epsilon$ -caprolactone) nanowires and nanofibers by template synthesis*. Nano Letters, 2007. 7(6): p. 1463-1468.



56. Liao, H.-S., et al., *Self-assembly mechanisms of nanofibers from peptide amphiphiles in solution and on substrate surfaces*. *Nanoscale*, 2016. 8(31): p. 14814-14820.
57. He, L., et al., *Fabrication and characterization of poly (l-lactic acid) 3D nanofibrous scaffolds with controlled architecture by liquid–liquid phase separation from a ternary polymer–solvent system*. *Polymer*, 2009. 50(16): p. 4128-4138.
58. Wu, J. and J.C. Meredith, *Assembly of Chitin Nanofibers into Porous Biomimetic Structures via Freeze Drying*. *ACS Macro Letters*, 2014. 3(2): p. 185-190.
59. Guan, H., et al., *Polyaniline nanofibers obtained by interfacial polymerization for high-rate supercapacitors*. *Electrochimica Acta*, 2010. 56(2): p. 964-968.
60. Ray, S.S., et al., *A comprehensive review: electrospinning technique for fabrication and surface modification of membranes for water treatment application*. *RSC Advances*, 2016. 6(88): p. 85495-85514.
61. Zhang, X. and M. Rolandi, *Engineering strategies for chitin nanofibers*. *Journal of Materials Chemistry B*, 2017. 5(14): p. 2547-2559.
62. Stojanovska, E., et al., *A review on non-electro nanofibre spinning techniques*. *RSC Advances*, 2016. 6(87): p. 83783-83801.
63. Eatemadi, A., et al., *Nanofiber: synthesis and biomedical applications*. *Artificial cells, nanomedicine, and biotechnology*, 2016. 44(1): p. 111-121.
64. Zhang, K.; Barhoum, A.; Xiaoqing, C.; Li, H.; Samyn, P. *Cellulose Nanofibers: Fabrication and Surface Functionalization Techniques*. In *Handbook of Nanofibers*; Springer International Publishing: Cham, 2019; pp 409–449.
65. Barhoum, A.; Li, H.; Chen, M.; Cheng, L.; Yang, W.; Dufresne, A. *Emerging Applications of Cellulose Nanofibers*. In *Handbook of Nanofibers*; Springer International Publishing: Cham, 2019; pp 1131–1156
66. Kaushik M, Moores A (2016) Green chemistry review: nanocelluloses as versatile supports for metal nanoparticles and their applications in catalysis †. *Green Chem* 18(3):622–637
67. Zhang, L., T. Tsuzuki, and X. Wang, *Preparation of cellulose nanofiber from softwood pulp by ball milling*. *Cellulose*, 2015. 22(3): p. 1729-1741.
68. Islam, M.T., et al., *Preparation of Nanocellulose: A Review*. *AATCC Journal of Research*, 2014. 1(5): p. 17-23.
69. Visanko, M., et al., *Mechanical fabrication of high-strength and redispersible wood nanofibers from unbleached groundwood pulp*. *Cellulose*, 2017. 24(10): p. 4173-4187.
70. Balea, A., et al., *Cellulose nanofibers from residues to improve linting and mechanical properties of recycled paper*. *Cellulose*, 2018. 25(2): p. 1339-1351.
71. Yousefi, H., V. Azari, and A. Khazaeian, *Direct mechanical production of wood nanofibers from raw wood microparticles with no chemical treatment*. *Industrial Crops and Products*, 2018. 115: p. 26-31.
72. Afra, E., et al., *Comparative effect of mechanical beating and nanofibrillation of cellulose on paper properties made from bagasse and softwood pulps*. *Carbohydrate Polymers*, 2013. 97(2): p. 725-730.
73. Samyn, P., et al., *nanoparticles and nanostructured materials in papermaking*. *Journal of Materials Science*, 2018. 53(1): p. 146-184.
74. Eichhlorn, S., et al., *Review, current international research into cellulose nanofibers and nanocomposites*. *J. Mater. Sci*, 2010. 45: p. 1-33.
75. Kafy, A., et al., *Cellulose long fibers fabricated from cellulose nanofibers and its strong and tough characteristics*. *Scientific Reports*, 2017. 7(1): p. 17683.
76. M. Breitwieser, C. Klose, M. Klingele, A. Hartmann, J. Erben, H. Cho, J. Kerres, R. Zengerle, S. Thiele, *Simple fabrication of 12 µm thin nanocomposite fuel cell membranes by direct*

- electrospinning and printing, *J. Power Sources*, 337 (2017) 137–144. doi:10.1016/J.JPOWSOUR.2016.10.094.
77. Lu, P., et al., *Rapid fabrication of transparent film directly from wood fibers with microwave-assisted ionic liquids technology*. *Carbohydrate polymers*, 2017. 174: p. 330-336.
  78. Yang, X., et al., *Integrated tungsten nanofiber field emission cathodes selectively grown by nanoscale electron beam-induced deposition*. *Applied Physics Letters*, 2005. 86(18): p. 183106.
  79. Teo, K.B.K., et al., *The Significance of Plasma Heating in Carbon Nanotube and Nanofiber Growth*. *Nano Letters*, 2004. 4(5): p. 921-926.
  80. Ajayan, P.M., et al., *Growth of manganese filled carbon nanofibers in the vapor phase*. *Physical Review Letters*, 1994. 72(11): p. 1722-1725.
  81. Tavangar, A., B. Tan, and K. Venkatakrisnan, *Synthesis of bio-functionalized three-dimensional titania nanofibrous structures using femtosecond laser ablation*. *Acta Biomaterialia*, 2011. 7(6): p. 2726-2732.
  82. Phan, L.T., S.M. Yoon, and M.-W. Moon, *Plasma-based nanostructuring of polymers: A review*. *Polymers*, 2017. 9(9): p. 417.
  83. Liu, Y., et al., *Hierarchical porous carbon fibers/carbon nanofibers monolith from electrospinning/CVD processes as a high effective surface area support platform*. *Journal of Materials Chemistry A*, 2017. 5(5): p. 2151-2162.
  84. Poveda, R.L. and N. Gupta, *Carbon nanofibers: structure and fabrication*, in *Carbon Nanofiber Reinforced Polymer Composites* 2016, Springer. p. 11-26.
  85. Xia, J.H., X. Jiang, and C.L. Jia, *The size effect of catalyst on the growth of helical carbon nanofibers*. *Applied Physics Letters*, 2009. 95(22): p. 223110.
  86. Chen, Q., et al., *Nano-epoxy resins containing electrospun carbon nanofibers and the resulting hybrid multi-scale composites*. *Composites Part B: Engineering*, 2014. 58: p. 43-53.
  87. I. Donmez, F. Kayaci, C. Ozgit-Akgun, T. Uyar, N. Biyikli, *Fabrication of hafnia hollow nanofibers by atomic layer deposition using electrospun nanofiber templates*, *J. Alloys Compd.* 559 (2013) 146–151. doi:10.1016/J.JALLCOM.2013.01.064.
  88. Firat, Y. and A. Peksoz, *Electrochemical synthesis of polyaniline/inorganic salt binary nanofiber thin films for electrochromic applications*. *Journal of Materials Science: Materials in Electronics*, 2017. 28(4): p. 3515-3522.
  89. Soumare, Y., et al., *Nickel nanofibers and nanowires: Elaboration by reduction in polyol medium assisted by external magnetic field*. *Solid State Communications*, 2011. 151(4): p. 284-288.
  90. Wang, W., et al., *A novel method to fabricate silica nanotubes based on phase separation effect*. *Journal of Materials Chemistry*, 2010. 20(41): p. 9068-9072.
  91. Ghayempour, S. and M. Montazer, *A modified microemulsion method for fabrication of hydrogel *Tragacanth* nanofibers*. *International journal of biological macromolecules*, 2018. 115: p. 317-323.
  92. Wang, Y., et al., *A nano-silica modified polyimide nanofiber separator with enhanced thermal and wetting properties for high safety lithium-ion batteries*. *Journal of Membrane Science*, 2017. 537: p. 248-254.
  93. Berenguer, R.I., et al., *Synthesis of Vanadium Oxide Nanofibers with Variable Crystallinity and V<sup>5+</sup>/V<sup>4+</sup> Ratios*. *ACS Omega*, 2017. 2(11): p. 7739-7745.
  94. Cheng, F., et al., *Template-directed materials for rechargeable lithium-ion batteries*. *Chemistry of Materials*, 2007. 20(3): p. 667-681.
  95. Nam, D.-H., et al., *Template-free electrochemical synthesis of Sn nanofibers as high-performance anode materials for Na-ion batteries*. *ACS nano*, 2014. 8(11): p. 11824-11835.

96. Park, K.-R., et al., *Simple electrochemical synthesis of ultra-long silver telluride nanotubes*. RSC Advances, 2015. 5(38): p. 29782-29785.
97. Zhao, Y., et al., *Facile electrochemical synthesis of antimicrobial TiO<sub>2</sub> nanotube arrays*. International journal of nanomedicine, 2014. 9: p. 5177.
98. Wen, Y., et al., *Synthesis of carbon nanofibers via hydrothermal conversion of cellulose nanocrystals*. Cellulose, 2017. 24(11): p. 4599-4604.
99. Wu, M.-C., et al., *Photocatalytic performance of Cu-doped TiO<sub>2</sub> nanofibers treated by the hydrothermal synthesis and air-thermal treatment*. Applied Surface Science, 2018. 430: p. 390-398.
100. Cao, T., et al., *A facile in situ hydrothermal method to SrTiO<sub>3</sub>/TiO<sub>2</sub> nanofiber heterostructures with high photocatalytic activity*. Langmuir, 2011. 27(6): p. 2946-2952.
101. Simpraditpan, A., et al., *Simple hydrothermal preparation of nanofibers from a natural ilmenite mineral*. Ceramics International, 2013. 39(3): p. 2497-2502.
102. Cao, S., et al., *Hydrothermal synthesis, characterization and gas sensing properties of the WO<sub>3</sub> nanofibers*. Materials Letters, 2016. 169: p. 17-20.
103. Barhoum, A., et al., *Sol-gel hot injection synthesis of ZnO nanoparticles into a porous silica matrix and reaction mechanism*. Materials & design, 2017. 119: p. 270-276.
104. Sui, R., A.S. Rizkalla, and P.A. Charpentier, *Formation of Titania Nanofibers: A Direct Sol-Gel Route in Supercritical CO<sub>2</sub>*. Langmuir, 2005. 21(14): p. 6150-6153.
105. Pirzada, T., et al., *Hybrid Carbon Silica Nanofibers through Sol-Gel Electrospinning*. Langmuir, 2014. 30(51): p. 15504-15513.
106. Watthanaarun, J., V. Pavarajarn, and P. Supaphol, *Titanium (IV) oxide nanofibers by combined sol-gel and electrospinning techniques: preliminary report on effects of preparation conditions and secondary metal dopant*. Science and Technology of Advanced Materials, 2005. 6(3): p. 240-245.
107. Liao, Y., et al., *Diameter control of ultrathin zinc oxide nanofibers synthesized by electrospinning*. Nanoscale Research Letters, 2014. 9(1): p. 267-267.
108. Kim, J.-H., et al., *Characterization and application of electrospun alumina nanofibers*. Nanoscale Research Letters, 2014. 9(1): p. 44-44.
109. Schwenke, A.M., S. Hoepfener, and U.S. Schubert, *Microwave synthesis of carbon nanofibers - the influence of MW irradiation power, time, and the amount of catalyst*. Journal of Materials Chemistry A, 2015. 3(47): p. 23778-23787.
110. Li, Y., et al., *Effects of ultrasonic irradiation on the morphology of chemically prepared polyaniline nanofibers*. Journal of applied polymer science, 2009. 113(2): p. 868-875.
111. Xu, H., B.W. Zeiger, and K.S. Suslick, *Sonochemical synthesis of nanomaterials*. Chemical Society Reviews, 2013. 42(7): p. 2555-2567.
112. Dallinger, D. and C.O. Kappe, *Microwave-assisted synthesis in water as solvent*. Chemical Reviews, 2007. 107(6): p. 2563-2591.
113. Nyutu, E.K., et al., *Systematic control of particle size in rapid open-vessel microwave synthesis of K-OMS-2 nanofibers*. The Journal of Physical Chemistry C, 2008. 112(17): p. 6786-6793.
114. Xie, J., et al., *Isolation and characterization of cellulose nanofibers from bamboo using microwave liquefaction combined with chemical treatment and ultrasonication*. Carbohydrate Polymers, 2016. 151: p. 725-734.
115. Liu, X. and P.X. Ma, *Phase separation, pore structure, and properties of nanofibrous gelatin scaffolds*. Biomaterials, 2009. 30(25): p. 4094-4103.
116. Zhao, J., et al., *Preparation, structure and crystallinity of chitosan nano-fibers by a solid-liquid phase separation technique*. Carbohydrate polymers, 2011. 83(4): p. 1541-1546.

117. Samitsu, S., et al., *Flash freezing route to mesoporous polymer nanofibre networks*. Nature communications, 2013. 4: p. 2653.
118. Zeng, D., A. Ribbe, and R.C. Hayward, *Anisotropic and Interconnected Nanoporous Materials from Randomly End-Linked Copolymer Networks*. Macromolecules, 2017. 50(12): p. 4668-4676.
119. Wang, B., X. Gao, and G. Piao, *Fabrication of C60 Fullerene Nanofibers by Volatile Diffusion Method*. Journal of Nanomaterials, 2013. 2013: p. 5.
120. Virji, S., et al., *Polyaniline nanofiber gas sensors: examination of response mechanisms*. Nano Letters, 2004. 4(3): p. 491-496.
121. Huang, J. and R.B. Kaner, *A general chemical route to polyaniline nanofibers*. Journal of the American Chemical Society, 2004. 126(3): p. 851-855.
122. Huang, J., et al., *Polyaniline nanofibers: facile synthesis and chemical sensors*. Journal of the American Chemical Society, 2003. 125(2): p. 314-315.
123. Huang, J. and R.B. Kaner, *Nanofiber formation in the chemical polymerization of aniline: a mechanistic study*. Angewandte Chemie, 2004. 116(43): p. 5941-5945.
124. Mirjalili, M. and S. Zohoori, *Review for application of electrospinning and electrospun nanofibers technology in textile industry*. Journal of Nanostructure in Chemistry, 2016. 6(3): p. 207-213.
125. Haider, A., S. Haider, and I.-K. Kang, *A comprehensive review summarizing the effect of electrospinning parameters and potential applications of nanofibers in biomedical and biotechnology*. Arabian Journal of Chemistry, 2015.
126. Pillay, V., et al., *A Review of the Effect of Processing Variables on the Fabrication of Electrospun Nanofibers for Drug Delivery Applications*. Journal of Nanomaterials, 2013. 2013: p. 22.
127. Teo, W.-E., R. Inai, and S. Ramakrishna, *Technological advances in electrospinning of nanofibers*. Science and Technology of Advanced Materials, 2011. 12(1): p. 013002.
128. Bhardwaj, N. and S.C. Kundu, *Electrospinning: a fascinating fiber fabrication technique*. Biotechnology advances, 2010. 28(3): p. 325-347.
129. Sahay, R., V. Thavasi, and S. Ramakrishna, *Design modifications in electrospinning setup for advanced applications*. Journal of Nanomaterials, 2011. 2011: p. 17.
130. Bubakir, M.M., et al., *Advances in Melt Electrospinning Technique*, in *Handbook of Nanofibers* 2018, Springer. p. 1-32.
131. Haichao, L., et al., *Engineering Nanofibers as Electrode and Membrane Materials for Batteries, Supercapacitors, and Fuel Cells*, in *Handbook of Nanofibers*, A. Barhoum, M. Bechelany, and A. Makhlof, Editors. 2018, Springer International Publishing: Cham. p. 1-27.
132. Zhang, B., et al., *Solvent-free electrospinning: opportunities and challenges*. Polymer Chemistry, 2017. 8(2): p. 333-352.
133. T.D. Brown, P.D. Dalton, D.W. Hutmacher, *Melt electrospinning today: An opportune time for an emerging polymer process*, Prog. Polym. Sci. 56 (2016) 116–166. doi:10.1016/J.PROGPOLYMSCI.2016.01.001.
134. Kamiyama, M. and M. Numata, *Islands-in-sea type composite fiber and process for producing the same*, 2009, Google Patents.
135. Yaqing, L., et al., *Magnetic-Field-Assisted Electrospinning of Aligned Straight and Wavy Polymeric Nanofibers*. Advanced Materials, 2010. 22(22): p. 2454-2457.
136. Han, D. and A.J. Steckl, *Triaxial electrospun nanofiber membranes for controlled dual release of functional molecules*. ACS applied materials & interfaces, 2013. 5(16): p. 8241-8245.
137. Zhang, L.-H., et al., *Recent advances in melt electrospinning*. RSC Advances, 2016. 6(58): p. 53400-53414.

138. He, H.-W., et al., *Solvent-free electrospinning of UV curable polymer microfibers*. RSC Advances, 2016. 6(35): p. 29423-29427.
139. He, H.-W., et al., *Solvent-free thermocuring electrospinning to fabricate ultrathin polyurethane fibers with high conductivity by in situ polymerization of polyaniline*. RSC Advances, 2016. 6(108): p. 106945-106950.
140. Moon, S., M. Gil, and K.J. Lee, *Syringeless Electrospinning toward Versatile Fabrication of Nanofiber Web*. Scientific Reports, 2017. 7: p. 41424.
141. Wang, G., et al., *Hierarchical activated carbon nanofiber webs with tuned structure fabricated by electrospinning for capacitive deionization*. Journal of Materials Chemistry, 2012. 22(41): p. 21819-21823.
142. R. Ramakrishnan, J. Gimbun, F. Samsuri, V. Narayanamurthy, N. Gajendran, Y. Sudha Lakshmi, D. Stranska, B. Ranganathan, *Needleless Electrospinning Technology – An Entrepreneurial Perspective*, Indian J. Sci. Technol. 9 (2016). doi:10.17485/ijst/2016/v9i15/91538.
143. Wang, J. and A.S. Nain, *Suspended micro/nanofiber hierarchical biological scaffolds fabricated using non-electrospinning STEP technique*. Langmuir, 2014. 30(45): p. 13641-13649.
144. Nain, A.S., et al., *Drawing suspended polymer micro-/nanofibers using glass micropipettes*. Applied Physics Letters, 2006. 89(18): p. 183105.
145. Mellado, P., et al., *A simple model for nanofiber formation by rotary jet-spinning*. Applied Physics Letters, 2011. 99(20): p. 203107.
146. Badrossamay, M.R., McIlwee, H.A., Goss, J.A., Parker, K.K., 2010. *Nanofiber assembly by rotary jetspinning*. Nano Letters 10, 2257e2261, Elsevier.
147. CHEN, R.-X., Y. LI, and J.-H. HE, *Mini-review on Bubbfil spinning process for mass-production of nanofibers*. Matéria (Rio de Janeiro), 2014. 19: p. 325-343.
148. Quintero, F., et al., *Laser spinning of bioactive glass nanofibers*. Advanced Functional Materials, 2009. 19(19): p. 3084-3090.
149. Quintero, F., et al., *Rapid production of ultralong amorphous ceramic nanofibers by laser spinning*. Applied physics letters, 2007. 90(15): p. 153109.
150. Sutti, A., T. Lin, and X. Wang, *Shear-enhanced solution precipitation: a simple process to produce short polymeric nanofibers*. Journal of nanoscience and nanotechnology, 2011. 11(10): p. 8947-8952.
151. Penide, J., et al., *Laser Spinning: A New Technique for Nanofiber Production*. Physics Procedia, 2014. 56: p. 365-370.
152. Yokoyama, Y., et al., *Novel wet electrospinning system for fabrication of spongiform nanofiber 3-dimensional fabric*. Materials letters, 2009. 63(9-10): p. 754-756.
153. Meier, C. and M.E. Welland, *Wet-Spinning of Amyloid Protein Nanofibers into Multifunctional High-Performance Biofibers*. Biomacromolecules, 2011. 12(10): p. 3453-3459.
154. Gagliardi, M., *Global Markets and Technologies for Nanofibers*, 2016, Report NAN043D, USA.
155. Lee, M.W., et al., *Self-healing nanofiber-reinforced polymer composites. 1. Tensile testing and recovery of mechanical properties*. ACS applied materials & interfaces, 2015. 7(35): p. 19546-19554.
156. Lu, Y., C. Chen, and X. Zhang, *Functional Nanofibers for Energy Storage*. Handbook of Smart Textiles, 2014: p. 1-28.
157. Sun, G., et al., *Electrospinning of Nanofibers for Energy Applications*. Nanomaterials, 2016. 6(7): p. 129.
158. Ding, B. and J. Yu, *Electrospun nanofibers for energy and environmental applications* 2014: Springer.
159. Victor, L. and K. Frank, *Biomedical applications of nanofibers*. Polymers for Advanced Technologies, 2011. 22(3): p. 350-365.

160. Ramakrishna, S., et al., *Electrospun nanofibers: solving global issues*. *Materials Today*, 2006. 9(3): p. 40-50.
161. Lee, M.W., et al., *Self-healing three-dimensional bulk materials based on core-shell nanofibers*. *Chemical Engineering Journal*, 2018. 334: p. 1093-1100.
162. Lee, M.W., et al., *Self-healing of nanofiber-based composites in the course of stretching*. *Polymer*, 2016. 103: p. 180-188.
163. R. Esmaeely Neisiany, J.K.Y. Lee, S. Nouri Khorasani, R. Bagheri, S. Ramakrishna, *Facile strategy toward fabrication of highly responsive self-healing carbon/epoxy composites via incorporation of healing agents encapsulated in poly(methylmethacrylate) nanofiber shell*, *J. Ind. Eng. Chem.* 59 (2018) 456–466. doi:10.1016/J.JIEC.2017.11.007.
164. Blaiszik, B.J., et al., *Self-Healing Polymers and Composites*. *Annual Review of Materials Research*, 2010. 40(1): p. 179-211.
165. Fang, Y., et al., *Robust Self-Healing Hydrogels Assisted by Cross-Linked Nanofiber Networks*. *Scientific Reports*, 2013. 3: p. 2811.
166. Jayawardena, K.I., et al., *'Inorganics-in-Organics': recent developments and outlook for 4G polymer solar cells*. *Nanoscale*, 2013. 5(18): p. 8411-8427.
167. Zhaodong, L., et al., *Highly Efficient Capillary Photoelectrochemical Water Splitting Using Cellulose Nanofiber-Templated TiO<sub>2</sub> Photoanodes*. *Advanced Materials*, 2014. 26(14): p. 2262-2267.
168. Barhoum, A., et al., *Review of recent research on flexible multifunctional nanopapers*. *Nanoscale*, 2017. 9(40): p. 15181-15205.
169. Persano, L., A. Camposeo, and D. Pisignano, *Active polymer nanofibers for photonics, electronics, energy generation and micromechanics*. *Progress in Polymer Science*, 2015. 43: p. 48-95.
170. Cho, H., S.Y. Min, and T.W. Lee, *Electrospun organic nanofiber electronics and photonics*. *Macromolecular Materials and Engineering*, 2013. 298(5): p. 475-486.
171. Thavasi, V., G. Singh, and S. Ramakrishna, *Electrospun nanofibers in energy and environmental applications*. *Energy & Environmental Science*, 2008. 1(2): p. 205-221.
172. Shalan, A.E., et al., *Nanofibers as Promising Materials for New Generations of Solar Cells*, in *Handbook of Nanofibers 2018*, Springer. p. 1-33.
173. Mitchell, R.R., et al., *All-carbon-nanofiber electrodes for high-energy rechargeable Li-O<sub>2</sub> batteries*. *Energy & Environmental Science*, 2011. 4(8): p. 2952-2958.
174. Wu, Q., et al., *Supercapacitors Based on Flexible Graphene/Polyaniline Nanofiber Composite Films*. *ACS Nano*, 2010. 4(4): p. 1963-1970.
175. Yu, S., et al., *Battery-like Supercapacitors from Vertically Aligned Carbon Nanofiber Coated Diamond: Design and Demonstrator*. *Advanced Energy Materials*, 2018. 8(12): p. 1702947.
176. Bhagwan, J., et al., *Nanofibers of spinel-CdMn<sub>2</sub>O<sub>4</sub>: A new and high performance material for supercapacitor and Li-ion batteries*. *Journal of Alloys and Compounds*, 2017. 703: p. 86-95.
177. Vu, N.H., P. Arunkumar, and W.B. Im, *High-performance spinel-rich Li<sub>1.5</sub>MnTiO<sub>4</sub> δ ultralong nanofibers as cathode materials for Li-ion batteries*. *Scientific Reports*, 2017. 7: p. 45579.
178. X. He, Y. Hu, Z. Shen, R. Chen, K. Wu, Z. Cheng, X.W. Zhang, P. Pan, *Channelized carbon nanofiber with uniform-dispersed GeO<sub>2</sub> as anode for long-lifespan lithium-ion batteries*, *J. Alloys Compd.* 729 (2017) 313–322. doi:10.1016/J.JALLCOM.2017.09.038.
179. Liu, Y., et al., *Self-improving anodes for lithium-ion batteries: continuous interlamellar spacing expansion induced capacity increase in polydopamine-derived nitrogen-doped carbon tubes during cycling*. *Journal of Materials Chemistry A*, 2015. 3(42): p. 20880-20885.

180. Yang, C., et al., *Polyvinylidene fluoride membrane by novel electrospinning system for separator of Li-ion batteries*. Journal of Power Sources, 2009. 189(1): p. 716-720.
181. Xiao, Q., et al., *A novel sandwiched membrane as polymer electrolyte for application in lithium-ion battery*. Journal of Membrane Science, 2009. 326(2): p. 260-264.
182. Kuo, P.-L., et al., *High performance of transferring lithium ion for polyacrylonitrile-interpenetrating crosslinked polyoxyethylene network as gel polymer electrolyte*. ACS applied materials & interfaces, 2014. 6(5): p. 3156-3162.
183. Miao, Y.-E., et al., *Electrospun polyimide nanofiber-based nonwoven separators for lithium-ion batteries*. Journal of Power Sources, 2013. 226: p. 82-86.
184. Zhang, X., et al., *Electrospun nanofiber-based anodes, cathodes, and separators for advanced lithium-ion batteries*. Polymer Reviews, 2011. 51(3): p. 239-264.
185. Liang, W., et al., *Synthesis of cellulose diacetate based copolymer electrospun nanofibers for tissues scaffold*. Applied Surface Science, 2018. 443: p. 374-381.
186. Hu, L., et al., *Highly conductive paper for energy-storage devices*. Proceedings of the National Academy of Sciences, 2009. 106(51): p. 21490-21494.
187. Li, W., et al., *Electrospinning with partially carbonization in air: Highly porous carbon nanofibers optimized for high-performance flexible lithium-ion batteries*. Nano Energy, 2015. 13: p. 693-701.
188. Chen, L., et al., *Core-shell structured carbon nanofibers yarn@ polypyrrole@ graphene for high performance all-solid-state fiber supercapacitors*. Carbon, 2018.
189. Yu, S., et al., *Supercapacitors: Battery-like Supercapacitors from Vertically Aligned Carbon Nanofiber Coated Diamond: Design and Demonstrator (Adv. Energy Mater. 12/2018)*. Advanced Energy Materials, 2018. 8(12): p. 1870054.
190. Chen, L., et al., *Flexible all-solid-state supercapacitors based on freestanding, binder-free carbon nanofibers@ polypyrrole@ graphene film*. Chemical Engineering Journal, 2018. 334: p. 184-190.
191. Fan, Z., et al., *Asymmetric Supercapacitors Based on Graphene/MnO<sub>2</sub> and Activated Carbon Nanofiber Electrodes with High Power and Energy Density*. Advanced Functional Materials, 2011. 21(12): p. 2366-2375.
192. Qiu, Y., et al., *Vertically aligned carbon nanotubes on carbon nanofibers: A hierarchical three-dimensional carbon nanostructure for high-energy flexible supercapacitors*. Chemistry of Materials, 2015. 27(4): p. 1194-1200.
193. Huang, Q., et al., *One-step electrospinning of carbon nanoweb on metallic textiles for high-capacitance supercapacitor fabrics*. Journal of Materials Chemistry A, 2016. 4(18): p. 6802-6808.
194. Shen, C., et al., *Flexible micro-supercapacitors prepared using direct-write nanofibers*. RSC Advances, 2017. 7(19): p. 11724-11731.
195. Chung, S., et al., *Improved water management of Pt/C cathode modified by graphitized carbon nanofiber in proton exchange membrane fuel cell*. Journal of Power Sources, 2018. 399: p. 350-356.
196. Zebda, A., et al., *Single Glucose Biofuel Cells Implanted in Rats Power Electronic Devices*. Scientific Reports, 2013. 3: p. 1516.
197. Liu, S., et al., *An oxygen tolerance conductive hydrogel anode membrane for use in a potentially implantable glucose fuel cell*. RSC Advances, 2016. 6(114): p. 112971-112980.
198. R. Sood, S. Cavaliere, D.J. Jones, J. Rozière, *Electrospun nanofibre composite polymer electrolyte fuel cell and electrolysis membranes*, Nano Energy. 26 (2016) 729–745. doi:10.1016/J.NANOEN.2016.06.027.

199. Shui, J., et al., *Highly efficient nonprecious metal catalyst prepared with metal–organic framework in a continuous carbon nanofibrous network*. Proceedings of the National Academy of Sciences, 2015. 112(34): p. 10629-10634.
200. Tamura, T. and H. Kawakami, *Aligned Electrospun Nanofiber Composite Membranes for Fuel Cell Electrolytes*. Nano Letters, 2010. 10(4): p. 1324-1328.
201. Abourached, C., M.J. English, and H. Liu, *Wastewater treatment by Microbial Fuel Cell (MFC) prior irrigation water reuse*. Journal of Cleaner Production, 2016. 137: p. 144-149.
202. Hou, H., et al., *Microfabricated microbial fuel cell arrays reveal electrochemically active microbes*. PLOS one, 2009. 4(8): p. e6570.
203. Jiang, H., L.J. Halverson, and L. Dong, *A miniature microbial fuel cell with conducting nanofibers-based 3D porous biofilm*. Journal of Micromechanics and Microengineering, 2015. 25(12): p. 125017.
204. Nasybulin, E., et al., *Morphological and spectroscopic studies of electrochemically deposited poly (3, 4-ethylenedioxythiophene)(PEDOT) hole extraction layer for organic photovoltaic device (OPVd) fabrication*. The Journal of Physical Chemistry C, 2011. 115(10): p. 4307-4314.
205. Kim, M., et al., *Flexible lateral organic solar cells with core–shell structured organic nanofibers*. Nano Energy, 2015. 18: p. 97-108.
206. Li, J., et al., *Silver nanoparticle doped TiO<sub>2</sub> nanofiber dye sensitized solar cells*. Chemical Physics Letters, 2011. 514(1): p. 141-145.
207. Sun, H., et al., *Recent progress in solar cells based on one-dimensional nanomaterials*. Energy & Environmental Science, 2015. 8(4): p. 1139-1159.
208. Jin, E.M., et al., *Enhancement of the photoelectric performance of dye-sensitized solar cells using Ag-doped TiO<sub>2</sub> nanofibers in a TiO<sub>2</sub> film as electrode*. Nanoscale Research Letters, 2012. 7(1): p. 97.
209. Qin, X.H. and S.Y. Wang, *Filtration properties of electrospinning nanofibers*. Journal of applied polymer science, 2006. 102(2): p. 1285-1290.
210. Ganesh, V.A., et al., *Electrospun SiO<sub>2</sub> nanofibers as a template to fabricate a robust and transparent superamphiphobic coating*. Rsc Advances, 2013. 3(12): p. 3819-3824.
211. Lee, K.J., et al., *Activated carbon nanofiber produced from electrospun polyacrylonitrile nanofiber as a highly efficient formaldehyde adsorbent*. Carbon, 2010. 48(15): p. 4248-4255.
212. Wu, Z.-Y., et al., *Carbon nanofiber aerogels for emergent cleanup of oil spillage and chemical leakage under harsh conditions*. Scientific Reports, 2014. 4: p. 4079.
213. Wang, W., et al., *Ferrite-grafted polyaniline nanofibers as electromagnetic shielding materials*. Journal of Materials Chemistry C, 2013. 1(16): p. 2851-2859.
214. Veleirinho, B., M.F. Rei, and J. Lopes-Da-Silva, *Solvent and concentration effects on the properties of electrospun poly (ethylene terephthalate) nanofiber mats*. Journal of Polymer Science Part B: Polymer Physics, 2008. 46(5): p. 460-471.
215. Weber, M., et al., *Atomic Layer Deposition for Membranes: Basics, Challenges, and Opportunities*. Chemistry of Materials, 2018. 30(21): p. 7368-7390.
216. Tabe, S., *Electrospun nanofiber membranes and their applications in water and wastewater treatment*, in *Nanotechnology for Water Treatment and Purification 2014*, Springer. p. 111-143.
217. Ling, S., et al., *Design and function of biomimetic multilayer water purification membranes*. Science advances, 2017. 3(4): p. e1601939.
218. Feng, Q., et al., *Electrospun AOPAN/RC blend nanofiber membrane for efficient removal of heavy metal ions from water*. Journal of Hazardous Materials, 2018. 344: p. 819-828.



219. Feng, C., et al., *Preparation and characterization of electro-spun nanofiber membranes and their possible applications in water treatment*. Separation and Purification Technology, 2013. 102: p. 118-135.
220. Lee, M.W., et al., *Electrospun Polystyrene Nanofiber Membrane with Superhydrophobicity and Superoleophilicity for Selective Separation of Water and Low Viscous Oil*. ACS Applied Materials & Interfaces, 2013. 5(21): p. 10597-10604.
221. Hassan, E., et al., *Use of Bacterial Cellulose and Crosslinked Cellulose Nanofibers Membranes for Removal of Oil from Oil-in-Water Emulsions*. Polymers, 2017. 9(9): p. 388.
222. Tijing, L.D., et al., *Superhydrophobic nanofiber membrane containing carbon nanotubes for high-performance direct contact membrane distillation*. Journal of Membrane Science, 2016. 502: p. 158-170.
223. Bechelany, M., et al., *Highly crystalline MOF-based materials grown on electrospun nanofibers*. Nanoscale, 2015. 7(13): p. 5794-5802.
224. Romanos, G.E., et al., *Hybrid Ultrafiltration/Photocatalytic Membranes for Efficient Water Treatment*. Industrial & Engineering Chemistry Research, 2013. 52(39): p. 13938-13947.
225. Song, J., et al., *Soft Zr-doped TiO<sub>2</sub> Nanofibrous Membranes with Enhanced Photocatalytic Activity for Water Purification*. Scientific Reports, 2017. 7(1): p. 1636.
226. Kanjwal, M.A., N.A. Barakat, and I.S. Chronakis, *Photocatalytic degradation of dairy effluent using AgTiO<sub>2</sub> nanostructures/polyurethane nanofiber membrane*. Ceramics International, 2015. 41(8): p. 9615-9621.
227. Singh, N., et al., *Quantum dot sensitized electrospun mesoporous titanium dioxide hollow nanofibers for photocatalytic applications*. RSC Advances, 2016. 6(53): p. 48109-48119.
228. Dong, Q.; Wang, G.; Wu, T.; Peng, S.; Qiu, J. Enhancing capacitive deionization performance of electrospun activated carbon nanofibers by coupling with carbon nanotubes. J. Colloid Interface Sci. 2015, 446, 373–378.
229. Zhang, R., et al., *Nanofiber air filters with high-temperature stability for efficient PM<sub>2.5</sub> removal from the pollution sources*. Nano letters, 2016. 16(6): p. 3642-3649.
230. Liu, C., et al., *Transparent air filter for high-efficiency PM 2.5 capture*. Nature communications, 2015. 6: p. 6205.
231. Chen, Y., et al., *Electrospun carbon nanofiber networks from phenolic resin for capacitive deionization*. Chemical Engineering Journal, 2014. 252: p. 30-37.
232. Yasin, A.S., et al., *ZrO<sub>2</sub> nanofibers/activated carbon composite as a novel and effective electrode material for the enhancement of capacitive deionization performance*. RSC Advances, 2017. 7(8): p. 4616-4626.
233. Zhang, S., Liu, H., Yin, X., Li, Z., Yu, J., Ding, B., 2017a. Tailoring mechanically robust poly(mphenylene isophthalamide) nanofiber/nets for ultrathin high-efficiency air filter. Scientific Reports 7, 40550.
234. Gao, H., et al., *A low filtration resistance three-dimensional composite membrane fabricated via free surface electrospinning for effective PM<sub>2.5</sub> capture*. Environmental Science: Nano, 2017. 4(4): p. 864-875.
235. Zhu, M., et al., *Electrospun nanofibers membranes for effective air filtration*. Macromolecular Materials and Engineering, 2017. 302(1): p. 1600353.
236. Balamurugan, R., S. Sundarajan, and S. Ramakrishna, *Recent trends in nanofibrous membranes and their suitability for air and water filtrations*. Membranes, 2011. 1(3): p. 232-248.
237. Aussawasathien, D., C. Teerawattananon, and A. Vongachariya, *Separation of micron to sub-micron particles from water: electrospun nylon-6 nanofibrous membranes as pre-filters*. Journal of membrane science, 2008. 315(1-2): p. 11-19.

238. Yeom, B.Y., E. Shim, and B. Pourdeyhimi, *Boehmite nanoparticles incorporated electrospun nylon-6 nanofiber web for new electret filter media*. *Macromolecular research*, 2010. 18(9): p. 884-890.
239. Jiang, S., et al., *Polyimide nanofibers by "Green" electrospinning via aqueous solution for filtration applications*. *ACS Sustainable Chemistry & Engineering*, 2016. 4(9): p. 4797-4804.
240. Gu, G.Q., et al., *Triboelectric Nanogenerator Enhanced Nanofiber Air Filters for Efficient Particulate Matter Removal*. *ACS Nano*, 2017. 11(6): p. 6211-6217.
241. Gugulothu, D., et al., *Structural Multifunctional Nanofibers and their Emerging Applications*, in *Handbook of Nanofibers*, A. Barhoum, M. Bechelany, and A. Makhlof, Editors. 2018, Springer International Publishing: Cham. p. 1-41.
242. Uludağ, H., *Grand challenges in biomaterials*. *Frontiers in bioengineering and biotechnology*, 2014. 2: p. 43.
243. D.-G. Yu, J.-J. Li, G.R. Williams, M. Zhao, *Electrospun amorphous solid dispersions of poorly water-soluble drugs: A review*, *J. Control. Release*. 292 (2018) 91–110. doi:10.1016/J.JCONREL.2018.08.016.
244. Place, E.S., et al., *Synthetic polymer scaffolds for tissue engineering*. *Chemical Society Reviews*, 2009. 38(4): p. 1139-1151.
245. Vasita, R. and D.S. Katti, *Nanofibers and their applications in tissue engineering*. *International journal of nanomedicine*, 2006. 1(1): p. 15-30.
246. Sankar, S., et al., *Electrospun fibers for recruitment and differentiation of stem cells in regenerative medicine*. *Biotechnology journal*, 2017. 12(12): p. 1700263.
247. Chaurey, V., et al., *Nanofiber size-dependent sensitivity of fibroblast directionality to the methodology for scaffold alignment*. *Acta Biomaterialia*, 2012. 8(11): p. 3982-3990.
248. Yang, F., et al., *Electrospinning of nano/micro scale poly (L-lactic acid) aligned fibers and their potential in neural tissue engineering*. *Biomaterials*, 2005. 26(15): p. 2603-2610.
249. Nedjari, S., F. Awaja, and G. Altankov, *Three Dimensional Honeycomb Patterned Fibrinogen Based Nanofibers Induce Substantial Osteogenic Response of Mesenchymal Stem Cells*. *Scientific Reports*, 2017. 7(1): p. 15947.
250. Lu, H., et al., *Synergistic effect of carbon nanofiber and carbon nanopaper on shape memory polymer composite*. *Applied physics letters*, 2010. 96(8): p. 084102.
251. Kai, D., et al., *Biocompatible electrically conductive nanofibers from inorganic-organic shape memory polymers*. *Colloids and Surfaces B: Biointerfaces*, 2016. 148: p. 557-565.
252. Lu, H., et al., *Self-assembled multi-layered carbon nanofiber nanopaper for significantly improving electrical actuation of shape memory polymer nanocomposite*. *Composites Part B: Engineering*, 2014. 59: p. 191-195.
253. Dahlin, R.L., F.K. Kasper, and A.G. Mikos, *Polymeric Nanofibers in Tissue Engineering*. *Tissue Engineering. Part B, Reviews*, 2011. 17(5): p. 349-364.
254. Zhang, Y., et al., *Coaxial electrospinning of (fluorescein isothiocyanate-conjugated bovine serum albumin)-encapsulated poly ( $\epsilon$ -caprolactone) nanofibers for sustained release*. *Biomacromolecules*, 2006. 7(4): p. 1049-1057.
255. Jun, Z., et al., *Poly (vinyl alcohol) nanofibres by electrospinning: influence of molecular weight on fibre shape*. *e-Polymers*, 2005. 5(1).
256. Huang, Z.-M., et al., *Electrospinning and mechanical characterization of gelatin nanofibers*. *Polymer*, 2004. 45(15): p. 5361-5368.
257. Tuzlakoglu, K., et al., *Design of nano-and microfiber combined scaffolds by electrospinning of collagen onto starch-based fiber meshes: a man-made equivalent of natural extracellular matrix*. *Tissue Engineering Part A*, 2010. 17(3-4): p. 463-473.

258. Buttafoco, L., et al., *Electrospinning of collagen and elastin for tissue engineering applications*. *Biomaterials*, 2006. 27(5): p. 724-734.
259. Pham, Q.P., U. Sharma, and A.G. Mikos, *Electrospun poly ( $\epsilon$ -caprolactone) microfiber and multilayer nanofiber/microfiber scaffolds: characterization of scaffolds and measurement of cellular infiltration*. *Biomacromolecules*, 2006. 7(10): p. 2796-2805.
260. Lee, C.H., et al., *Nanofiber alignment and direction of mechanical strain affect the ECM production of human ACL fibroblast*. *Biomaterials*, 2005. 26(11): p. 1261-1270.
261. Xu, C., et al., *Electrospun nanofiber fabrication as synthetic extracellular matrix and its potential for vascular tissue engineering*. *Tissue engineering*, 2004. 10(7-8): p. 1160-1168.
262. Sahoo, S., et al., *Characterization of a novel polymeric scaffold for potential application in tendon/ligament tissue engineering*. *Tissue engineering*, 2006. 12(1): p. 91-99.
263. Rim, N.G., C.S. Shin, and H. Shin, *Current approaches to electrospun nanofibers for tissue engineering*. *Biomedical materials*, 2013. 8(1): p. 014102.
264. Chen, S., et al., *Recent advances in electrospun nanofibers for wound healing*. *Nanomedicine*, 2017. 12(11): p. 1335-1352.
265. Zahedi, P., et al., *A review on wound dressings with an emphasis on electrospun nanofibrous polymeric bandages*. *Polymers for Advanced Technologies*, 2010. 21(2): p. 77-95.
266. Kang, Y.O., et al., *Chitosan-coated poly (vinyl alcohol) nanofibers for wound dressings*. *Journal of Biomedical Materials Research Part B: Applied Biomaterials: An Official Journal of The Society for Biomaterials, The Japanese Society for Biomaterials, and The Australian Society for Biomaterials and the Korean Society for Biomaterials*, 2010. 92(2): p. 568-576.
267. Rho, K.S., et al., *Electrospinning of collagen nanofibers: effects on the behavior of normal human keratinocytes and early-stage wound healing*. *Biomaterials*, 2006. 27(8): p. 1452-1461.
268. Charernsriwilaiwat, N., et al., *Lysozyme-loaded, electrospun chitosan-based nanofiber mats for wound healing*. *International Journal of Pharmaceutics*, 2012. 427(2): p. 379-384.
269. Sadri, M., et al., *New wound dressing polymeric nanofiber containing green tea extract prepared by electrospinning method*. *Fibers and Polymers*, 2015. 16(8): p. 1742-1750.
270. Matthews, J.A., et al., *Electrospinning of collagen nanofibers*. *Biomacromolecules*, 2002. 3(2): p. 232-238.
271. Chen, D.W.-C. and S.-J. Liu, *Nanofibers used for delivery of antimicrobial agents*. *Nanomedicine*, 2015. 10(12): p. 1959-1971.
272. Fink, H., et al., *Real-time measurements of coagulation on bacterial cellulose and conventional vascular graft materials*. *Acta Biomaterialia*, 2010. 6(3): p. 1125-1130.
273. Andrade, F.K., et al., *Improving bacterial cellulose for blood vessel replacement: Functionalization with a chimeric protein containing a cellulose-binding module and an adhesion peptide*. *Acta Biomaterialia*, 2010. 6(10): p. 4034-4041.
274. Esguerra, M., et al., *Intravital fluorescent microscopic evaluation of bacterial cellulose as scaffold for vascular grafts*. *Journal of Biomedical Materials Research Part A: An Official Journal of The Society for Biomaterials, The Japanese Society for Biomaterials, and The Australian Society for Biomaterials and the Korean Society for Biomaterials*, 2010. 93(1): p. 140-149.
275. Lin, N. and A. Dufresne, *Nanocellulose in biomedicine: Current status and future prospect*. *European Polymer Journal*, 2014. 59: p. 302-325.
276. Namekawa, K., et al., *Fabrication of zeolite-polymer composite nanofibers for removal of uremic toxins from kidney failure patients*. *Biomaterials Science*, 2014. 2(5): p. 674-679.
277. Dadsetan, M., et al., *Effect of hydrogel porosity on marrow stromal cell phenotypic expression*. *Biomaterials*, 2008. 29(14): p. 2193-2202.

278. Barhoum, A., et al., *Nanofiber Technology: History and Developments*, in *Handbook of Nanofibers* 2018. p. 1-42.
279. Gibson, P., H. Schreuder-Gibson, and C. Pentheny, *Electrospinning technology: direct application of tailorable ultrathin membranes*. *Journal of Coated Fabrics*, 1998. 28(1): p. 63-72.
280. McCreery, M.J., *Topical skin protectants*, 1997, Google Patents.
281. Stevens, W., et al., *Basic Research Needs for Countering Terrorism*, 2002, USDOE Office of Science (SC).
282. Kathirvelu, S., L. D'Souza, and B. Dhurai, *Nanotechnology applications in textiles*. *Indian Journal of Science and technology*, 2008. 1(5): p. 1-10.
283. Chen, J., J.H. Gu, and Y. Liu. *Perspective on development of nanotechnology in textiles*. in *Advanced Materials Research*. 2010. Trans Tech Publ.
284. Vanangamudi, A., et al., *Nanofibers for Membrane Applications*, in *Handbook of Nanofibers*, A. Barhoum, M. Bechelany, and A. Makhlof, Editors. 2018, Springer International Publishing: Cham. p. 1-24.
285. Barhoum, A., et al., *Seed-mediated hot-injection synthesis of tiny Ag nanocrystals on nanoscale solid supports and reaction mechanism*. *ACS applied materials & interfaces*, 2016. 8(16): p. 10551-10561.
286. Rehan, M., et al., *Towards multifunctional cellulosic fabric: UV photo-reduction and in-situ synthesis of silver nanoparticles into cellulose fabrics*. *International journal of biological macromolecules*, 2017. 98: p. 877-886.
287. Fantini, D. and L. Costa, *Dye, fluorophores and pigment coloration of nanofibers produced by electrospinning*. *Polymers for Advanced Technologies*, 2009. 20(2): p. 111-121.
288. Yan, X., et al., *Colorful Hydrophobic Poly (Vinyl Butyral)/Cationic Dye Fibrous Membranes via a Colored Solution Electrospinning Process*. *Nanoscale research letters*, 2016. 11(1): p. 540.
289. Khatri, Z., et al., *Cationic-cellulose nanofibers: preparation and dyeability with anionic reactive dyes for apparel application*. *Carbohydrate Polymers*, 2013. 91(1): p. 434-443.
290. Khatri, Z., et al., *Dyeing and characterization of cellulose nanofibers to improve color yields by dual padding method*. *Cellulose*, 2013. 20(3): p. 1469-1476.
291. Samyn, P. and A. Barhoum, *Chapter 9 - Engineered nanomaterials for papermaking industry*, in *Fundamentals of Nanoparticles*, A. Barhoum and A.S. Hamdy Makhlof, Editors. 2018, Elsevier. p. 245-277.
292. Mathur, V. and B. Brennand. *Novel silicate nano-fibers and super nano carbonates for dematerialization—basis weight reduction*. in *Paper conference and trade show, PaperCon*. 2013.
293. Zhao, Z., J. Gou, and A. Khan, *Processing and structure of carbon nanofiber paper*. *Journal of Nanomaterials*, 2009. 2009: p. 5.
294. Carosio, F., et al., *Clay nanopaper as multifunctional brick and mortar fire protection coating—wood case study*. *Materials & Design*, 2016. 93: p. 357-363.
295. Kalinová, K., et al., *Resonant effect of nanofibrous sound absorptive material in room acoustics*. *Building Research Journal*, 2009. 57: p. 55-76.
296. Khan, W.S., R. Asmatulu, and M.B. Yildirim, *Acoustical Properties of Electrospun Fibers for Aircraft Interior Noise Reduction*. *Journal of Aerospace Engineering*, 2012. 25(3): p. 376-382.
297. Youssef, A. M.; Moustafa, H. A.; Barhoum, A.; Hakim, A. E.-F. A. A.; Dufresne, A. Evaluation of the Morphological, Electrical and Antibacterial Properties of Polyaniline Nanocomposite Based on Zn/Al-Layered Double Hydroxides. *ChemistrySelect* 2017, 2 (27), 8553–8566.

298. Rasouli, R.; Barhoum, A. Advances in Nanofibers for Antimicrobial Drug Delivery. In Handbook of Nanofibers; Springer International Publishing: Cham, 2019; pp 733–774.
299. Rasouli, R.; Barhoum, A.; Bechelany, M.; Dufresne, A. Nanofibers for Biomedical and Healthcare Applications. *Macromol. Biosci.* 2019, 19 (2), 1800256.
300. Barhoum, A.; Shalan, A. E.; El-Hout, S. I.; Ali, G. A. M.; Abdelbasir, S. M.; Abu Serea, E. S.; Ibrahim, A. H.; Pal, K. A Broad Family of Carbon Nanomaterials: Classification, Properties, Synthesis, and Emerging Applications. In Handbook of Nanofibers; Springer International Publishing, 2019; pp 1–40.
301. Chen, X.; Cheng, L.; Li, H.; Barhoum, A.; Zhang, Y.; He, X.; Yang, W.; Bubakir, M. M.; Chen, H. Magnetic Nanofibers: Unique Properties, Fabrication Techniques, and Emerging Applications. *ChemistrySelect* 2018, 3 (31), 9127–9143.
302. Turkey, A. O.; Barhoum, A.; Mohamed Rashad, M.; Bechlany, M. Enhanced the Structure and Optical Properties for ZnO/PVP Nanofibers Fabricated via Electrospinning Technique. *J. Mater. Sci. Mater. Electron.* 2017, 28 (23), 17526–17532.
303. Makhoulf, A.; Barhoum, A. Emerging Applications of Nanoparticles and Architectural Nanostructures: Current Prospects and Future Trends; 2018.
304. Jeevanandam, J.; Barhoum, A.; Chan, Y. S.; Dufresne, A.; Danquah, M. K. Review on Nanoparticles and Nanostructured Materials: History, Sources, Toxicity and Regulations. *Beilstein J. Nanotechnol.* 2018, 9 (1).
305. Jeevanandam, J.; Barhoum, A.; Chan, Y. S.; Dufresne, A.; Danquah, M. K. Review on Nanoparticles and Nanostructured Materials: History, Sources, Toxicity and Regulations. *Beilstein Journal of Nanotechnology*. Beilstein-Institut Zur Forderung der Chemischen Wissenschaften April 3, 2018, pp 1050–1074.
306. M. Rehan, A. Barhoum, T.A. Khattab, L. Gätjen, R. Wilken, Colored, photocatalytic, antimicrobial and UV-protected viscose fibers decorated with Ag/Ag<sub>2</sub>CO<sub>3</sub> and Ag/Ag<sub>3</sub>PO<sub>4</sub> nanoparticles, *Cellulose*. 26 (2019) 5437–5453. doi:10.1007/s10570-019-02497-8.
307. A. Barhoum, M. Bechelany, A.S.H. Makhoulf, eds., Handbook of Nanofibers, Springer International Publishing, Cham, 2019. doi:10.1007/978-3-319-53655-2.
308. S. Prasad, V. Kumar, S. Kirubanandam, Engineered nanomaterials: nanofabrication and surface functionalization, *Emerg. Appl. Nanoparticles Archit. Nanostructures*. (2018) 305–340. doi:10.1016/B978-0-323-51254-1.00011-7.