



Structural Multifunctional Nanofibers and their Emerging Applications

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Abstract

Nanofibers are an exciting new class of nanomaterials (NMs) produced by using innovative manufacturing process technologies. Nanofibers are developed from a wide variety of materials of diverse architecture and nature. Nanofibers are divided into the following classes: (1) based on the raw material, nanofibers are classified into organic, inorganic, and carbon and composite fibers, and (2) based on the structure, nanofibers are divided into nonporous, mesoporous, hollow, and core-shell fibers. The geometrical shape (structure) of the fiber materials can be tuned from the non-woven web, yarn, to bulk structures using nanofiber fabrication techniques. Nanofibers have been widely used in a range of applications, such as energy generation, production, and storage, environmental protection and improvement, tissue engineering, pharmaceutical, and biomedical applications. This chapter discusses the nanofibers' types, structures, fabrication techniques, inherent properties, and how these properties affect their potential usage.

Keywords

Nanostructured fibers · Mesoporous nanofibers · Hollow nanofibers · Core-shell nanofibers · Natural nanofibers · Engineered nanofibers

Introduction

Nanofibers are flexible one-dimensional nanomaterial (1D-NMs) with a diameter of 100 nm or less. As the fiber diameter is shrunk from micrometers to nanometers, the nanofibers show some unique properties. Assorted attractive characters like the high surface area to volume ratio, flexibility on surface functionalities, and superior mechanical properties can be obtained, when the diameter of the fiber is reduced to the nanoscale [1]. Nanostructured fibers (mesoporous, core-shell, hollow, surface-decorated fibers) acquire distinctive characteristics that make them appropriate for biomedical, environmental, and energy-related applications, to name a few [2]. Various preparation approaches such as drawing, template synthesis, phase separation, self-assembly, and electrospinning have been employed for the synthesis of polymer nanofibers [1]. Among these approaches, electrospinning has been acknowledged as a resourceful method for the manufacture of structural nanofibers, including mesoporous, core-shell, hollow, multicomponent, and surface-decorated nanofibers. Due to the inherent features of electrospinning process, it can manage deposition of

nanofibers on a target substrate with a different orientation, including random, aligned, and layer-by-layer deposition [3].

Electrospinning is a fiber production method which uses electric force to draw charged threads of polymer solutions or polymer melts with diameters in the range of 5 to 100 nm. In the existence of the persuade of an electric field, a pendant droplet of the polymer solution at the spinneret is exact to a conical shape. The electrospinning process could consider the capacity to synthesizes nanofibers using an electrically charged jet of polymer solution or polymer melts. Some polymers are not spinnable due to inadequate solubility in a proper solvent for electrospinning. An unsinkable polymer can be fabricated as nanofibers using co-spinning with a spinnable polymer solution. The different structures of nanofiber, such as core-shell, biocomponent, multicomponent, hollow, and porous structures, could be fabricated by using specially designed spinnerets [4].

Various polymers have been successfully electrospun into ultrafine fibers in recent years, mostly in solution form and some in melt form. Synthetic polymers represent straightforward processability for electrospinning and additionally favor various nanofibrous morphologies than natural polymers. Water-soluble natural polymers are repeatedly noted to be complex for directing into nanofibers owed to their deranged nature, for example, being vulnerable to handling parameters and having inferior mechanical characters [4]. Figure 1 shows various types of nanofibers with different structures [5]. While modifying or changing the electrospinning process conditions, different shapes can be obtained, such as uniaxially, biaxial aligned, ribbon, porous fibers, necklace-like, nano-webs, hollow, a nanowire in hollow fibers, and multichannel tubular.

Polymer-Based Nanofibers

Polymer-based nanofibers are ubiquitous in many spheres of human life. clothing, fishing nets, air-conditioning filters, cigarette filters, surgical masks, heart valves, and vascular grafts are few examples. The fibers used in these applications are typically micron-sized and made from a variety of polymers of both synthetic and natural origin. The literature suggests that around hundred different polymers have been effectively electrospun into very fine fibers with a diameter ranging from 10 nm to 1 μm . Polymers, which are molten at high temperature, can also be prepared into nanofibers with electrospinning. As an alternative to a solution, the polymer melt is sent into the capillary tube. While employing high-melting-point polymers for electrospinning process, the capillary tube, traveling-charged melt fluid jet, and metal collecting screen have to be enclosed in a vacuum [6]. Most of the polymers are dissolved in solvents before electrospinning, as the processing conditions involved are simple and straightforward. Attention has been focused on functionalization of polymer nanofibers via different approaches, for example, coaxial electrospinning, blend electrospinning, emulsion electrospinning, combining nanofibers

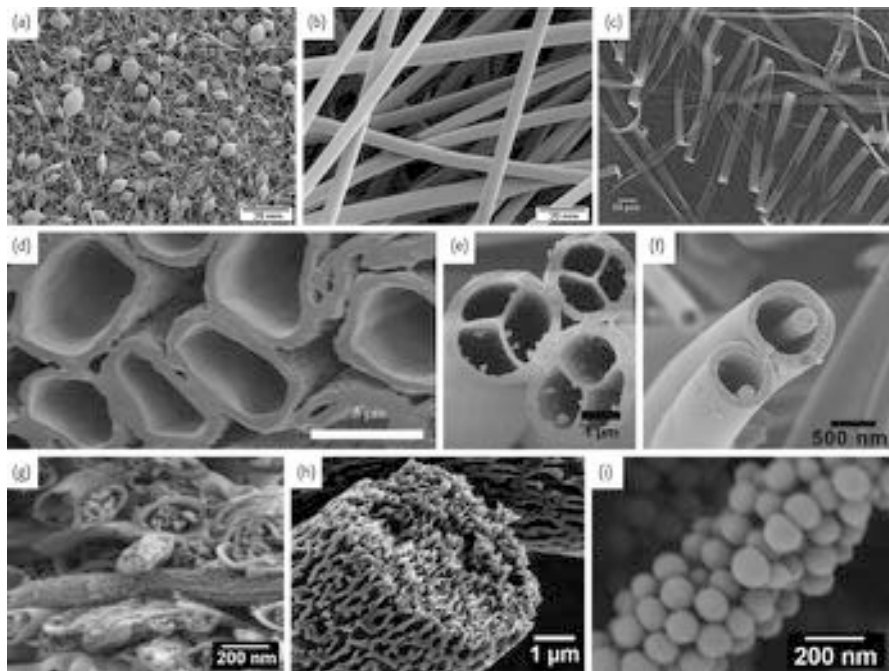


Fig. 1 Illustrate the diverse shapes of polymer-based micro- and nanofibers: (a) beaded, (b) smooth, (c) ribbon, (d) hollow, (e) multichannel tubular, (f) nanowire-in-microtube, (g) multicore cable-like, and (h, i) porous 16 fibers. (Reprinted from [5], Copyright (2010), with permission from Elsevier)

with nanocontainers, and nanofiber surface functionalization (Fig. 2). A comprehensive summary of polymers which have been successfully electrospun into superfine fibers is listed by Huang et al. [7] and Frenot et al. [3]. Numerous parameters could affect the conversion of polymer solutions into nanofibers during electrospinning. These parameters consist of the (a) viscosity, elasticity, conductivity, and surface tension of the solutions, (b) hydrostatic pressure in the capillary tube, electric potential at the tube tip, and the gap (distance between the tip and the collecting screen), and (c) final solution temperature, humidity, and air velocity in the electrospinning assembly [7, 8]. Typically, the nanofibers are collected in the collector as a non-woven mat, with no special orientation. The nanofibers can be also aligned into a uniaxial array by using different types of collectors to control the distribution of the electric field [9]. The air gap allows one to simply transfer the aligned fibers from the collector onto other solid supports and further stack them into a multilayered structure. By changing an array of electrodes on the insulating substrate, one can guide the fibers to direct deposit into a multilayered film by the irregular high-voltage application scheme. With this process, random nanofibers can be deposited on the conductive metal substrates, whereas the fibers were uniaxially aligned across the air gap [10].

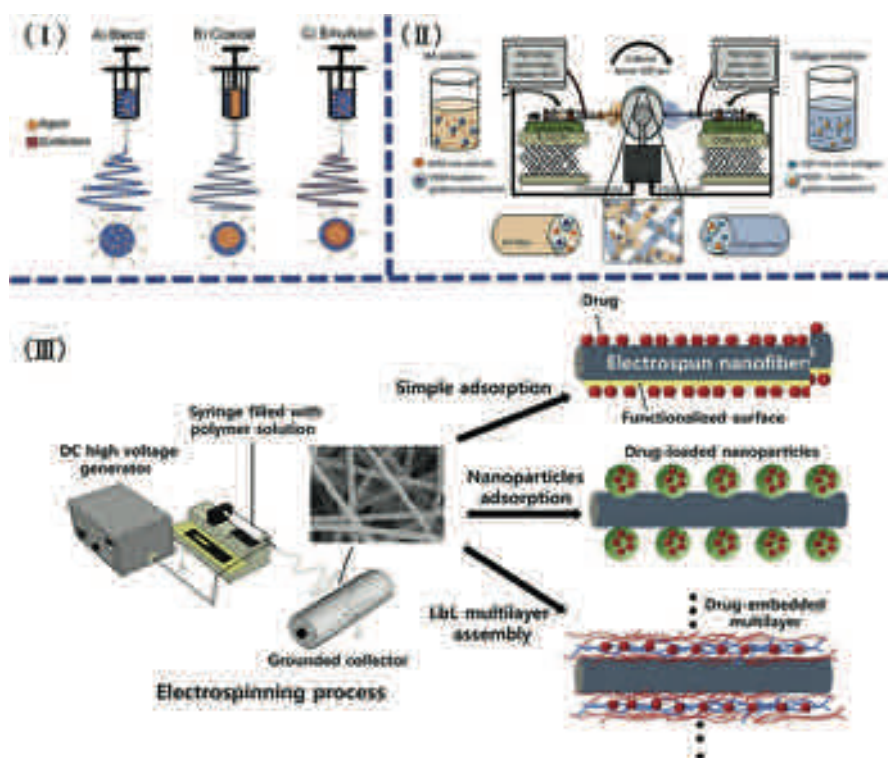


Fig. 2 Schematic illustration of the modified polymer-based electrospinning setup: (I) schematic illustration of blend electrospinning, coaxial electrospinning, and emulsion electrospinning. (II) The synergistic combination of nanocontainers and nanofibers. (III) Surface functionalization of electrospun nanofibers. (Reprinted from [7], Copyright (2017), with permission from Elsevier)

Collagen Nanofibers

Collagen is the major structural protein in the extracellular space in numerous tissues, such as the muscles, bones, skin, blood vessels, digestive system, and tendons. In the human body, collagen constitutes 1–2% of muscle tissue and 6% in total weight of tendons [4]. The biomedical use of the collagen is widespread, and different types of collagen have been recognized and described. Depending upon the degree of mineralization, collagen-bearing tissues may be rigid (bone) and compliant (tendon) or have a gradient from rigid to compliant (cartilage) [3].

Collagen is generally present in the form of nanofibers, and therefore, electrospinning that is capable of manufacturing nanofibers has attracted special attention for collagen processing. Type I collagen, the most common form of collagen in the body, has been electrospun into nanofibers for biomedical applications with the range of micro- to the nanoscale diameter of the fibers [5]. Pure collagen nanofibers are generally prepared by an electrospun process of Rho et al. [11]. Briefly, type I collagen was dissolved in the organic solvent Hexafluoroisopropanol (HFIP) or

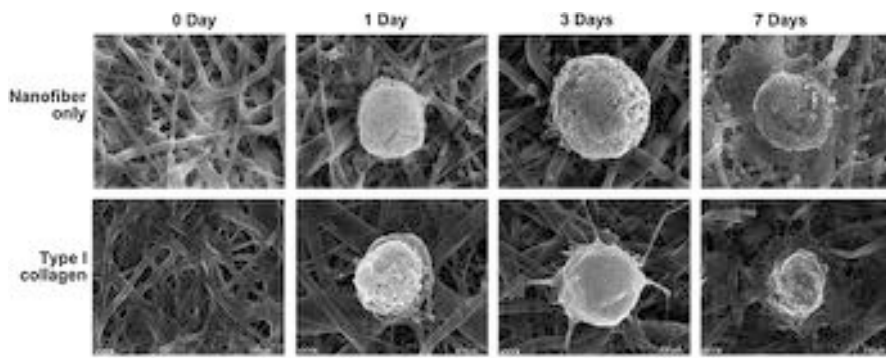


Fig. 3 Electrospinning of collagen nanofibers for wound healing applications. SEM images show the contact between normal human oral keratinocytes (NHOK) and uncoated collagen nanofibers and collagen nanofibers coated with type I collagen on 0, 1, 3, and 7 days of culture. Scale bar, 10 μ m. (Reprinted from [11], Copyright (2006), with permission from Elsevier)

acidic solutions. Using this process, the bead-free pure collagen nanofibers have been fabricated with diameters ranging from 100 to 500 nm. The water-soluble collagen nanofibers are cross-linked by using chemical agents that give good mechanical strength even in aqueous solution.

Collagen nanofibers can provide a suitable three-dimensional structure for cell attachment, growth, and migration. Zheng et al. [1] reported that the developed biodegradable nanofiber scaffolds are able to sustain cell attachment and proliferation of human bone marrow-derived mesenchymal stem cells and normal human keratinocytes as compared to conventional fibers. Rho et al. [11] fabricated collagen nanofibers by the electrospinning process for wound healing application. The collagen nanofibers were chemically cross-linked by glutaraldehyde vapor and then treated with aqueous glycine to block unreacted aldehyde groups. The obtained collagen nanofibrous matrices were treated with type I collagen or laminin. The authors studied the effects on the behavior of normal human oral keratinocytes (NHOK) and early-stage wound healing. The results show that the collagen nanofibrous matrices coated with type I collagen were functionally active in responses in NHOK comparing with uncoated collagen nanofibers. Figure 3 shows the cell morphology and interaction between cells and unmodified and modified collagen nanofibers *in vitro* [11].

Gelatin Nanofibers

Gelatin is a transparent, colorless, brittle (when dry), flavorless food derivative obtained from various parts of the animal body. It is the denatured form of collagen derived from the partial hydrolysis of collagen extract from the skin, bones, and connective tissues [12]. For electrospinning of gelatin from its solution with a nontoxic solvent, specific parameters can be optimized to get uniform fibers. Gelatin

nanofibers have been prepared using an electrospun process by solubilizing gelatin in organic solvents such as HFIP and 2,2,2-trifluoroethanol (TFE) or acidic solutions. Gelatin nanofibers are obtained with diameters from 50 to 500 nm by electrospinning. Like collagen, gelatin needs to be cross-linked before use in cell culture process. Furthermore, gelatin nanofiber blends can be electrospun with other polymers in a single solution for obtaining different size nanofibers. For example, PCL nanofibers blended with gelatin exhibited better cell attachment and good proliferation and enhanced nerve differently as compared to plain PCL nanofiber scaffolds [12].

Huang et al. [13] developed randomly oriented or aligned PVA and PVA-gelatin nanofibers and studied their topography-induced biological effects. Figure 4 shows the interaction between the cell and PVA and PVA-gelatin nanofibers. Owing to the

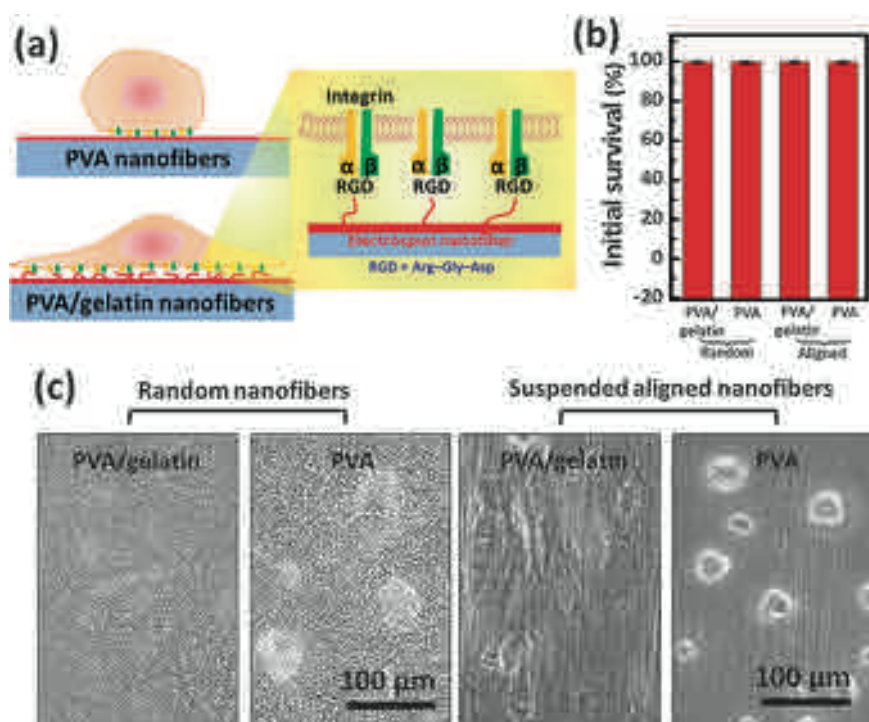


Fig. 4 Evaluation of cell actions of electrospun PVA and PVA-gelatin nanofibers with random and aligned arrangements. **(a)** Schematic representation of cell growth on PVA and PVA-gelatin nanofibers. **(b)** Primary survival of cells on nanofibers after 24 h. **(c)** SEM image shows the cell morphology of growing cell on the PVA and PVA-gelatin random and aligned nanofibers. (Copyright 2016, Nature [13], This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>)

low protein affinity of PVA which limits the interaction of secreted ECM (Fig. 4a), the 3 T3 cells can attach and stretch out only after being cultured on PVA-gelatin fibers (Fig. 4c). The cells exhibited distinctive adhesive properties on PVA and PVA-gelatin fibers, and they all remain highly viable after the seeding on the scaffold in the primary 24 h (Fig. 4b) [13]. The fibroblasts growing on PVA-gelatin fibers showed significantly larger projected areas as compared with those cultivated on PVA fibers. This is likely due to the better suitability of the PVA-gelatin surfaces to cell attachment [13].

Elastin Nanofibers

Elastin is an extremely elastic protein in connective tissue and permits tissues to maintain their shape after stretching or contracting. It exists in the human body as an elastic fiber with amorphous elastin and fibrillar fibrillin. Elastin is mainly made from the smaller amino acids such as glycine, valine, alanine, and proline and is widespread in various tissues such as the skin, arteries, bladder, lungs, ligaments, and cartilage. Elastin contains a tropoelastin protein, which is available in soluble form. Insoluble tropoelastin (~65 kDa) will form insoluble complexes by cross-linking.

α -Elastin and tropoelastin fibers have been prepared by electrospinning using HFIP and aqueous acidic with a diameter ranging from the one to several microns. The electrospun elastin nanofibers have been exhibiting a ribbon-like morphology as different to the uniform cross-section filament shape. The elastin nanofibers are typically cross-linked with chemical agents, such as glutaraldehyde, 1,6-diisocyanatohexane and 1-ethyl-3-[3-dimethylaminopropyl]carbodiimide (EDC), before use in cell culture [14]. Daamen et al. [15] developed elastin nanofibers by electrospinning process (Fig. 5). α -Elastin and tropoelastin fibers form wider and flatter, shaped-like ribbons, with their size similar to that of naturally occurring elastin fibers under the same experimental conditions. The AFM images of nanofibers of the elastin/tropoelastin ribbons show a significant increase in their thickness at the edges (Fig. 5d).

Chitosan Nanofibers

Chitosan is a natural polycationic linear polysaccharide biomaterial obtained from chitin. It is consisting of randomly arranged β -(1 $\rightarrow$ 4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit). Chitosan has been synthesized from the hard outer skeleton of shellfish, including crab, lobster, and shrimp. Chitosan binds strongly with lipids present in the gastrointestinal tract, thus decreasing their absorption. The poor solubility of chitosan in neutral and alkaline solution limits its application. However, the chemical modification of chitosan increases its water solubility and brings to it new functional properties

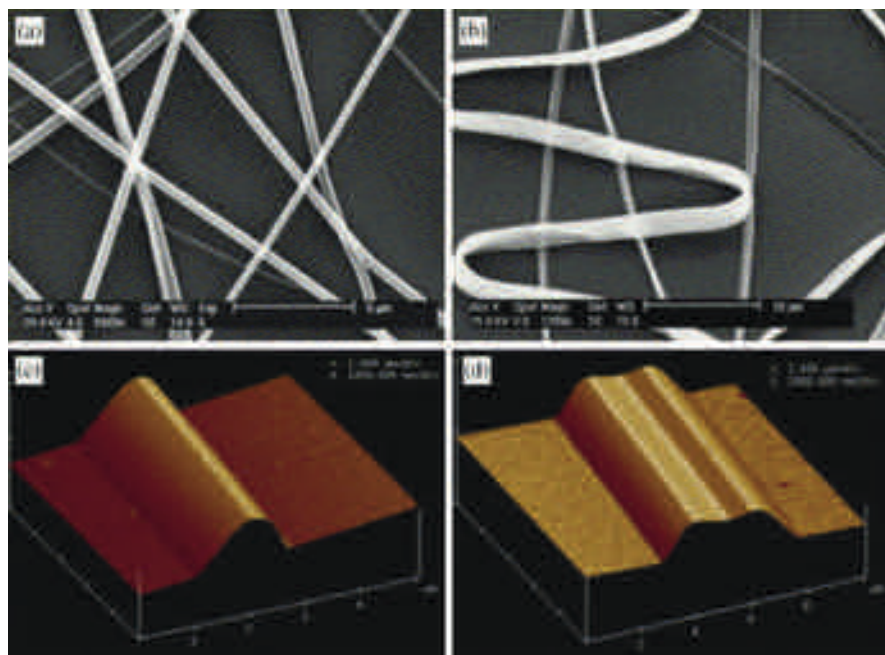


Fig. 5 Comparative evaluation of collagen and tropoelastin fibers by SEM and AFM images. (a) SEM images of collagen fibers. (b) SEM image of tropoelastin fibers. (c) AFM image of round shape collagen fiber. (d) AFM image of ribbon shape tropoelastin fiber. (Reprinted from [15], Copyright (2005), with permission from Elsevier)

suitable for various applications, such as biomedical and surgical applications, filler in tablets, as a carrier in controlled-release formulations, and in water processing as a part of a filtration process to bind metal ions and anionic dyes. Additionally, it has natural antibacterial properties [16].

Chitosan nanofibers are prepared by electrospinning process owing to limited solubility, ionic character, and 3D networks of strong hydrogen bonds. High molecular weight chitosan nanofibers are effectively electrospun using high concentration acid solutions (diameter = 130 nm) and organic solvents (diameter = 60–330 nm). Chitosan can be mixed with other polymers in organic solvents or aqueous acid for the preparation of nanofiber blends. Low concentration of polyethylene oxide (PEO, e.g., 10%) mixed with chitosan can be easily electrospun into nanofibers with a diameter ranging from 150 to 200 nm. These nanofibers are employed with beneficial properties in tissue engineering applications by Geng et al. [16]. Meng et al. [17] developed randomly oriented and aligned poly(D, L-lactide-co-glycolide) (PLGA)/chitosan nanofibers by electrospinning (Fig. 6a). PLGA and PLGA/chitosan nanofibers (randomly oriented) were formed with beadles and smooth surface with average diameters of 146 ± 35 nm, 189 ± 51 nm, 246 ± 44 nm, and 229 ± 71 nm corresponding to the PLGA/chitosan ratios of 10:0, 9.375:0.625,

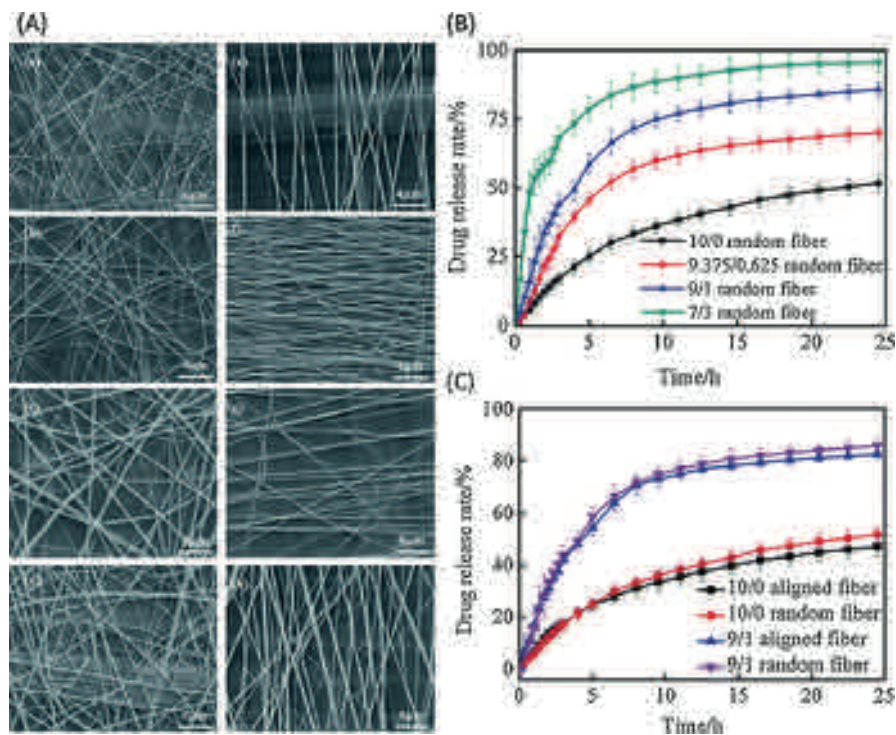


Fig. 6 In vitro drug release pattern of electrospun PLGA/chitosan nanofiber scaffolds. (A) SEM images of randomly oriented PLGA and chitosan nanofibers (a–d) and aligned nanofibers (e–h) with different PLGA/chitosan (10/0, 9.375/0.625, 9/1 and 7/3) ratios. (B) FBF release pattern of PLGA and PLGA/chitosan nanofibers with different PLGA/chitosan ratios. (C) FBF release profiles of randomly oriented and aligned PLGA/chitosan nanofibers with PLGA/chitosan 10/0 and 9/1 ratios. (Reprinted from [17], Copyright (2011), with permission from Elsevier)

9:1, and 7:3, respectively. The average diameters of the fibers increased with increasing chitosan content, which may be due to the high viscosity of chitosan in the composite solution. Figure 6b shows the release characteristics of fenbuphen (FBF) from the FBF-loaded randomly oriented PLGA and PLGA/chitosan nanofibrous scaffolds. The result indicates the FBF released from the PLGA nanofiber scaffold is gradual. In case of PLGA/chitosan nanofiber scaffold, the drug release rate was increased with the increase of chitosan content in the nanofibers. In case of aligned scaffolds, the drug release pattern was the similar trend with that of the randomly oriented scaffold for the period of the first 5 h which may be due to the surface drug rapidly released from the fiber; though the drug release rate was a little different (3–5%) after 5 h (Fig. 6c), which might be due to the scaffold structure changed by nanofibrous arrangement, the drug concentration difference has become low at the surface of the fiber [17].

Dextran Nanofibers

Dextran is a complex branched glucan polysaccharide chain of different lengths (3–2000 KDa). It is obtained from cane or beet sugar, where it is formed by the action of a contaminating bacterium *Leuconostoc mesenteroides*. Traditionally, dextran had been long familiar as contaminants in sugar processing and other food production. Dextran is used therapeutically as plasma volume expanders, as anticoagulants, and as a stationary phase in chromatography [18].

Dextran is a highly water-soluble polymer. Dextran nanofibers with a wide range of fiber diameters have been developed using aqueous acidic solutions as well as organic solvents, for example, with dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) mixtures. Methacrylated dextran nanofibers can be photo-cross-linked after the electrospinning process for getting stable hydrogels in the aqueous environment. PLGA and dextran nanofiber blends have been fabricated using electrospinning process and have been established for tissue engineering applications [18]. Zhang et al. [19] have fabricated biodegradable cross-linked nanofibrous scaffolds consisting of PLA-g-dextran and methacrylated dextran by means of a coaxial reactive electrospinning technology coupled with in situ photo-cross-linking. PLA-g-dextran aqueous solution produced smooth fibers with an average diameter of 342 ± 99 nm (Fig. 7a), and the fibers swelled to 565 ± 173 nm after water immersion for 24 h (Fig. 7c) due to water absorption of the grafted dextran. With 20% grafted dextran, only bead-like fibers were produced (Fig. 7b), and the beads were different in morphology from the round beads present in the electrospun mesh of a physical mixture of PLA and dextran. Extended threads were observed from both ends of a significant percentage of the beads, whose shape was retained even after water immersion for 24 h (Fig. 7d) [19].

Fibrinogen Nanofibers

Fibrinogen (FBG) is a glycoprotein that circulates in the blood. It consists of two sets of α , β , and γ -chains which are linked by disulfide bridges. Upon injury, it is enzymatically transformed by thrombin to fibrin and consequently to a fibrin-based clot. The FBG micro- and nanofibers are a natural matrix for tissue turnover [20]. FBG and fibrin (FBN) can be easily electrospun into nano-/microporous scaffolds, such as microspheres, microfibers, microtubes, nanoparticles, nanofibers, and hydrogels for various tissue engineering applications [20]. The electrospinning fibrinogen nanofibers could be used in tissue engineering, wound dressing, and hemostatic bandage [21].

The FBG nanofibers were prepared in the electrospinning method by Wnek et al. [22] with diameters ranging from 80 to 700 nm by dissolving FBG in organic solvents (e.g., HFIP). The FBG nanofiber scaffolds were capable of conserving their structure when hydrated without a cross-linking agent and confirmed superior

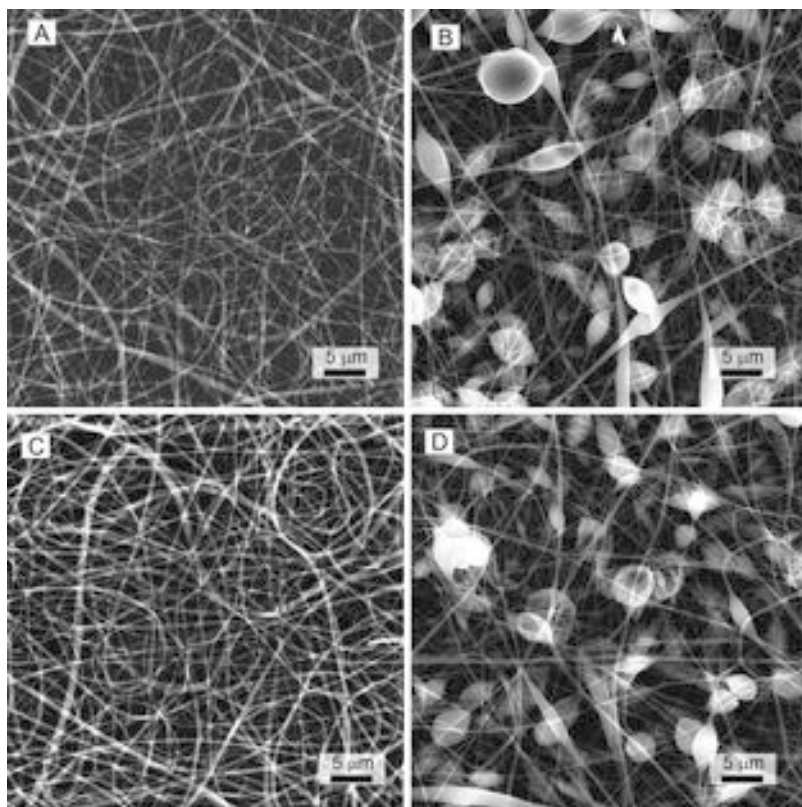


Fig. 7 SEM images of electrospun PLA-g-dextran nanofibers. (a) PLA-g-10% dextran (342 ± 99 nm) before water immersion, (b) PLA-g-20% dextran before water immersion, (c) PLA-g-10% dextran (565 ± 173 nm) after water immersion, (d) PLA-g-20% dextran after water immersion. (Reprinted from [19], Copyright (2017), with permission from Elsevier)

cell interaction in *in vitro* culture studies. The protease inhibitor apparitions were mixed with cell culture media and exhibited less degradation rate of FBG nanofibers [22]. Nedjari et al. [23] developed 3D honeycomb-patterned FBG nanofibers and showed substantial osteogenic response by mesenchymal stem cells (Fig. 8). The diameters of the thick and thin 3D honeycomb scaffolds were 462 ± 117 nm and 195 ± 50 nm, respectively, while the diameter of the thick and thin aligned 3D honeycomb scaffolds was 491 ± 182 nm and 195 ± 63 nm, respectively. The diameter of the thick and thin random 3D honeycomb scaffolds was 445 ± 147 nm and 213 ± 50 nm, respectively. During the electrospinning process of honeycomb scaffolds, the walls of the honeycomb were produced mostly from thick fibers, whereas the thinner ones were formed in the base of the honeycomb niches. This may be due to, during electrospinning process, thicker portions of the jet that are highly charged and more “sensitive” to the electric field; thus the fibers deposit preferentially on the top of the walls, by selecting the grounded electrode.

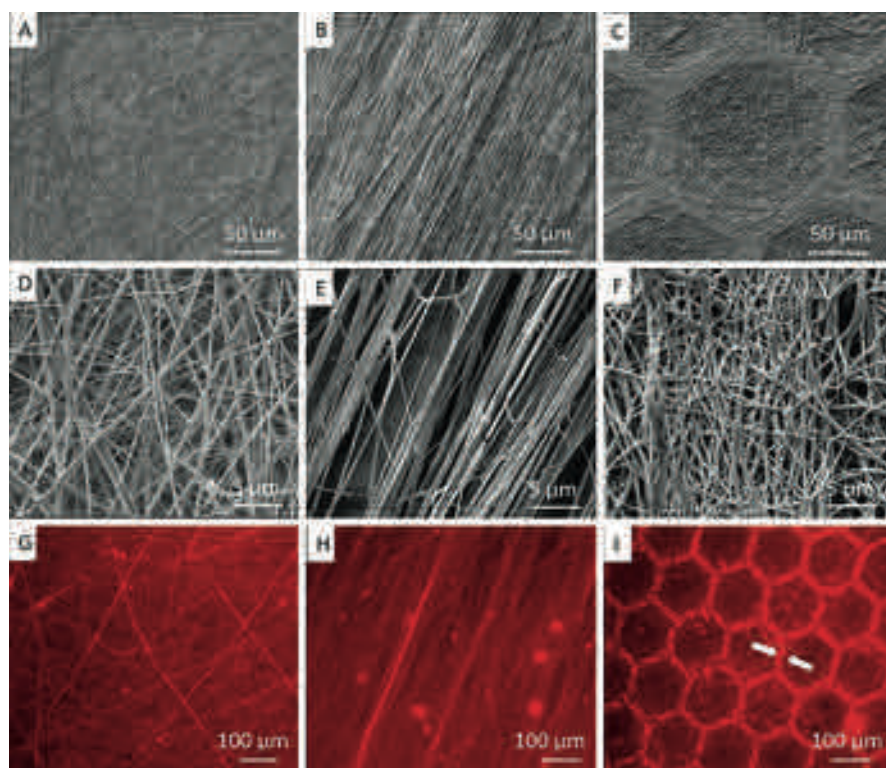


Fig. 8 SEM images of (a, d) random nanofibers, (b, e) aligned nanofibers, and (c, f) honeycomb-shaped poly(L-lactide-ε-caprolactone)-fibrinogen nanofiber scaffolds. The bottom row illustrates the immunofluorescent observation of FBG within the fibers (red) on random (g), aligned (h), and honeycomb (i)-shaped scaffolds. The arrows on (i) show the higher amount of FBG on the walls of honeycomb shapes. (Copyright 2017, Nature [23], This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made)

Equally, the thinner portions of the jet have higher freedom to deposit equally inside the niches. Figure 8 (inserts G, H, I) illustrates the presence of FBG inside the fibers, which was confirmed by immunofluorescence. 3D honeycomb walls contain the higher amount of FBG compared with the thicker wall of the scaffold [23].

Laminin Nanofibers

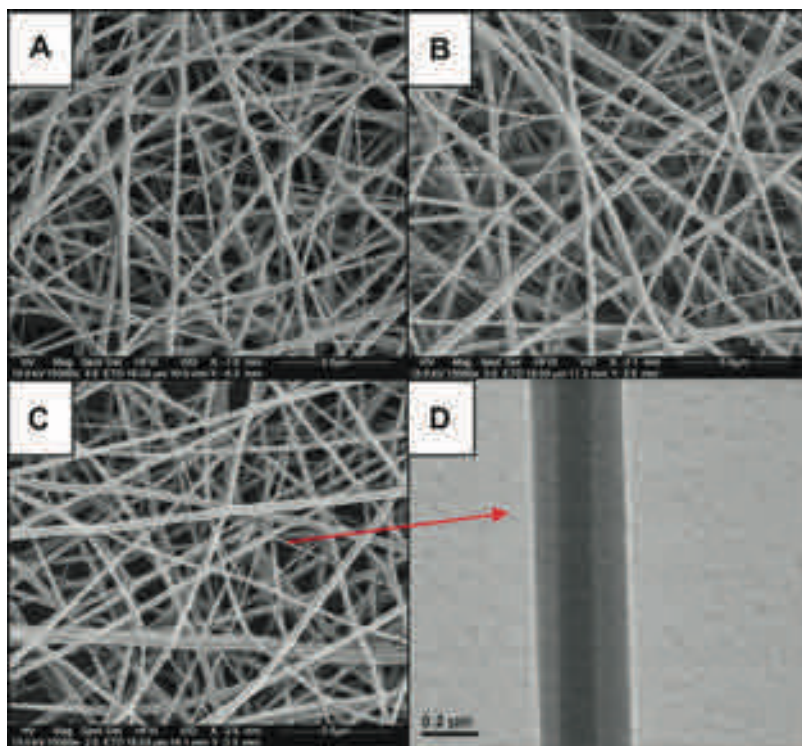
Laminins are naturally available high molecular weight (~400 to ~900 kDa) proteins of the extracellular matrix in humans and animals, and it is biologically an active part of the basal lamina, influencing cell differentiation, migration, and adhesion. The

molecules can bind to each other and to other tissues, thus holds tissues and organs together. Laminin contains “arms” that link with other laminin molecules to structure sheets and bind to cells. Laminin and other ECM proteins effectively “glue” the cells to a foundation of connective tissue. Laminin containing scaffolds have been shown to endorse Schwann cell proliferation and migration, which could potentially afford guidance cues to the ensuing axons, migrating from the proximal to the distal ends [24]. Recently, laminin was purified from Engelbreth-Holm-Swarm (EHS) tumor, solubilized in HFIP, and subjected to electrospinning to obtain 90 to 300 nm diameter nanofibers [10]. The bioactivity of laminin nanofibers was tested in vitro with neural stem cells (PC12) and human adipose stem cells. Laminin nanofibers maintained their structure under a hydrated environment without cross-linking agents [25]. Kijenska et al. [26] fabricated poly(L-lactic)-co-poly (ε-caprolactone) (PLA-PCL)/laminin nanofiber mats using two different techniques: (i) by electrospinning process by missing PLA-PCL solution with laminin in HFIP and (ii) by coaxial electrospinning process, mixing of laminin in water (core material) with PLA-PCL in HFIP as the shell (material). The SEM images of electrospun PLA-PCL, blended PLA-PCL/laminin, and core-shell PLA-PCL/laminin nanofibers are illustrated in Fig. 9. The average diameters for PLA-PCL, blended PLA-PCL/laminin, and core-shell PLA-PCL/laminin nanofibers were found to be 302 ± 101 , 350 ± 112 , and 316 ± 110 nm, respectively. The water contact angle results of PLA-PCL, blended PLA-PCL/laminin (B), and core-shell PLA-PCL/laminin nanofibers were found to be 126.3 ± 0.9 , 122.8 ± 1.3 , and 125.9 ± 1.8 , respectively [26]. TEM illustrates the coaxial electrospun core-shell PLA-PCL/laminin scaffolds (Fig. 9d), indicating laminin to be completely encapsulated in polymeric shell core-shell structure nanofibers [26].

Hyaluronic Acid Nanofibers

Hyaluronic acid (HA) is an anionic, nonsulfated glycosaminoglycans (GAGs) dispersed extensively in connective, epithelial, and neural tissues. The molecular weight of HA could be large (>1 M Da). HA has the dramatic ability to attract and hold a huge quantity of moisture, which is critical for its function in the skin (elasticity) and cartilage (lubrication). Human bodies approximately contain 15 grams of HA, and it has been purified from various sources and extensively available in capsules, skin creams, and even injectables. Though HA has outstanding biocompatibility, the anionic and hydrophilic properties of many HA materials do not support the direct attachment of cells. Combining HA materials with other materials, such as collagen, makes them more cell-friendly. Otherwise, creating 3D or a porous scaffold can help for the proliferation of cells. Such scaffolds can be formed by electrospinning [27].

HA has been produced in the form of nanofibers for use in tissue engineering. HA nanofibers are very complex to fabricate, and the high viscosity and surface tension of HA makes it difficult to electrospun, as both are important parameters in the



production of nanofibers. Recently, a combination of an acidic solution with heated air blown around the electrospinning jet was employed to obtain uniform HA fibers. The pure HA nanofibers (diameter = 110 nm) have been fabricated by electrospinning. The scaffolds are assembled and were recognized to have good in vitro cell interaction properties [28]. Brenner et al. [29] fabricated pure HA mats with an average fiber diameter of 40 nm using a new solvent system, i.e., aqueous ammonium hydroxide (NH_4OH) solvent and $\text{NH}_4\text{OH}/\text{DMF}$ solution, they also successfully reported the electrospinning of HA nanofibers from NaOH/DMF system. Figure 10 shows the different morphology of HA nanofiber mats prepared from NaOH/DMF and $\text{NH}_4\text{OH}/\text{DMF}$ solution [29]. With using 2:1 $\text{NH}_4\text{OH}/\text{DMF}$ solvent system, no degradation effects were observed, and the continuous electrospinning of pure HA fibers was possible.

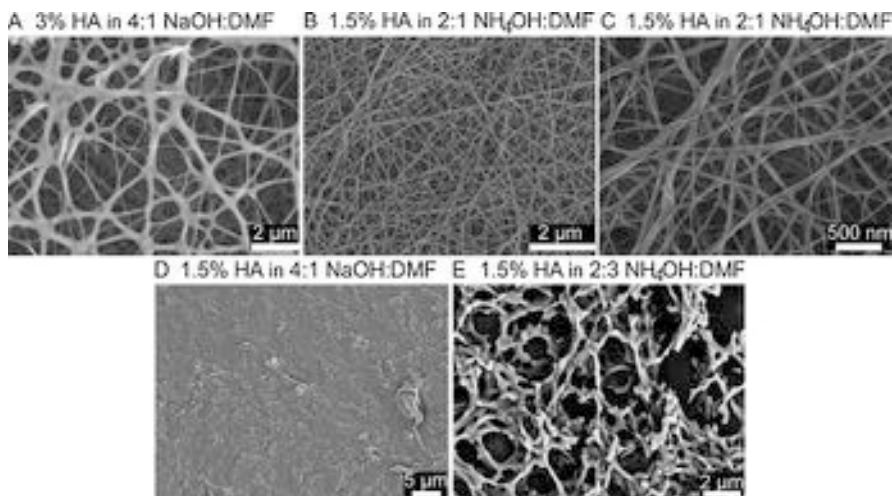


Fig. 10 SEM images displaying the morphology of HA nanofiber mats: (a) 3% HA solubilized in 4:1 NaOH/DMF mixture, (b and c) 1.5% HA solubilized in 2:1 NH_4OH /DMF mixture, (d) 1.5% HA solubilized in 4:1 NaOH/DMF mixture, and (e) 1.5% HA solubilized in 2:3 NH_4OH /DMF mixture. The electrospinning process was completed within 5 min to prevent degradation of HA. (Reprinted from [29], Copyright (2012), with permission from Elsevier)

Inorganic-Based Nanofibers

The fabrication of inorganic nanofibers based on metals, metal oxides, and ceramic materials has been of vast scientific and technological importance [30]. Inorganic nanofibers frequently reveal novel thermal, electrical, mechanical, and optical properties as their size approaches nanometer scale dimensions. For many advanced applications, ranging from energy production and storage, current research is progressively more focused on exploiting the high porosity and suppleness of nanofibers for the assembly of complex nanomaterials. For example, the exceptional electronic and optical properties of inorganic nanofibers can find future applications in flexible batteries, supercapacitors, fuel cells, and solar cells. Structures together with core-shell nanofibers and multicomponent hierarchical assemblies can demonstrate superior properties and new functionalities arising from the close proximity of chemically distinct, nanostructured components [30]. An extensive range of structural inorganic nanofibers was effectively developed by electrospinning technique. **Literature** shows various types of inorganic nanofibers with different structures. By modifying the electrospinning process conditions, inorganic nanofibers of different shapes are obtained, for example, mesoporous nanotubes, and nanorods were grown to form nanofibers, hollow nanofibers, multichannel microtubes, nanowire-in-microtube, and core-shell nanofibers [31].

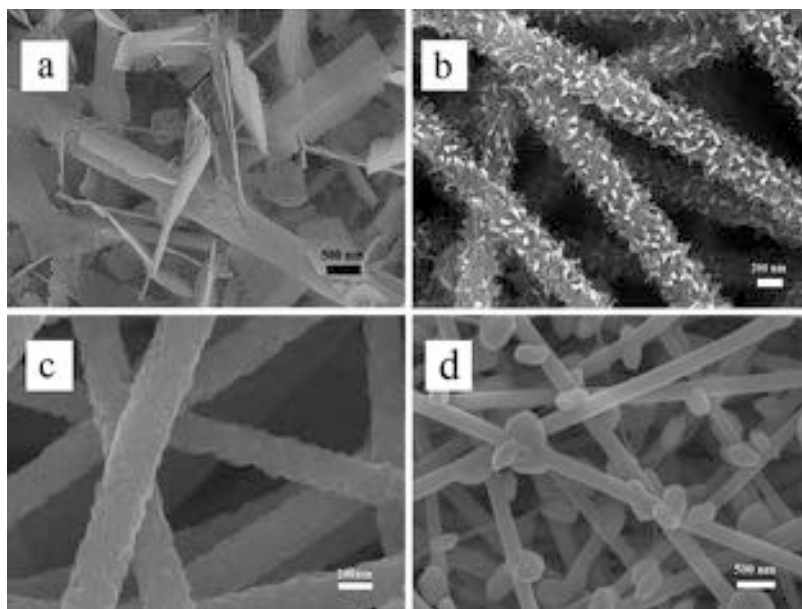


Fig. 11 Controllable synthesis strategy of hierarchical heterostructure metal oxide/TiO₂ nanofibers with improved Li-ion battery performance. (a) Low- and (b) high-magnification SEM images of hierarchical heterostructure Fe₂O₃/TiO₂ nanofibers. (c) Low- and high-magnification TEM images of hierarchical heterostructure Fe₂O₃/TiO₂ nanofibers. (d) TEM image of the Fe₂O₃ nanorod surface. (Copyright 2012, Nature [32], This work is licensed under a Creative Commons Attribution-NonCommercial-No Derivative Works 3.0 Unported License)

Wang et al. [32] developed a controllable synthesis strategy of hierarchical heterostructure metal oxide/TiO₂ nanofibers using the electrospinning and hydrothermal method. Four typical metal oxides, namely, Co₃O₄, Fe₂O₃, Fe₃O₄, and CuO, are adopted as secondary nanostructures grown on primary TiO₂ nanofiber to verify the feasibility and versatility of metal oxides/TiO₂ hierarchical heterostructures. The low- and high-magnification SEM images (Fig. 11a and b) show the secondary Fe₂O₃ nanorods grown on the primary TiO₂ nanofiber to form Fe₂O₃/TiO₂ hierarchical heterostructures with diameters of about 290 nm. The structure is further investigated by TEM in more detail. Figure 11c shows that Fe₂O₃ nanorods are uniformly attached to the primary TiO₂ nanofiber surface and the selected circular area is enlarged (Fig. 11c, inset). The diameter and length of Fe₂O₃ nanorods are estimated to be about 22 and 45 nm, respectively. TEM (Fig. 11d) further confirms the single-crystalline structure of the Fe₂O₃ nanorods with a lattice fringe spacing of 0.37 nm from the (311) plane [32]. The hierarchical heterostructure metal oxide/TiO₂ nanofibers are investigated as the Li-ion batteries anode materials, and the obtained electrodes showed excellent rate capability with respect to the pristine TiO₂ nanofibers. The hierarchical heterostructures and synergetic effect between the metal

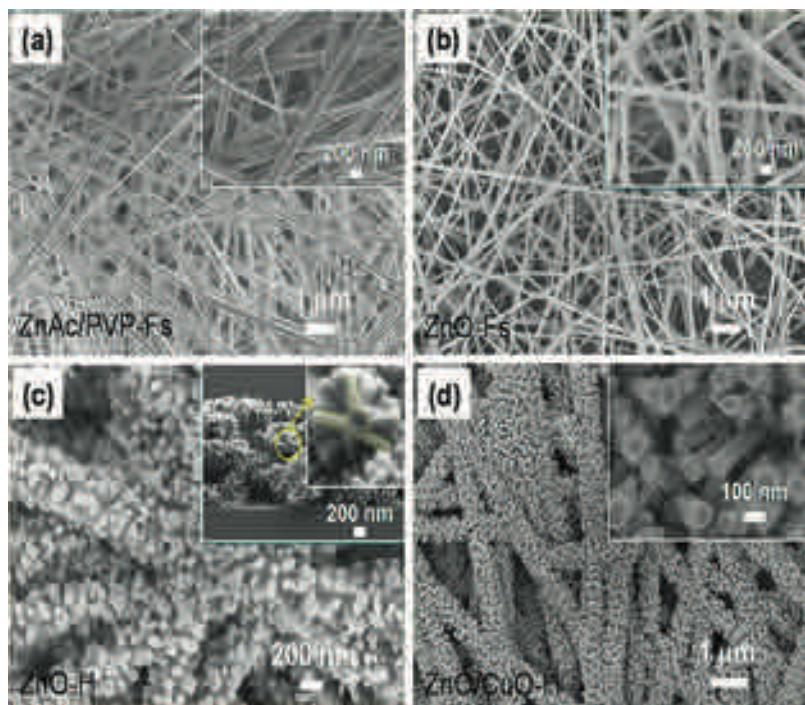


Fig. 12 Hierarchical CuO-decorated ZnO nanostructures as efficient and established sensing materials for H_2S gas sensors. Morphological structure of the prepared nanofibers: (a) ZnAc-PVP nanofibers, (b) ZnO nanofibers (ZnO-Fs) produced by oxidation at 500°C , (c) hierarchical ZnO nanofibers (ZnO-H) produced by hydrothermal method using ZnO-Fs in (b) as seed template, and (d) hierarchical ZnO nanofibers coated with CuO NPs. (Copyright 2016, Nature [33], This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material)

oxide and TiO_2 are probably responsible for the enhanced electrochemical performance.

Nguyen and co-workers [33] developed highly sensitive hydrogen sulfide (H_2S) gas sensors from CuO-decorated hierarchical ZnO nanofibers by the following steps: (i) preparation of ZnAc-PVP nanofibers using electrospinning method, (ii) thermal oxidation of ZnAc-PVP nanofibers to obtain ZnO nanofibers (ZnO-Fs), (iii) preparation of hierarchical ZnO nanofibers (ZnO-H) by hydrothermal method using ZnO-Fs, and (iv) CuO decoration of hierarchical ZnO nanofibers by a wet chemistry method. Figure 12 shows images of ZnO and PVP nanofibers at high magnification and cross-section correspondingly. Figure 12a illustrates the ZnO nanofibers and PVP composite nanofibers with diameters of 100 nm and 250 nm, respectively, with relatively smooth surfaces due to the polymeric nature and amorphous characters of Zinc acetate dihydrate (ZnAc). Figure 12b illustrates ZnO nanofiber after the

oxidation of ZnAc/PVP at 500 °C. Figure 12c shows the SEM image of the hierarchical ZnO nanofibers obtained by the hydrothermal growth of ZnO nanorods with an average thickness of around 1.1 μm . Figure 12 shows the SEM of the hierarchical ZnO nanofibers coated with CuO NPs. In the process, the ZnO nanorods (Fig. 12c) were coated with a copper salt solution. The CuO were formed on the nanofiber surface by employing UV illumination followed by oxidation. Gas sensors made of CuO-decorated hierarchical ZnO nanofibers exhibited a significant improvement in its H_2S sensing. This enhanced performance is due to the formation of p-CuO nanoparticle/n-ZnO nanofiber junctions [33].

Aluminum oxide has many applications in which its properties of extraordinary hardness and thermal stability are exploited. It is an extensively employed material in ceramics preparations. Al_2O_3 nanofibers were employed as fillers in thermoplastic polymers for fabricating the tested composites. The high surface area and chemisorption properties of Al_2O_3 nanofibers have been used to remove metal ions from the aqueous phase [29]. The Al_2O_3 nanofibers typically exhibit the desired adsorption capacity, cycle performance, and the ability to regenerate easily. Also, Al_2O_3 nanofibers have significant potential as support materials in heterogeneous catalysis, for example, methane reforming and Fischer-Tropsch reactions. Peng et al. [34] successfully fabricated porous hollow $\gamma\text{-Al}_2\text{O}_3$ nanofibers by the single-capillary electrospinning of an $\text{Al}(\text{NO}_3)_3$ /polyacrylonitrile (PAN) solution, followed by sintering treatment. Figure 13 illustrates the structure of the fibers with different weight ratios of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ to PAN. Figure 13 illustrates the image of $\gamma\text{-Al}_2\text{O}_3$ cylindrical porous nanofibers after decomposition of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and the absence of PAN. The nanofibers, prepared with weight ratios of 5:10 and 10:10 of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ /PAN, have exhibited much smaller pores compared with nanofibers obtained of other weight ratios. So the pores on the surface of the fibers can be adjusted by changing the weight ratio of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ to PAN. Furthermore, the average diameter of $\gamma\text{-Al}_2\text{O}_3$ nanofibers was increased with the weight ratio of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ to PAN, whereas the mean diameter was 172 nm for 1:10 and around 350 nm for 10:10, respectively (Fig. 13a2, c2) [34]. These porous hollow $\gamma\text{-Al}_2\text{O}_3$ nanofibers were employed as adsorbents to eliminate organic dyes (i.e., methyl blue, Congo red, and acid fuchsin) from aqueous solutions. The nanofibers exhibited excellent dye adsorption efficiency with a removal efficiency greater than 90% after 60 min of adsorption [34].

Stannic oxide (SnO_2) is an oxide semiconductor material with a lot of applications in the areas of sensors and optoelectronic devices. The SnO_2 is available in numerous forms like nanoparticles, nanowires, nanobelts, and nanofibers. In comparison with solid nanofibers, hollow and mesoporous nanofibers are more advantageous in practical applications to catalysts and gas sensors, owing to their high surface area to volume ratio. Normally the conventional methods for applications of hollow and mesoporous SnO_2 nanofibers by self-assembly and templates directed process are often suffering from firm synthesis conditions or tedious procedures [35]. Lee et al. [36] have fabricated hollow porous SnO_2 nanofibers using electrospinning technique. Generally, the formation mechanism of hollow nanofibers which were fabricated via the electrospinning process followed by heat treatment is accredited to

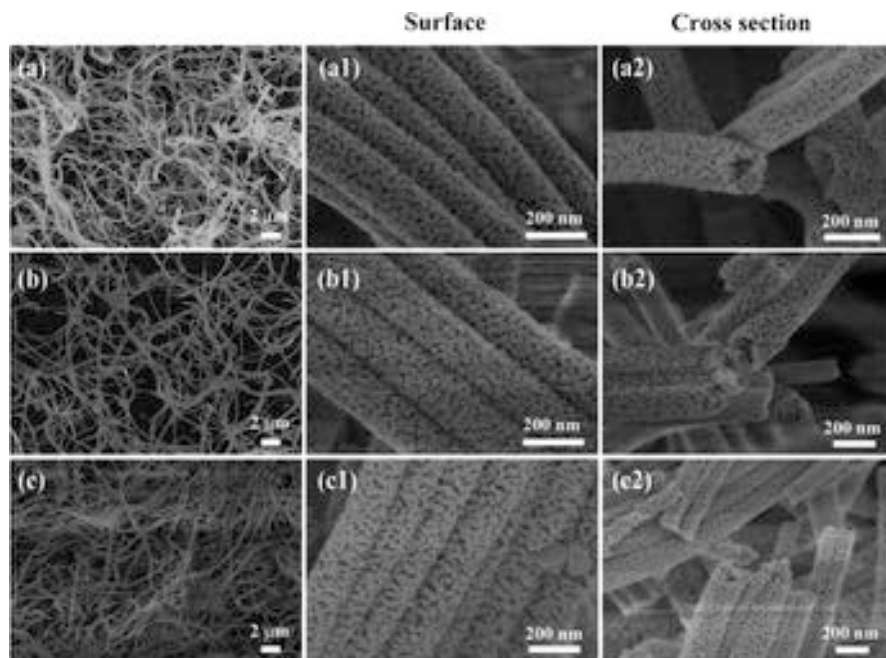


Fig. 13 Fabrication of porous hollow γ - Al_2O_3 nanofibers by facile electrospinning and its application for water remediation. Low-magnification and high-magnification SEM images of the surface and a cross-section of the porous hollow γ - Al_2O_3 nanofibers sintered at 800°C with various weight ratios of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ to PAN (a) 1:10, (b) 2:10, (c) 3:10, (d) 5:10, and (e) 10:10. (Reprinted from [34], Copyright (2015), with permission from Elsevier)

the decomposition of the sacrificial template of the organic polymer. Xia et al. [37] fabricated hollow SnO_2 nanofibers by annealing electrospun polyvinylpyrrolidone (PVP)/Sn precursor nanofibers. The composite core-shell PVP/ SnO_2 nanofibers have been prepared with a capricious diameter ranging between 50 and 300 nm and clear boundaries of a phase separation between the PVP and Sn precursor. The hollow SnO_2 nanofibers were obtained by the calcination treatment of as-spun core-shell PVP/ SnO_2 nanofibers. The nanofibers produced have a tubular structure with dense shells, which consist of nanograins of approximately 17 nm in diameter [37].

Du et al. [38] synthesized composite $\text{SnO}_2/\text{In}_2\text{O}_3$ nanofibers by employing a co-electrospinning system with positive and negative polarity electric fields with two jets, followed by treating with oxygen plasma at radio-frequency power of 450 W (Fig. 14). The diameters of SnO_2 nanofibers are relatively uniform ranging between 200 and 250 nm, while the surfaces of In_2O_3 nanofibers are comparatively irregular and slightly rough. The diameter of In_2O_3 nanofibers was in the range of 100–150 nm (Fig. 14a, b). They contain many rod-like nanoparticles with 40–50 nm diameters. The surfaces of both SnO_2 and In_2O_3 nanofibers suit moderately asymmetrical and rough (Fig. 14c, d). However, both SnO_2 and In_2O_3

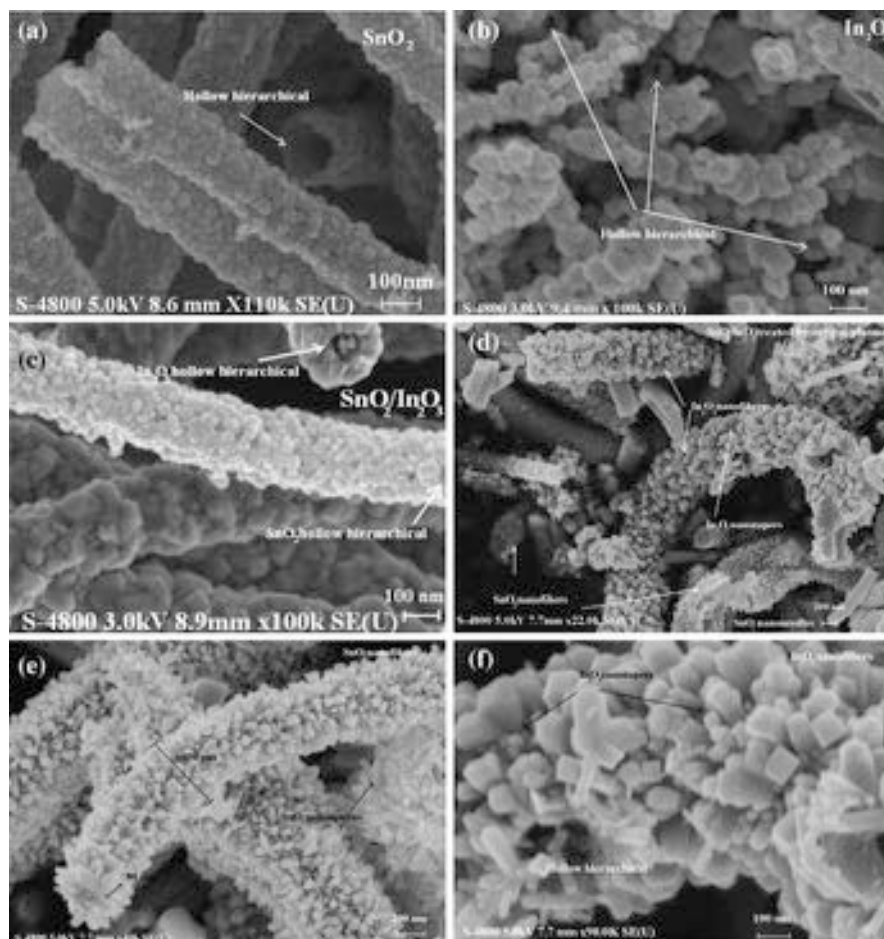


Fig. 14 Fabrication of $\text{SnO}_2/\text{In}_2\text{O}_3$ composite nanofibers. SEM illustrate the (a) untreated SnO_2 nanofibers with oxygen plasma, (b) untreated In_2O_3 nanofibers with oxygen plasma, (c) untreated $\text{SnO}_2/\text{In}_2\text{O}_3$ nanofibers with oxygen plasma, (d) treated $\text{SnO}_2/\text{In}_2\text{O}_3$ nanofibers with oxygen plasma, (e) treated SnO_2 in composite nanofiber mat with oxygen plasma, and (f) treated In_2O_3 in composite material with oxygen plasma. (Reprinted from [38], Copyright (2015), with permission from Elsevier)

nanofibers still maintained hollow and hierarchical structure after treatment with oxygen plasma, and the diameters of both SnO_2 and In_2O_3 nanofibers increased to 450 nm and 500 nm, correspondingly. Figure 14e and f illustrates the slight differences in the morphology of treated SnO_2 nanofibers [43]. The oxygen plasma-treated $\text{SnO}_2/\text{In}_2\text{O}_3$ nanofiber sensors were effectively identified in the formaldehyde concentration range of 0.5–50 ppm. Furthermore, these fibers revealed good selectivity to formaldehyde-interfering gases such as ethanol, ammonia, acetone, toluene, and methanol. The superior response of $\text{SnO}_2/\text{In}_2\text{O}_3$ composite nanofiber sensors

to detection of formaldehyde may be due to the increased conducting electron concentrations, the porosity, and the specific surface area after treatment with oxygen plasma [38].

Carbon-Based Nanofibers

Carbon nanofibers (CNFs) have been pursued for both fundamental research and practical applications. Vapor grown carbon nanofibers (VGCNFs) are cylindrical nanostructure with graphene layers arranged as stacked cones, cups, or plates. Catalytic chemical vapor deposition (CCVD) or simply CVD with other methods such as thermal and plasma assisted is the foremost efficient approaches for fabrication of VGCNF. CNFs can be also fabricated by the electrospinning method. CNFs have been extensively used in many fields such as hydrogen fuel production, electrochemical capacitors (EDLCs), Li-ion batteries (LIBs), supercapacitors, and fuel cells. Polyacrylonitrile (PAN) is a popularly known ancestor for fabrication of CNFs. CNFs are promising excellent material resources due to their superior strength, conductivity, flexibility, and durability characters. However, the synthesis process is complex, and its surface area is lower than other nanostructured carbonaceous nanomaterials, e.g., graphene and carbon nanotubes [39].

An exceptional concept of making nanocomposite paper from CNFs has been explored. Carbon nanopapers made of CNFs have been recognized as a promising platform to transfer the exceptional electrical, thermal, and mechanical properties of CNFs at the nanoscale to macroscopic engineering applications. The uniform network structure CNF papers were fabricated by filtration of well-dispersed CNF suspension under controlled process parameters. CNF papers can be also prepared by using liquid molding processes by integrating conventional fiber reinforced into composite laminates (Fig. 15) [40].

CNFs are well-established fillers employed for improving the mechanical properties of polymers. Because the strengthening capacity of nanofibers increases with decreasing diameter [41], nanofibers have greater strengthening potential compared with microfibers. Figure 16 shows different types of carbon fibers with different sizes and morphologies. Typically, as the CNFs diameter was decreased, the ultimate tensile strength of nanofiber was increased, due to the minimization of a number of defects. Furthermore, the surface area/volume ratio and flexibility of the CNFs was increased due to the enhancement of the contact area between the filler and the polymer matrix. Due to this, fiber can bend without breaking and maintain good mechanical strength [46]. Therefore, the extreme investigation is going on polymer nanocomposite based on carbon nanotubes (CNTs), clay platelets, and CNFs [42, 43]. Because of the smaller diameter and lower density of SWCNT and MWCNT than VGCNFs, they exhibit better mechanical properties than VGCNFs. However, due to the low price of VGCNFs, they have been employed as low-cost alternatives for CNTs [44]. The VGCNFs are also the substitute of traditional carbon fibers due to their nanoscale dimensions, unique properties, and economically feasible applications [45]. VGCNFs can be used as reinforcing, electromagnetic interference (EMI)

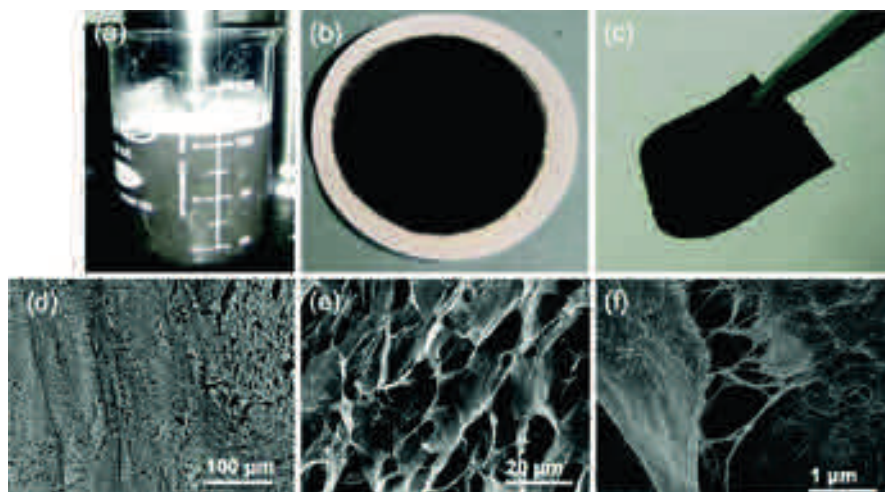


Fig. 15 Fabrication of carbon nanofiber (CNFs) composite flexible paper. (a) The aqueous dispersion of CNTs and CNFs. (b) A web film made of slurry in (a). (c) A freeze-dried conductive nanopaper (200 μm thick). (d)–(f) SEM of conductive nanopaper with different magnifications. (Reprinted from [40], Copyright (2013), with permission from Elsevier)

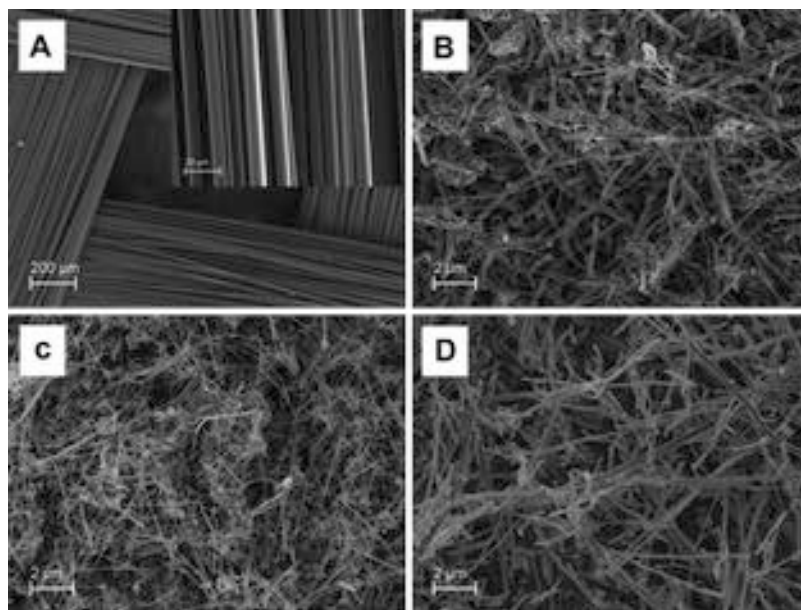


Fig. 16 SEM images showing the representative morphologies of (a) commercial T300 carbon fabrics, (b) vapor grown CNFs (VGCNFs), and (c) graphene-based CNFs, as well as (d) electrospun CNFs after being shortened. (Reprinted from [44], Copyright (2014), with permission from Elsevier)

Table 1 Shows a summary of major properties of various carbon fibers [48]. (Copyright 2002, American Institute of Physics)

Property	VGCNFs	SWCNTs	MWCNTs	CFs
Diameter (nm)	50–200	0.6–0.8	5–50	7300
Aspect ratio	250–2000	100–10,000	100–10,000	440
Density (g/cm ³)	2	1.3	1.75	1.74
Thermal conductivity (w/m K)	1950	3000–6000	3000–6000	20
Electrical resistivity (Ωcm)	1×10^{-4}	1×10^{-3} – 1×10^{-4}	2×10^{-3} – 1×10^{-4}	1.7×10^{-3}
Tensile strength (Gpa)	2.92	50–500	10–60	3.8
Tensile modulus (Gpa)	240	1500	1000	227

shielding, as electrostatic discharge (ESD) protection applications, and as a catalyst and encapsulation of DNA for biological applications and many more areas [46]. For example, the EMI shielding can be prepared by employing a 2 mm plate of a polymer composite with 7.5 Vol% VGCNF solutions. For the ESD applications, 0.5Vol % VGCNF solutions were used for making a conductive network for insulating polypropylene (PP) [45, 46].

VGCNFs have been fabricated by pyrolysis of a hydrocarbon feedstock (natural gas, acetylene, etc.) or CO on a metal catalyst such as iron. This method is the most popular, proficient, relatively low cost to obtain low diameter fibers [41]. In this process, iron nanoparticles are used as a catalyst, and these are obtained by the pyrolysis of reaction between organic and metallic compounds such as ferrocene $\text{Fe}(\text{C}_5\text{H}_5)_2$ and iron pentacarbonyl $\text{Fe}(\text{CO})_5$ [47]. The average diameter of iron nanoparticles, operating parameters, and catalyst activity significantly affects the thickness of nanofibers. Table 1 shows the summaries of the major properties of vapor grown carbon fibers (VGCNFs), single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotube (MWCNTs), and carbon fibers (CFs) [48].

Structural Nanofibers

Structural nanofibers with different size and morphologies have been gaining great interest due to their unique properties. The structure of nanofibers depends on the type of precursor used, and the method of production allows for controlling the shape and arrangement of nanofibers. The most common structures of nanofibers were hollow, mesoporous, nonporous, and core-shell types of nanofibers. Also, there are many common structures reported in the literature such as herringbone, platelet, and ribbon-structured nanofibers. In herringbone-structured CNFs, the graphite layers are arranged diagonally with reverence to the fiber axis. In the case of the platelet-structured CNFs, the graphite layers are arranged vertically to the fiber axis, and in

the case of the ribbon-structured CNFs, the graphite layers are arranged parallel to the growth axis of a fiber [49]. The composition and arrangement of these extracellular fibers play a vital role in imparting the mechanical properties to the tissue. Sometimes the network of the fibrous material acts as a bone-like structure and provides the favorable environment for the osteogenic function of resident cells. Molecules of the nanofibers can arrange themselves into patterns or structures through the non-covalent forces such as intra- and inter-hydrogen bonding, hydrophobic forces, and electrostatic forces of attractions. Interestingly, recent studies showed that self-assembly of amphiphilic nanofiber can generally occur by providing the suitable pH environment [49].

Hollow Nanofibers

Hollow nanofibers (HNFs) are largely gaining interest from the scientific community for diverse applications in the fields of environment, energy, sensing, and health. HNF walls can be made up of a wide range of materials including polymer, metal oxide, ceramics, or composite. Their unique characteristics such as the presence of the porous structure, large surface area, high tensile strength, and modulus depend upon the helicity and arrangement of rings in their walls [50]. Fabrication of HNFs can be made by electrospinning two immiscible liquids through a coaxial, two-capillary spinneret, followed by selective removal of the cores. Electrospinning is a versatile and efficient process to fabricate HNFs of metal oxides, carbon, metals, composites, and others. The diameter and helicity of the HNFs indeed promote the electronic properties of the nanofibers [51]. The structure of HNFs depends on parameters such as viscosity, conductivity, surface tension, polymer molecular weight, dielectric constant, and dipole moment [52].

HNFs have been fabricated from a wide range of organic and inorganic materials. TiO₂/PVP hollow nanofibers were developed by removing the oil phase as core [53]. In another study, hollow-microsized TiO₂ fibers were prepared by removing the organics and inner materials. The photocatalytic activity of such microsized TiO₂ fibers was enhanced for degrading acetaldehyde gaseous by adding interior hollow channel numbers [54]. Electrospinning parameters such as feed ratio can have an effect on the size and wall thickness of these nanofibers. The successful synthesis of HNFs is likely to depend on choosing the right solvent and controlling the heating rate. HNFs are able to fill with different substances for expanding their applications. PCL nanofibers were fabricated for controlling the release of bovine serum albumin (BSA) or lysozyme. PEG was used as a core material and proved that the release rate could be controlled by adding PEG, water-soluble macromolecules in the sheath material [55].

Lee et al. [56] developed hollow CNFs by coaxial electrospinning of styrene acrylonitrile (SAN) and polyacrylonitrile (PAN) solutions. In this study, PAN was used as a shell and SAN as the core, where SAN was found to be a very suitable material for the sacrificial core. The intrinsic properties of SAN prevented the PAN shell from shrinking during the stabilization and carbonization process. Lee et al.

[57] observed that the concentration of the solution and flow rate were effective in controlling the outer diameters and the wall thickness of hollow CNFs. Highly porous polymeric HNFs were prepared by the coaxial electrospinning method using silicon oil as the core material and poly(methyl methacrylate)(PMMA) as a polymer. The polycarbonate (PC) is used as the shell material. It was found that the nature and concentration of the solvent affect the diameter as well as the wall thickness of the developed HNFs. The electric insulating a material constant of the solvent was abbreviated the diameter of HNFs. Nanofiber wall width and average pore size were improved by increasing the molecular weight of the polymer, but the specific surface area is slightly decreased. Ahmed et al. [58] developed a highly proficient hollow CNF electrode for capacitive deionization produced by using coaxial electrospinning of PMMA(core)and PAN(shell)polymer solutions, followed by oxidative stabilization and carbonization process. The specific capacitance of the obtained hollow CNFs (222.3 F g^{-1}) was almost four times higher than that of solid CNFs (63 F g^{-1}). In addition, the surface area of the hollow CNFs ($186 \text{ m}^2 \text{ g}^{-1}$) was almost ten times greater to the surface area of the solid CNFs ($17.7 \text{ m}^2 \text{ g}^{-1}$). The developed hollow CNFs showed an excellent desalination performance (86%) and a better cycling ability [58].

Kim et al. [47] discovered the mechanism for the formation of hollow SnO_2 nanofibers fabricated by one-step electrospinning technique followed by a heat treatment step, applied to decompose the sacrificial template of the organic polymer. The work mainly aimed at investigating the effect of calcitration and crystal growth formation of hollow SnO_2 nanofibers. In this work, the hallow SnO_2 nanofibers were fabricated by electrospinning through a single capillary from PVP/ SnO_2 using a calcination treatment during which astringent structure of core-shell provides the advantage of preserving the fibrous pore structures based on the sacrificial PVP template. The formation of hollow structural fiber was initiated by the Kirkendall effect followed by the enlargement of an interior to produce surface diffusion process [47].

A multi-fluidic coaxial electrospinning technique has also been used to produce ultrathin, core-shell nanofibers with a unique nanowire-in-microtube design, as shown in Fig. 17a–c. In this approach, a spinneret comprising three coaxial capillaries was used, in which a chemically inert fluid acts as a buffer between the outer and inner polymer solutions. The buffer middle fluid is then removed, creating a void between the inner solid nanofiber and the outer solid microtube. This approach was successfully demonstrated in fabricating a TiO_2 nanofiber encased in a TiO_2 microtube. In addition to its usefulness in fabricating hollow structures, the triple-coaxial electrospinning technique can be adapted to produce novel fiber architectures [67]. The basic coaxial electrospinning is illustrated in Fig. 17d–f and consists of the hierarchically assembled compound nozzle comprising two or more metal capillaries separately leading to a single blunted metallic needle. Careful selection of the outer shell polymer solution, middle fluid, and inner core polymer solutions in terms of miscibility is critical in the stable ejection of the multi-fluidic compound jet to produce multichannel microtubes wherein the middle wall can be further

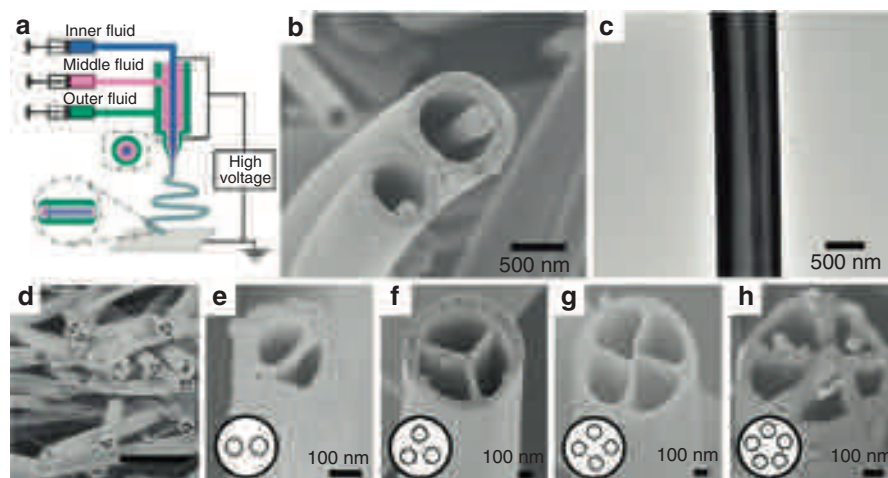


Fig. 17 Schematic illustration of the multi-fluidic coaxial electrospinning experimental setup used to generate hollow fibers with the nanowire/nanotube structure; (b) SEM and (c) TEM images of TiO_2 with nanowire/nanotube structure; (d) side view SEM image of the sample after the organics has been removed; (e–h) SEM images of multichannel tubes with varying diameter and channel number from 2 to 5. (Reprinted from [59], Copyright (2017), with permission from Elsevier)

divided into two to four channels, proving the versatility and simplicity of this technique [59].

Porous Nanofibers

A porous medium or a porous material is a material containing pores (voids). The porous materials are materials with pores (cavities, channels, or interstices). The skeletal portion of the material is often called the “matrix” or “frame.” The characteristics of a porous material vary depending on the size, shape, and arrangement of the pores as well as composition of the material itself. The porous materials can be mainly categorized into microporous, mesoporous, and macroporous. Microporous materials are categorized along with macroporous materials due to their pore diameters of greater than 50 nm and microporous materials having pore diameters of smaller than 2 nm. Mesoporous materials cover novel and important aspects of porous solids with pore sizes between 2 to 50 nm. Mesoporous nanofibers have attracted attention because of their unique structure and widespread applications. Mesoporous nanofibers with controlled diameter from 50 to 250 nm and tunable pore size range from 2 to 50 nm and length of millimeters range have been reported in the literature. Up to date, several methods have been invented to fabricate mesoporous nanofibers, such as template-assisted process, hydrothermal route, structure-selective synthesis, electrospinning technique, and so on. The different mesoporous nanofibers, such a circular, hexagonal column, a circular lamellar

cylinder, and a parallel, hexagonal column, have been synthesized by using different preparation procedures [60]. However, it is still a great challenge to fabricate mesoporous nanofibers with high uniformity and purity in a simple manner.

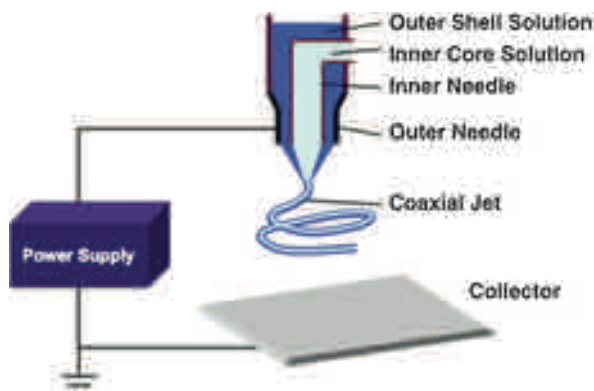
Nonporous nanofibers were the plain fibers without any pores; therefore the surface area for nonporous nanofibers is less when compared to porous surfaces. The method of fabrication includes nanomaterial incorporation onto a fiber structure after formation of the fiber structure. Nanofiber structure can be a part of a nanoparticle carrier material, a nanoparticle disposal medium, a lighting medium, and a catalysis medium. There are different fabrication methods for producing nanofiber structures with surface porosity and coating techniques for porous and nonporous nanofibers. Nanofibers with the porous membrane have higher surface area than smooth/nonporous nanofibers [60]. Mesoporous structure with abundant inner spaces enables electrolyte access easily for the nanofibers, which can lead to the improvement in charge transfer [60]. Sihui et al. [61] developed highly porous nanofibers using a PS mixture with the combination of DMF/tetrahydrofuran (THF) solution as a core material and PVP/TiO₂ mixture in combination with ethanol as a shell liquid. These two, PS and PVP/TiO₂, polymer solution combinations were aligned, and the PS phase was detached by calcining nanofibers to form highly porous nanofibers [61]. Kim et al. [62] prepared electrospun polymer nanofibers made of PLA, PS, and poly(vinyl acetate) (PVA) with a porous surface morphology. In this work, the surface morphology of the obtained nanofibers, e.g., pore size, depth, shape, and distribution of non-woven mats, was optimized by varying the collector temperature.

Nayani et al. [63] developed highly porous and hollow PAN fibers using nonsolvent-induced phase separation (NIPS). A highly porous structure is obtained when the polymer is absorbed in a nonsolvent bath(water), and the specific surface area of porous PAN nanofibers was increased comparing with solvent-induced phase separation [63]. In another study, porous PAN fibers were fabricated with a ternary system of PAN/DMF/water. The porous structure was formed when the spinodal decomposition phase separation was occurring. In addition, the thickness of nanofibers was tuned by raising the surface tension and viscosity of PAN solutions [64]. Liangmiao et al. [65] fabricated small wire-based 3D hierarchy boehmite hollow spheres without any surfactants and templates. Size and internal structure and morphological characteristics of hollow spheres were optimized by altering the aggregation of boehmite clusters into spheres and their subsequent reactions such as dissolution and redeposition process.

Core-Shell Nanofibers

Core-shell electrospinning is capable of using an electrospinnable material as a carrier to fabricate nanofibers for non-electrospinnable material (Fig. 18) [66]. Given that a core-shell fiber is prepared out of two independent materials, each material might impart exceptional and independent functionality to the composite

Fig. 18 Schematic diagram of the core-shell electrospinning setup. (Reprinted from [66], Copyright (2014), Elsevier)



fiber. The core is protected until it is time for its release. The core-shell nanofibers can be differentiated into core and shell with an overall diameter varying from 20 to 100 nm. Distribution and orientation of molecules and ions are influenced by several factors such as crystalline, interaction between the material mixture, and molecular mobility. The core-shell polymers produce flexibility of lightweight with the high mechanical strength, chemical stability, and heat stable inorganic particles [66, 67]. To bring the functional properties onto the surface of the nanofibers (shell), as keeping the intrinsic properties of the nanofibers (core), core-shell nanofibers are introduced. In this type of nanofiber, the external layer may include active agents for getting functional properties, such as shells holding immobilized specific enzymes. Various methods, together with the multistep template synthesis, surface-initiated atom transfer radical polymerization “ATRP,” and coaxial electrospinning, are introduced for fabricating core-shell nanofibers. Among them, coaxial electrospinning is usually counted as one of the most versatile methods for fabricating these kinds of nanofiber [68]. A coaxial jet is formed, when two different liquids simultaneously flow through outer and inner spinneret capillaries in the presence of a high-voltage power supply. Then, nanofibers are subjected for solvent evaporation and a stretching process. The inlet volume of two different liquids into spinneret capillaries is influencing the uniformity of nanofiber and stability of the core material [65]. Also, flow rates of liquids in the inner and outer capillary affect the thickness of core-shell nanofibers. Additionally, the opening capacity of the spinneret capillaries, electric field, miscibility of two liquids and conductivity, and their viscosity plays important roles in the formation of uniform core-shell nanofibers and morphology. Liangmiao et al. [65] developed core-shell nanofibers with two miscible and immiscible polymer solutions using phase separation process. Achieving continuous and uniform core-shell nanofibers can be ascertained by proper stretching of the droplet (Cone Taylor). Core deformation or its breakage into droplets may happen due to a viscous force obtained by the shell, transforming itself into droplets (due to the weakness of electric fields) or its rapid stretching, thus exerting strong viscous stress tangential to the core. Several studies have used a coaxial jet and produced special nanofibers through it [65].

Recently, a novel kind of shape memory polyurethane (SMPU) nanofibers with core-shell nanostructure is fabricated using coaxial electrospinning. Pyridine(Py)-co-urethane as a shell and caprolactone-co-urethane as the core were coaxially electrospun for fabricating shape memory nanofibers. In this study, the ratio of the core polymer and shell were customized for best shape revival [69]. The developed fibers exhibited high-dimensional stability and good shape revival under thermal-induced tests. Collagen as the shell and PCL as the core were applied for creating a non-woven mat. According to cell culture results, collagen-coated PCL nanofibrous mat was attuned with fibroblast cell migration and proliferation in assessment with other controls (pure PCL nanofibers and single collagen and PCL nanofibrous or their mixtures) [70]. Li et al. [71] developed PMMA-PAN nanofibers by using a conventional single-nozzle electrospinning technique. In this study, PMMA and PAN were applied as core and shell, respectively. The same technique was also used for PEO and chitosan. In this study, the fraction effect of each component in the solution was investigated. The core-shell structure transformation was caused by dissimilar phase separation mechanisms with a continuous decrease of PEO fraction. Uniform-sized and monodispersed boehmite core-shell and hollow spheres have been successfully developed by Zhang et al. [72] by applying a template-free solvothermal process. The various parameters like reaction duration, the trisodium citrate amounts, and solvents were shown to affect the formation of the AlOOH core-shell and hollow nanospheres.

Weinqi et al. [73] developed hollow core-shell ZnO-SnO₂ nanofibers via a two-step process. A ZnO shell with a thickness of 10–15 nm was effectively grown on hollow SnO₂ nanofibers, resulting in an additional core-shell nanostructure. SnO₂ sensor exhibited significantly improved ethanol sensing performance as compared to the ZnO-SnO₂ sensor at below 200 °C temperature. This type of performance can be ascribed to the exceptional hollow structure, oxygen vacancies, and the n-n heterojunction. Moreover, the energy band structure of the heterojunction between the SnO₂ core and ZnO shell-core and the electron depletion theory was frayed to construe the gas sensing mechanism. Nair et al. [74] reported the fabrication of non-woven porous mats of PS-Py core-shell nanofibers by electrospinning polymeric solutions containing chemical oxidants. Polymers with high molecular weights are dissolved in solvents that produce polymeric solutions with optimum viscosity, evaporation rate, and dielectric constants. PS can be electrospun in various solvents; it is in combination with ferric oxide used as a template for polymerization of pyrrole to fabricate polymeric shells on the structural polymeric core. The morphology of nanofibers exhibits higher conductivity due to the growth of poly-Py shells over PS template fibers. From the obtained results, it was suggested that the use of ferric tosylate instead of ferric chloride produced faster growth and higher crystallinity, leading to higher conductivity [74].

Nanostructure materials play an important role in the automotive technology, especially in the development of high-performance supercapacitors and portable power devices. Particularly the nanofibers with mesoporous structures possess unique dimensional structure and high surface area to volume ratio which favors

the electrode-electrolyte interface to provide high electrochemical properties [75]. Xinghong et al. [75] reported on the preparation of coaxial electrospinning titanium nitride-vanadium nitride core-shell-structured mesoporous fibers with the spinneret of coaxial capillaries for developing the supercapacitors. Results indicated that the mesoporous structures of nanofibers were a good candidate for high-performance supercapacitors and can be used in Li-ion batteries. Li et al. [76] developed tetradecanol/PMMA nanofibers by melt coaxial electrospinning process. The sheath consisted of optical transmission PMMA, and core contains 1-tetradecanol. The TEM image reveals the clear interface between 1-tetradecanol core and PMMA polymer shell with inner and outer diameters of 200 nm and 500 nm, respectively. The core material was completely encapsulated independently and phase separated from the shell wall of the polymer matrix. These types of nanofibers are most important in thermo-responsive, energy-storage, and phase-transformation applications [76].

Emerging Applications of Structural Nanofibers

Structural nanofibers can be produced from various polymers, metal oxide, and ceramic materials and therefore have different physical properties and application potentials, such as in energy production and storage, sensors, automotive, aerospace, smart textile design, tissue engineering, medical implants, pharmacy, and cosmetics. Attention is given to the future of research in these areas in order to advance and increase the application of nanofibers and commercialization. Various potential applications of functional nanofibers have been described in detail.

Energy Production and Storage

The potential applications of nanofibers have been demonstrated for energy production and storage applications. They provide solutions for energy crisis as they have the ability to convert different forms of energies into electrical energy. Presently, various types of fuel cells, like direct methanol fuel cells, proton exchange mat fuel cells, solid oxide fuel cells, and alkaline fuel cells, are available [77, 78]. It was reported that nanofibers have been applied in construction for various parts of batteries, supercapacitors, solar cells, hydrogen storage and generation devices, and piezoelectric power generators. The outstanding properties of nanofibers such as high surface area-to-volume ratio and high porosity are being utilized in electrolytes for long-term storage and rapid electron/ion transport. Figure 19 shows fabrication of highly porous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /carbon nanofiber electrodes that exhibit excellent cyclability, high capacity, and super-high rate capability in hybrid supercapacitors and Li-ion batteries [79]. The highly porous structure of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /carbon nanofibers facilitates the electrolyte infiltration, enabling full utilization of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and fast transport of Li^+ and e^- .

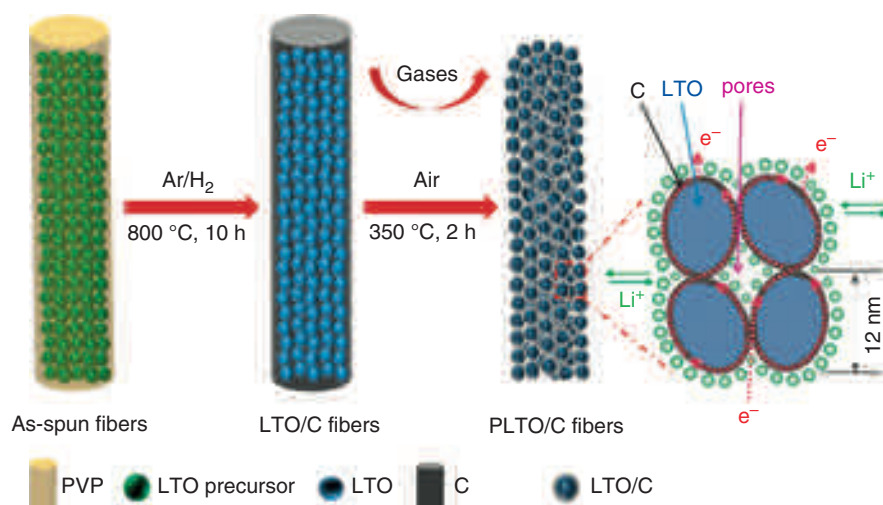


Fig. 19 Schematic presentation of the formation of the porous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /carbon nanofibers through electrospinning and a subsequent two-step heat treatment. (Reprinted from [78], Copyright (2014), Elsevier)

Environmental Protection and Improvement

With increasing harmful pollutions in recent years, the need for environmental monitoring and access to clean air and water has become important. To achieve this, the fabrication and applications of nanofibers with tunable physicochemical properties and features are required. Rapid developments have been demonstrated in the applications of nanofibers for water treatment and environmental protection, notably in ultrafiltration, photocatalysis, and chemical sensing. Nanofibers have typically high porosity, a controllable pore size, which is advantageous for purification of water and air. Nanofibers possess high adsorption capacity and surface area, thus enhancing the filtration efficiency and sensing performance to remove the inorganic pollutants such as heavy metals Hg, Pb, Cu, and Cd from the environment [80]. Environmental remediation includes the removal of industrial pollutants, agricultural pollutants, bacteria, germs, fungus, and hard-to-decompose organic compounds present in wastewater. Figure 20 illustrates the idea of environmental remediation using a metal oxide as photocatalysis [81].

In industry, nanofibers have been used as filter media for the past two decades for cleaning air pollutants such as volatile organic compounds (VOCs) and nitrogen dioxide (NO_2). Nanofiber filters also provide higher filtration efficiency due to smaller fiber size. Thin-plate die technology of M/s Non-woven Technologies Inc. (Georgia) had developed submicron fibers for filtration products. They find applications in the pulse clean cartridges for dust collection and in-cabin air filtration of mining vehicles.

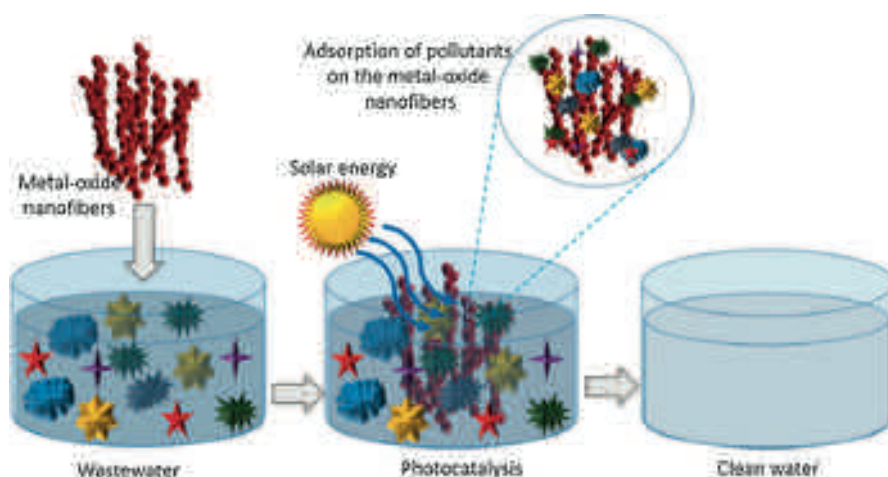


Fig. 20 Representation of environmental remediation by metal oxide nanofibers as photocatalysis. (Copyright 2017, MDPI [81], This is an open access article distributed under the Creative Commons Attribution License which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. (CC BY 4.0))

Biological and Healthcare Applications

Polymeric nanofibers have found wide biomedical applications [82] with several US patents [83–86] describing techniques for making vascular prostheses and breast prostheses. Porous, thin film protein nanofibers were applied to a prosthetic device for implantation into the body [87]. Tissue engineering is a promising substitute for damaged or deteriorated tissues which cannot be repaired with common methods. The tissue-engineered nanofibers may possess many advantages like versatility for biofunctionalization and promotion of desired cell behaviors. The future success of nanofiber will depend on the fabrication of nanofiber scaffolds at a reasonable cost [88–91].

The various naturally available biomaterials like keratin, viral spike protein, silk, collagen, tubulin and actin, cellulose, chitin, and mucin are established as nanofibrous materials in the form of the nm-to mm-scale. The goal is to design 3D scaffolds of synthetic biodegradable matrices that provide temporary templates for cell seeding, invasion, multiplication, and differentiation, thereby reviving the biological tissue. Biodegradable scaffolds from nanoscale nanofibers may hold the key in adjusting the degradation rate of a specified biomaterial in vivo [85–87]. It has been recently demonstrated that smooth muscle cells oriented themselves along the aligned nanofibers [87, 88].

Electrospun nanofibers of the poly(ethylene-co-vinyl acetate) and PLA loaded with the antibiotic drugs like tetracycline and Mefoxin exhibited promising results in various disease treatments. Thus, drug delivery with nanofibers can be expected in a

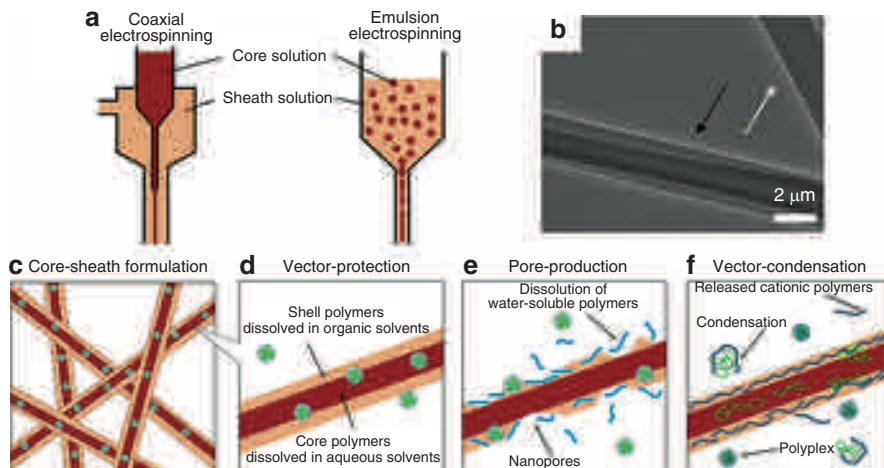


Fig. 21 Preparation of core-shell nanofibers for controlled gene delivery using coaxial electrospinning process and emulsion electrospinning. **(a)** Preparation of nanofibers with two methods **(b)** shows the TEM images core-shell nanofibers prepared by using coaxial electrospinning. **(c)** Shows the encapsulation of gene vector encapsulation for controlled release into core-shell nanofibers. **(d)** Shows the avoiding completely contact of gene vectors with core-shell nanofibers, **(e)** controlled delivery of gene vector from core-shell nanofiber, and **(f)** improved delivery of nanofiber layer modified with the polycationic polymers. (Copyright 2014, Springer Nature [97], This article is published under license to BioMed Central Ltd. This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly credited. The Creative Commons Public Domain Dedication waiver (<http://creativecommons.org/publicdomain/zero/1.0/>) applies to the data made available in this article, unless otherwise stated)

clinical setting in the near future [92–97]. Nanofibers were promising in the treatment of wounds and burns. Recently, biodegradable electrospun nanofibers produced mat dressing when applied onto skin wounds. This dressing facilitates the growth of normal skin without the formation of a scar. Non-woven nanofibrous membranes protect the wound by aerosol particle capture mechanism against the bacteria [92]. The encapsulation of gene vectors within electrospun nanofibers for consequent diffusion through porous routes can result in the sustained release of gene vectors. Figure 21 shows the encapsulation of gene vectors into nanofiber [98].

Presently available skin care products may cause allergies and/or inflammation [99] due to the migration of the product to the more sensitive areas of the body. Therefore, polymer nanofibers are being tested as skin care products. Due to the high surface area, nanofibrous skin masks facilitate higher use and transfer rate of the additives to the skin. Such cosmetic skin products made from electrospinning can be softly and painlessly applied for treatment of the skin. During combat, electrospun woven nanofiber clothing may increase the chances of survivability of soldiers against harsh environmental conditions. Nanofibers have been identified as ideal

candidates for protective clothing applications due to their lightweight, high porosity, large surface area, resistant to penetration of harmful chemical agents, and good filtration efficiency [100, 101].

Sensors, Electric, and Optical Devices

Researchers are using nanofibers to make sensors that change color as they absorb chemical vapors. Piezoelectric nanofibers of polyvinylidene fluoride were used in developing functional sensors. They were found to be more sensitive owing to the high surface area [102, 103]. Recently, highly sensitive optical sensors based on fluorescent polymer nanofiber films have been established. Initial results indicate that the sensitivities of nanofiber films distinguish ferric and mercury ions and a nitro compound (2,4-dinitrotoluene) is two to three times more significant than sensitivities obtained from thin film sensors. A single nanofiber coated with two metals forms a thermocouple to rapidly detect inflammation of coronary arteries. Such a nano-thermocouple scan also is inserted into a cell to monitor the metabolic activities [104]. Additional, nano-thermocouples can be incorporated into a catheter balloon to determine the arterial wall temperature. CNFs have a great perspective to create the next generation of electrochemical biosensors owing to their exceptional structural, mechanical, and electrical properties. Figure 22 shows the fabrication of active humidity sensors based on lead-free NaNbO_3 piezoelectric nanofibers. The devel-

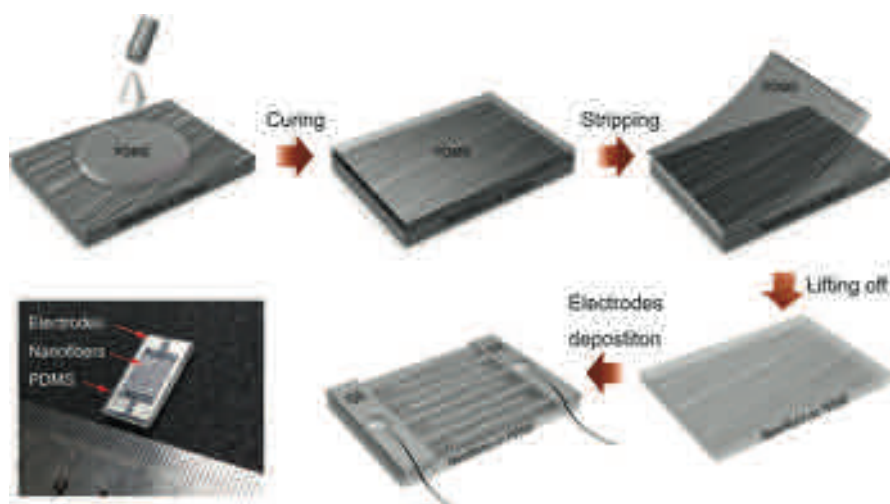


Fig. 22 Piezoelectric active humidity sensors based on lead-free NaNbO_3 piezoelectric nanofibers. (Copyright 2015, Hindawi [105], This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any original work is properly cited)

oped equipment could detect humidity at ambient temperature conditions as well [105].

Flexible electronics have become the focus of major research since they can be the next-generation devices with lightweight and portable electronics. Transparent conductive films made of nanofibers have played important roles in different flexible electronic applications, including electronic displays and solar cells. There are several ways in which electrospun nanofibers may be made conductive. One of the simplest methods is by blending conductive additive such as CNTs to the polymer solution to be electrospun. These nanofibers can be used in fabricating small electronic devices such as Schottky junctions, sensors, and actuators. In high-performance batteries, conductive nanofibrous membranes are also suitable for use as porous electrodes due to more surface area. Researchers have developed piezoelectric nanofibers that are flexible enough to be woven into clothing. Photoelectric conductive nanofibrous membranes have been proposed to have significant application in corrosion protection, electrostatic dissipation, and electromagnetic interference shielding and photovoltaic devices [105]. The primary part of the liquid crystal device consists of a fiber/liquid crystal composite with a submicron thickness. The refractive index differences between the liquid crystal material and the fibers govern the transmissivity of the device. For this application, the potential and performance of nanofibers need to be further assessed.

Conclusion

Nanofibers are fibers having dimensions of 100 nm or less. The surface and/or interior of such nanofibers can be further functionalized with molecular species or nanoparticles during or after an electrospinning process. In addition, electrospun nanofibers can be assembled into ordered arrays or hierarchical structures by manipulation of their alignment, stacking, and/or folding. Functional nanofibers, based on the nature of materials used for construction, are broadly divided into organic, inorganic, and inorganic carbon and hybrid nanofibers. Further, depending on structural features, nanofibers are classified into hollow, mesoporous, nonporous, and core-shell nanofibers. Nanofibers found a wide range of applications in our daily life. The properties of nanofibers have stimulated researchers and companies to consider using them in several fields, including controlled drug delivery, cosmetics, tissue engineering scaffolds, sensor devices, optical devices, wound healing, and protective clothing, to name a few. Numerous publications have appeared in recent years on specific functional nanofibers and their processing methods and uses. However, there are several areas that require attention for further development of the field. At the laboratory scale, potential applications of nanofibers have been identified. Significant efforts will be required to commercialize these applications so that research and development into nanofibers will continue to attract the attention of scientists in the future.

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