Chapter 1
Engineering Ceramic Fiber Nanostructures Through Polymer-Mediated Electrospinning

Avinash Baji and Yiu-Wing Mai

Abstract Electrospinning is increasingly used as a simple and straightforward technique to fabricate one-dimensional fibers from both organic and inorganic materials. These one-dimensional fibers with controlled sizes possess some unique features such as large surface area to volume ratio, high porosity, and low density. Compared to other conventional materials, these features make them attractive for applications such as energy harvesting, energy storage, super-hydrophobic membranes, and sensors. This chapter provides an overview on the synthesis of inorganic fibers through polymer-mediated electrospinning. Some of the common techniques employed by many researchers, such as solgel combined with electrospinning, emulsion electrospinning, and electrospinning combined with solid–gas reaction, to fabricate metal oxide fibers are discussed. In addition, techniques to fabricate ceramic and metal oxide fibers having different morphologies and hierarchical structures are described. Recent applications of electrospun metal oxide fibers are finally highlighted with a focus on filtration, sensors, photocatalysis, and energy.

1.1 Introduction

The interest in nanostructured materials has grown tremendously in the last few years mainly due to the development in techniques that enable us to fabricate structures with controlled geometry and dimensions [1–7]. These nanostructures with controlled size and geometry display some unique characteristics and functions

A. Baji (✉)
Engineering Product Development (EPD) Pillar, Singapore University of Technology and Design (SUTD), Singapore 487372, Singapore
e-mail: avinash_baji@sutd.edu.sg

Y.-W. Mai (✉)
Centre for Advanced Materials Technology (CAMT), School of Aerospace, Mechanical and Mechatronic Engineering, The University of Sydney, Sydney, NSW 2006, Australia
e-mail: yiu-wing.mai@sydney.edu.au

Z. Lin et al. (eds.), *Polymer-Engineered Nanostructures for Advanced Energy Applications*, Engineering Materials and Processes,
DOI 10.1007/978-3-319-57003-7_1

that are important for the design and development of advanced devices and systems [4, 5, 7]. In particular, the one-dimensional structures such as fibers and wires due to their large aspect ratio and surface area have attracted great attentions of researchers and are being considered as building blocks for nanoscale electronics and electrochemical devices [8–10]. The geometry and size of these nanostructured fibers ensure that the fibers display enhanced electrical conductivity and thermal transport characteristics. The nanostructured fibers also show good interaction with surrounding matrix and therefore are used to enhance its mechanical stiffness and strength [6, 10–12].

Among all the fabrication techniques used to produce one-dimensional fibers and wires, electrospinning is regarded as a simple and efficient technique to produce continuous fibers with controlled dimensions from a range of organic and inorganic materials [13–15]. Also, electrospinning can be used to obtain fibers with various structures and morphologies [16–18]. For example, modifying the conventional electrospinning setup and using a coaxial spinneret can yield core–shell or hollow fibers [19, 20]. Similarly, modifying the collector used in conventional electrospinning can lead to the collection of yarns or aligned fibers [15, 21]. Fibers with unique surface structures can also be obtained by decorating the surface of the fibers with nanoparticles or by introducing substructures on the surface of the fibers [22, 23]. Introduction of such nanoscale features on the surface of the fibers can greatly impact the surface properties of the fibers, which can expand their applications. In particular, inorganic metal oxide fibers obtained using electrospinning of precursor metal oxide salts followed by thermal annealing display some unique morphology on the fiber surfaces [13, 24]. Such fibers with high surface area and interconnected porosity are technologically important materials for various functional applications. For example, it is reported that the charge transport in metal oxide fibers can be a few orders of magnitude higher than that in their counterparts which are based on nanoparticles [8, 11]. Similarly, metal oxide fibers have been actively investigated for novel electrode materials for electrochemical storage devices [12, 25]. Thus, metal oxide fibers have found applications in nanoelectronics, sensors, fuel cells, solar cells, catalysis, hydrogen storage batteries, etc. [26–31].

Since the first report published in 2002–2003 on fabrication of metal oxide fibers using electrospinning combined with solgel technique [32, 33], many researchers have adopted this polymer-mediated electrospinning technique to produce a variety of ceramic and metal oxide fibers [13, 20, 24, 34, 35]. They have gone even further to fabricate hybrid and hierarchical ceramic and metal oxide fibers [18, 36], hollow and core–shell ceramic fibers [7, 37], porous ceramic fibers, and carbon nanotube-filled ceramic fibers [38]. Recently, some researchers have also fabricated hierarchical fibers by growing substructures on the surface of inorganic fibers. For example, electrospinning and hydrothermal treatment have been applied to grow ZnO nanostructures on the surface of Co_3O_4 fibers [39]. In a similar way, Ostermann et al. [36] fabricated nanorod-on-fiber structures by growing V_2O_5 nanorods on the surface of TiO_2 fibers.

We acknowledge that there are many articles in the literature on electrospinning which have extensively reviewed the electrospinning mechanisms and applications of electrospun fibers in the areas of tissue engineering and biomedical engineering. We will not duplicate the existing work here. Hence, in this chapter, we will review some of common electrospinning setups and techniques used to fabricate ceramic and metal oxide fibers. We will show how the fiber size and morphology can be controlled because they are important factors in engineering these complex structures for use in different advanced and novel applications. We will also present the use of electrospinning to fabricate hybrid and hierarchical fibers based on ceramics. Some recent applications of these inorganic fibers are given.

1.2 Electrospinning: Fabrication of Inorganic Fibers

Ceramic or metal oxide fibers have captured wide interest as promising candidates for electrodes in lithium-ion batteries due to their high-energy densities [1, 7, 10, 29]. Although there are various methods such as electrodeposition, lithography, and electron beam to produce such one-dimensional ceramic fibers [8, 40–42], most of them are cumbersome and expensive. By contrast, polymer-mediated electrospinning offers an attractive alternative route to produce one-dimensional (1D) ceramic fibers in large quantities. Below, we present some common electrospinning techniques used to produce 1D ceramic and metal oxide fibers.

1.2.1 Solgel Method

Electrospinning combined with solgel approach is often used to obtain inorganic fibers [13, 32, 34, 43]. This method is particularly efficient and useful as the metal oxides produced using this method are typically pure and the method enables us to obtain the ceramic or metal oxide from molecular precursors [29]. The process can be controlled, and hence, 'tailor-made' materials can be obtained using this method. Typically, two different processing techniques are used in the preparation of the sol solution. The first approach is based on hydroxylation and condensation of molecular precursors [44]. Here, the metal precursor salts are hydrolyzed in alcohol or water. Following this, the hydrolyzed precursor salts are condensed in organic acid. This leads to the formation of metal-oxo or metal-hydroxo polymeric gels that are spinnable.

The second approach is a common technique that is used to fabricate ceramic or metal oxide fibers. Typically, to obtain such inorganic fibers, metal salt precursors are dispersed homogeneously in a solvent [34, 42, 44]. Then, a suitable polymer is dissolved in this solvent to prepare the solution for electrospinning. Electrospinning this solution with metal salts and polymer leads to polymer fibers with well-dispersed metal oxide precursor, which can be thermally annealed to reduce

the precursor to ceramic or metal oxide. Finally, the polymer is removed to obtain neat metal oxide or ceramic fibers. To obtain continuous and uniform ceramic fibers, it is essential that the weight ratio of the precursor to polymer in electrospinning be between 50 and 80%. As an example, this approach is used to fabricate bismuth ferrite fibers [34]. Here, $Bi(NO_3)_{3.5}H_2O$ and $Fe(NO_3)_{3.9}H_2O$ are chosen as the precursor salts which are dispersed in a solution mixture of 2-methoxyethanol and glacial acetic acid. Polyvinylpyrrolidone (PVP) is dissolved in a dimethylformamide/ethanol solution mixture. Finally, the precursor solution mixture and the PVP solution are blended and electrospun to obtain homogenous precursor fibers. Thermal annealing of these fibers produces neat $BiFeO_3$ fibers. We have also used this method to fabricate barium titanate ($BaTiO_3$) fibers [27]. A solgel solution is first prepared by adding known quantities of barium acetate, titanium isopropoxide, and acetic acid. This solution is then added into a PVP–ethanol solution and electrospun to obtain the precursor fibers. Figure 1.1a shows the scanning electron microscopy (SEM) image of precursor fibers. The fibers are thermally annealed to obtain $BaTiO_3$ fibers. Figure 1.1b, c shows the SEM and

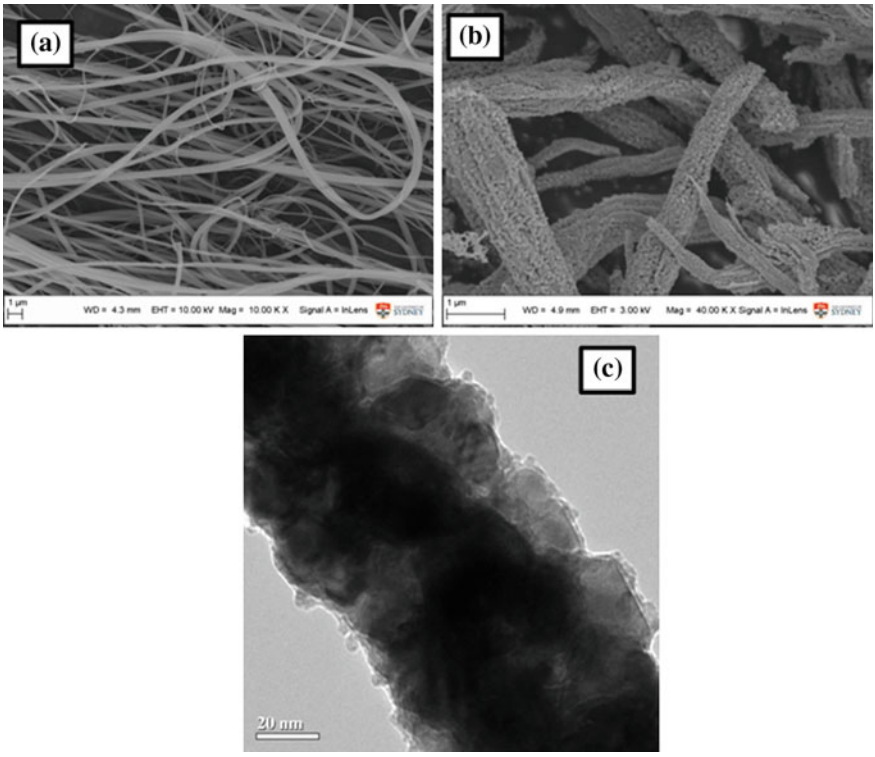

Fig. 1.1 **a** SEM image of PVP fibers with $BaTiO_3$ precursors, **b** SEM image of $BaTiO_3$ fibers obtained after thermal annealing, and **c** TEM image of $BaTiO_3$ fibers (reproduced from Ref. [27] with kind permission of © 2011 Elsevier)

transmission electron microscopy (TEM) images of the obtained fibers. It is evident from Fig. 1.1b, c that $BaTiO_3$ fibers are made of many fine-grained structures [27].

The size of the fibers can be determined by controlling the electrospinning processing variables, the annealing temperature and annealing time [15]. During annealing, the organic polymer phase is selectively burnt off while the inorganic phase is evolved to a polycrystalline phase. For example, TiO_2 precursor with polyvinyl pyrrolidone (PVP) polymer is electrospun and thermally annealed to obtain TiO_2 fibers. It is shown that during annealing, the polymer is removed and the size of the fibers is reduced [38, 45, 46]. Polycrystalline TiO_2 fibers are obtained after the thermal annealing stage, and the crystalline phase formation is determined by the annealing temperature used. TiO_2 fibers with anatase phase are obtained when the annealing temperature is 510 °C. This anatase phase is converted to a rutile phase if 800 °C for 3 h is used for annealing [47]. Similar observations are noted for WO_3 fibers [48, 49]. Either tetragonal or orthorhombic phases are obtained that depend on the temperature used for annealing.

1.2.2 Dispersion of Metal Oxide Particles

Electrospinning combined with solgel has been used to fabricate a wide range of ceramic and metal oxide fibers. However, when this technique is used, the fiber diameter varies with the hydrolyzing time [50]. Furthermore, the solution can be electrospun only during, but not before or after, the solgel reaction. A more direct and straightforward technique to produce inorganic fibers relies on dispersing the nanoparticles of the metal or metal oxides of known concentration directly into a polymer solution [51–53] which can be electrospun to obtain polymer fibers filled with nanoparticles. Then, the fibers are thermally treated to sinter the nanoparticles. During thermal treatment, the polymer matrix is burnt off leaving behind neat sintered particles in the form of fibers.

Ding et al. [53] used this technique to fabricate porous silica fibrous structures and showed that the porosity could be controlled by adjusting the concentration of silica added into the electrospinning solution. By using this approach, the variability that is associated with solgel hydrolyzing time can be avoided. However, with this technique, it is crucial to disperse the nanoparticles uniformly in the polymer solution such that polymer fibers with uniformly filled particles can be obtained. Studies also report that the size of nanoparticles used influences their aggregation in the polymer fibers [54]. For homogenous particle dispersion, it is important that the particles and the polymer share a common solvent [52]. For example, silica nanoparticles can be dispersed homogeneously in water-soluble polymers [52]. However, the fibers obtained using water-soluble polymers are often cross-linked to expand their applications that involve the use of water. Newsome et al. [52] dispersed silica nanoparticles in water-soluble PVP and cross-linked the polymer by heating the fibers at 200 °C. The polymer was later burnt off to sinter the nanoparticles and obtain fibers composed of pure silica nanoparticles.

1.2.3 Gas–Solid Reaction

The method of dispersing metal oxide particles in the electrospinning solution to obtain metal oxide fibers is a convenient and straightforward method. However, the particles tend to aggregate and cannot be homogeneously dispersed in the electrospinning solution, making it difficult to obtain uniform fibrous structures after the sintering process. Similar to the method of dispersing nanoparticles in the polymer solution, inorganic fibers fabricated using gas–solid reaction method are obtained by first dissolving the doped precursor particles of metal or metal oxide into the electrospinning polymer solution [42]. Then, gas–solid reaction treatment is applied to the fibers to synthesize metal or metal oxide particles within the polymer fibrous matrix. The polymer matrix can then be removed to obtain neat metal or metal oxide particles as fibers. Lu et al. [55] dispersed lead acetate in PVP polymer solution and electrospun to obtain PVP/lead acetate fibers. These fibers are then exposed to H_2S gas to convert lead acetate to PbS. Thus, after gas treatment, PbS nanoparticles dispersed in PVP are obtained. In a similar study [56], a solution consisting of polyacrylonitrile (PAN) and silver nitrate ($AgNO_3$) is prepared and electrospun to obtain $AgNO_3$–PAN fibers and exposed to HCl gas. The exposure to HCl synthesized AgCl particles and led to the collection of PAN fibers filled with AgCl particles with uniform size. It is further shown that the size and density of the particles with in the PAN fibers can be controlled by adjusting the $AgNO_3$ concentration within the electrospinning solution. Other researchers have used this gas–solid reaction method to obtain neat metallic or metal oxide fibers. Hence, Bognitzki et al. [57] dispersed copper nitrate in a poly(vinyl butyral) (PVB) solution that was electrospun to obtain copper nitrate–PVB fibers. These fibers are then thermally treated to remove the polymer and subsequently annealed in hydrogen atmosphere at 300 °C to obtain neat copper fibers.

1.2.4 Emulsion Electrospinning

Recently, emulsion electrospinning has been increasingly used to fabricate inorganic fibers [23, 42, 58]. This technique is similar to conventional electrospinning; however, a water-in-oil emulsion is used instead of a solution. Electrospinning this emulsion results in the separation of the phases within the fibers. Hence, this technique is useful to obtain highly porous fibers or hollow tubes. It eliminates the need of a complex coaxial spinneret to obtain core–shell fibers. With this technique, two different polymer solutions are first prepared and mixed to form an emulsion, followed by electrospinning to obtain fibers with two separated polymer phases. Lu et al. [23] used emulsion electrospinning to prepare highly porous TiO_2 nanotubes that are decorated with WO_3 nanoparticles on the internal and external sidewalls of the nanotubes. In their study, a solution consisting of titanium acetate and PVP solution is prepared. To this viscous gel, known quantity of viscous oil is added to

prepare the emulsion. This emulsion is then electrospun into fibers that are thermally treated to obtain porous TiO_2 nanotubes. Typically, in this process, oil along with the solvent evaporates from the surface of the fibers once the jet is ejected from the electrospinning nozzle. This produces a region near the surface of the fibers that is rich in PVP and precursor salts. The residual oil gathers at the inner regions of the fiber to obtain core–shell fibers. When the fibers are thermally annealed, the oil present in the core region of the fibers is removed and hollow nanotubes are obtained. Following this step, Lu et al. [23] used a thermal evaporation method to deposit tungsten carbide nanoparticles on the inside as well as outside walls of the hollow fibers. The fibers are then thermally treated in air to convert tungsten carbide particles to WO_3 particles. This has led to the synthesis of TiO_2 nanotubes decorated with WO_3 nanoparticles. A similar fabrication technique is used in another study [58] to obtain porous TiO_2 fibers.

1.3 Ceramic and Metal Oxide Fibers with Controlled Structures

The use of electrospinning to fabricate ceramic or metal oxide fibers has many advantages as the morphology and the structure of the fibers can be easily controlled. Some of the techniques that are used to control the morphology as well as the structure of the fibers are discussed in this section.

1.3.1 Unique Fiber Structures

The fiber morphology can be controlled by adjusting the electrospinning processing variables or the temperature and/or time during the annealing stage [59]. For example, ultra-thin zinc oxide fibers can be fabricated using a combined solgel and electrospinning technique. Zinc acetate, a precursor for zinc oxide, is added to the polyvinyl alcohol (PVA) solution and electrospun to fibers that are thermally annealed to obtain zinc oxide fibers. SEM and TEM images are used to show that zinc oxide particles are self-assembled and arranged to yield zinc oxide fibers [59, 60]. Similar results are observed when fabricating $BaTiO_3$ fibers whose SEM image in Fig. 1.2 shows that the fibers comprise $BaTiO_3$ particles. These particles are self-arranged and organized to obtain fibrous structures.

Research demonstrates that the size of the fiber can be controlled by adjusting the PVA concentration within the electrospinning solution and the morphology of the fiber can be varied by adjusting the thermal annealing temperature and/or annealing time. Apart from tailoring the electrospinning variables, the morphologies of ceramic fibers which are obtained using the solgel route are also influenced by the heating rate, cooling rate, and the atmosphere in which the sample is

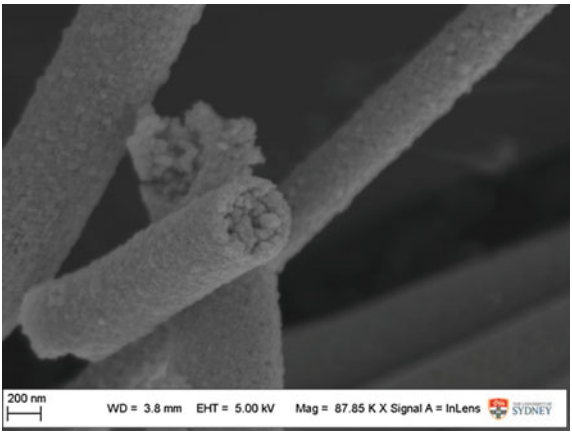

Fig. 1.2 SEM image of $BaTiO_3$ fibers demonstrating self-assembly and organization of $BaTiO_3$ particles (reproduced from Ref. [59] with kind permission of © 2013 Elsevier)

annealed. Fibers consisting of multi-grain structures can be developed by controlling the annealing temperature. It is reported that the size of the particles increases with annealing temperature. Hence, the use of high temperature causes crystallization and allows the grains to coalesce. For example, Xia et al. [61] investigated the effect of thermal annealing temperature on the morphology of $SrTiO_3$ fibers. Their results demonstrate that when the precursor fibers are thermally annealed at 800 °C, the morphology of the fibers is smooth and homogeneous. However, when the thermal annealing temperature is increased to 900 or 1000 °C, coarse fibers are obtained due to the irregular growth of the particles within the fibers. Figure 1.3 shows a $BaTiO_3$ coarse fiber obtained by controlling the annealing temperature. When 750 °C is used for annealing, the fibers have a continuous surface structure

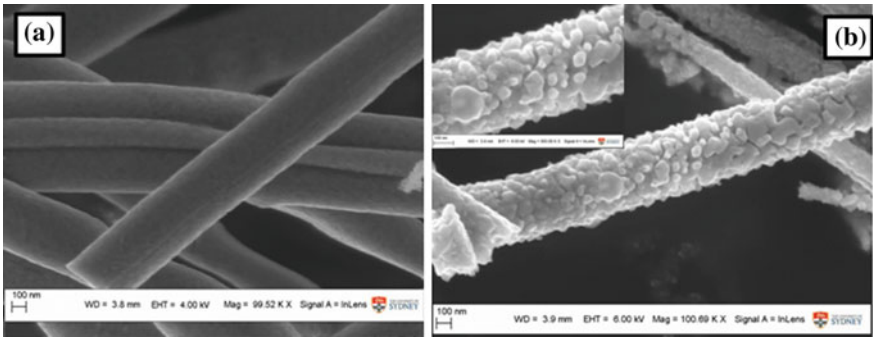

Fig. 1.3 SEM images of $BaTiO_3$ fibers obtained by thermally annealing the precursor fibers at **a** 750 °C and **b** 1000 °C. The *inset* shows the magnified image of the fiber (reproduced from Ref. [61] with kind permission of © 2015 Elsevier)

(see Fig. 1.3a). However, coarse fibers are obtained when the annealing temperature is increased.

In an another study, Anjusree et al. [45] showed that when PVP was used as the polymer along with a TiO_2 precursor, the fibers obtained were continuous and uniform. However, when polyvinyl acetate (PVAc) was used in the electrospinning solution instead of PVP, rice-shaped fibers were obtained. They also showed that leaf-like TiO_2 fibers could be obtained when both PVAc and PVP were used as the polymer in the electrospinning solution. They argued that the chemical nature of the polymer used in the electrospinning solution and the interactions between the polymer and the inorganic precursor defined the morphology of the ceramic fibers. For example, the hydrolysis of precursor metal oxide occurs when it is dissolved in polar PVP in a solvent. The hydroxyl groups of the precursor metal salts interact with PVP via hydrogen bonding. This suggests that the precursor metal oxide is attached to PVP, and hence, it assumes the shape of the fibers. Therefore, after thermal annealing treatment, the metal oxide retains the uniform and continuous shape. Rice-shaped fibers (Fig. 1.4) are obtained when PVP is replaced by PVAc. These unique shaped structures are caused by the reduced chemical interaction of the metal oxide precursor with PVAc. Microscale phase separation happens when the fibers are annealed. One phase is rich in metal oxide domains while the other phase is predominantly PVAc domains. The coexistence of these two phases within the fiber prolongs these domains during annealing, leading to the formation of rice-like structures of the metal oxide. Lastly, leaf-shaped structures can be obtained when a mixture of PVP and PVAc is used to electrospin TiO_2 fibers. The metal oxide precursor interacts with both PVP and PVAc at the same time. Thus, when these fibers are thermally annealed, the anisotropy in TiO_2 morphology leads to the formation of the leaf-like structures. Similar results are reported by Jo et al. [24] in their study which investigated the effect of polymer type used in the solgel solution that was used to prepare the inorganic fibers. The miscibility of the polymer with the precursor solgel and its interaction with the precursor metal oxide define the morphology of the fibers.

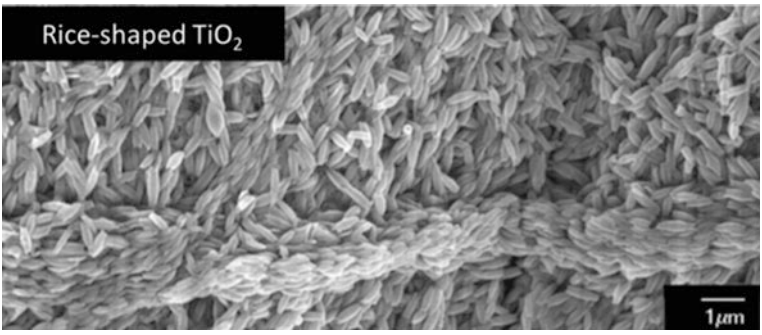

Fig. 1.4 SEM image of rice-shaped TiO_2 fibers obtained via electrospinning technique (reproduced from Ref. [45] with kind permission of © 2013 Royal Society of Chemistry)

1.3.2 Porous Fibrous Structures

It is desirable to fabricate inorganic porous fibers with high specific surface area for functional applications as the functionality of these fibers can be optimized. For example, these porous fibrous structures show tremendous potential as electroactive materials for energy harvesting applications [29, 31]. These structures are capable of demonstrating considerable improvement in power and energy density when compared to electrodes that are made using bulk materials [29, 31]. The one-dimensional structure of the fiber enables efficient transport of electrons along the fiber axis direction. The large surface area afforded by these porous fibers also promotes quick lithium-ion transfer. Thus, the charge transport can be orders of magnitude higher than the bulk counterparts.

Porous inorganic fibers can be easily obtained using electrospinning by controlling the concentrations of the polymer and the inorganic precursor in the electrospinning solution. Pores are formed when the metal salts and the polymer in the fibers are decomposed during thermal annealing [20, 60]. Kumar et al. [16] showed that porous fibers could be obtained by controlling the annealing temperature used to obtain the inorganic fibers and that the pores were formed when the polymer phase was removed from the fibers during the annealing process. Figure 1.5 shows an example of porous fibers obtained in the laboratory by controlling the concentration of polymer in the electrospinning solution.

Recently, emulsion electrospinning is an efficient tool to fabricate highly porous ceramic or metal oxide fibers [46, 58]. It can be used to produce fibers with high surface area to volume ratio compared to fibers prepared using the conventional electrospinning approach. In this approach, the emulsion solution used to prepare the fibers is the key factor that controls the fiber porosity. Lu et al. [58] used this method to prepare highly porous TiO_2 fibers. First, PVP–titanium acetate solution is prepared that forms a viscous gel. Then, a homogeneous and stable gel is prepared by adding a known quantity of mineral oil to the PVP–titanium acetate gel solution

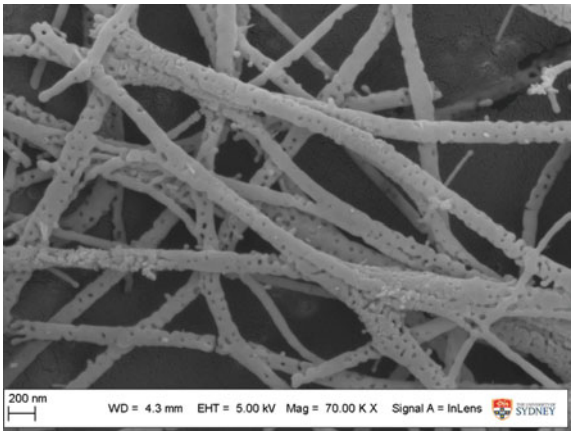

Fig. 1.5 SEM image of porous $BaTiO_3$ fibers obtained by controlling the concentration of polymer in the electrospinning solution (reproduced from Ref. [16] with kind permission of © 2011 Royal Society of Chemistry)

which can be used for electrospinning. When the fibers are ejected from the nozzle, the oil present on the fiber surface and the solvent evaporates. The evaporation of the solvent from the fiber surface ensures that the surface comprises PVP and precursor of the metal oxide. This leads to the formation of core–shell fibers with oil present in the core region of the fiber, while the outer shell consists of PVP and metal oxide precursor. When the oil from the inner core is evaporated, PVP hollow tubes and metal oxides are deposited on the collector. Finally, TiO_2 nanotubes are produced when the obtained fibers are annealed. Porous nanotubes are obtained during this process because the residual oil present in the shell region of the fiber is evaporated during thermal treatment. Uniformly distributed pores with 12 nm diameter are found on the surface of the fiber. A similar approach is used by Liu et al. [62] to produce porous TiO_2 fibers. They argue that the presence of tiny droplets of mineral oil in the surface region of the fibers is responsible for the porosity. Similarly, Chen et al. [46] prepared porous TiO_2 fibers using microemulsion combined with electrospinning. PVP and metal oxide precursor are first dissolved in a solvent solution to which paraffin oil is added to prepare the microemulsion mixture. The solution is then electrospun to obtain the precursor fibers. Paraffin oil is dispersed within the fibers and serves as the pore-forming agent. Metal oxide precursors are the matrix phase. During subsequent annealing, paraffin oil is removed and pores are formed. They explained that the multi-scale porous structures are obtained because paraffin oil droplets merge during electrospinning to form different sizes of the droplets. Thus, multi-scale porous structures are obtained when the fibers are thermally annealed.

1.3.3 Hollow Fibers

Electrospinning has also been used as a processing technique to fabricate ceramic fibers with complex architectures such as hollow fibers or coaxial fibers. Such hollow or tubular ceramic fibers have found applications in a wide variety of fields including gas storage, energy harvesting, catalysis, gas and chemical sensors, dye-sensitized solar cells, and electrodes for supercapacitors [4, 11, 20, 23, 34]. These hollow metal oxide fibers have captured the interest of researchers due to their unique catalytic, electrical, sensing, and electrochemical properties. The high surface to volume ratio and unique transport properties that arise owing to the fiber geometry and confinement effects can be attributed to the properties of the hollow ceramic fibers. Two separate fabrication techniques based on electrospinning are widely employed to obtain hollow ceramic fibers.

One of the fabrication techniques relies on using sacrificial templates for obtaining hollow fibers [63–65]. Here, the fabrication of polymer fibrous membrane using electrospinning is first effected. These polymer fibers are used as templates. Precursors of the inorganic materials are then coated on the surface of these fibers. Following this step, the polymer core is selectively removed or etched away to obtain hollow ceramic or metal oxide fibers. Choi et al. [63], in their study, used

this approach to fabricate hollow fibers with several centimeters in length and submicron diameters. The wall thickness of the hollow fibers is several tens of nanometers. Briefly, electrospinning is used in the first step to obtain polyvinyl acetate (PVAc) fibers that serve as sacrificial templates. Then, precursor materials of inorganic zinc oxide (ZnO) are used to coat the fibers by physical vapor deposition. Finally, the fibers are thermally treated to decompose the PVAc core and obtain inorganic ZnO as the shell.

The second technique used to produce hollow fibers is based on coaxial electrospinning [64]. This straightforward approach uses a coaxial spinneret to produce core–shell fibers. Here, two immiscible solutions are fed independently into the core and shell capillaries of the coaxial spinneret. It is critical that the core and shell solutions are immiscible to obtain well-defined coaxial fibers. Typically, the precursor for the inorganic material is fed into the shell capillary and mineral oil into the core capillary of the coaxial setup. The fiber formation mechanism is similar to that of conventional electrospinning. When a voltage is applied, the solution ejected from the spinneret is electrically charged and the electrostatic forces stretch the jet to form the fibers. The solution emanating from the inner capillary of the spinneret is stretched due to the shear stresses developed from stretching of the shell solution. Once the fibers are formed, they are heat treated to remove the mineral oil from the core region of the fiber and obtain the inorganic shell phase. Li et al. [33] used this method to produce hollow TiO_2 fibers. Figure 1.6 shows the SEM image of the hollow fibers obtained using this technique.

The size of the fibers can be tailored by controlling the feeding rate of the core and the shell solutions. A higher feeding rate of the mineral oil results in hollow fibers with thin walls. However, only some segments of the fibers are seen to be hollow when the feeding rate of the mineral oil is low. Zhang et al. [66] used this approach to fabricate hollow TiO_2 fibers. Briefly, the precursor material consisting of titanium isopropoxide and polyvinylpyrrolidone (PVP) is dissolved in a solvent. This solution is fed to the shell capillary, while heavy mineral oil is fed to the inner

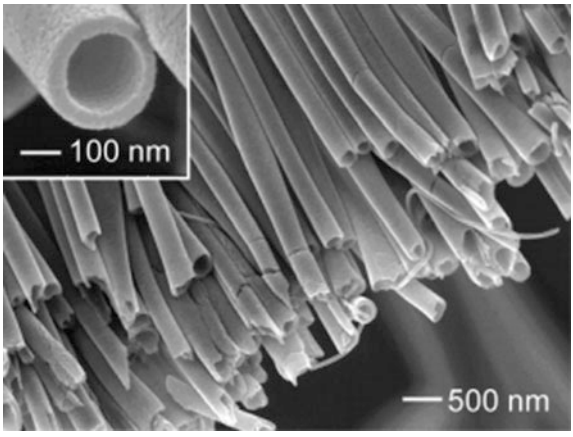

Fig. 1.6 SEM image of hollow TiO_2 fibers obtained using core–shell electrospinning (reproduced from Ref. [33] with kind permission of © 2003 American Chemical Society)

core capillary. The as-spun fibers are immersed in octane for 12 h to remove the heavy mineral oil. Following this, the fibers are thermally treated to obtain crystalline hollow TiO_2 fibers whose diameter is determined by the concentration of PVP used in the precursor solution. Researchers have also demonstrated that hollow inorganic fibers can be obtained using conventional single spinneret electrospinning. In this process, the inorganic precursor solution is mixed with two different polymer solutions. For this purpose, immiscible polymers are chosen such that they phase separate during electrospinning. Thus, Zhang et al. [67] prepared a solution consisting of polyacrylonitrile (PAN), PVP, and zinc acetate. Fibers are then formed using conventional electrospinning. Their results indicate that due to phase separation, PAN forms the core of the fiber, while PVP and zinc acetate constitute the fiber shell. Hollow zinc oxide (ZnO) fibers are obtained after thermal treatment and after the polymer phases are burnt off.

1.3.4 Controlled Assembly

Electrospinning setup can be modified to collect controlled assembly of fibers such as aligned and ordered structures. It has been shown that such aligned fibers can have tremendous potential for device applications including electrical and photonic devices. Also, anisotropic properties are displayed when the fibers are aligned. Li et al. [68] show that aligned arrays of SnO_2 fibers have anisotropic properties. Aligned SnO_2 fibers have 15 times higher electrical conductivity along the fiber axis compared to that transverse to the fiber axis. Similarly, other studies have demonstrated that the energy generation efficiency can be improved by aligning the fibers [69].

Typically, the setup for conventional electrospinning can be changed to collect aligned array of metal oxide fibers [15, 21, 70]. The electrospinning solution is prepared in a similar manner as for conventional electrospinning for obtaining aligned array of metal oxide fibers. The precursor of the inorganic material is dispersed in a polymer solution and electrospun using a modified electrospinning setup to collect the aligned fibers. Example of one such modified setup that is commonly used to collect aligned fibers is based on parallel plates. Aligned fibers are collected using grounded parallel plates as these grounded electrodes affect the electric field near the collecting area [15, 70]. The electrostatically charged electrospinning jet is sensitive to the electric field created by the grounded collector causing the fibers to deposit transverse to the plates and across the air gap between them. This results in deposition of an aligned array of fibers.

It is argued that the electrical conductivity of the electrospinning solution must be within a critical range to enable deposition of the fibers across the parallel plates. When the solutions with a low electrical conductivity are electrospun, the electrostatic forces are insufficient to pull the fiber across the air gap, and hence, the parallel plate method is ineffective to collect aligned array of fibers. Conversely, when the solutions with high electrical conductivity are electrospun, the jet motion

is dominated by the random whipping instabilities and aligning the fibers becomes difficult. Hence, the electrical conductivity of the solution and applied voltage should be carefully controlled when using the parallel plate method for collecting aligned array of fibers.

Wu et al. [71] in their study modified the conventional electrospinning setup in order to fabricate aligned inorganic fibers. In their approach, the fibers are collected between the electrodes. Briefly, a metallic triangular tip with 60° apex angle is the spinneret. The triangular shape of the tip helps establish the Taylor cone during electrospinning. The counter electrode has a grounded coin placed 3 cm away from the tip which, in turn, is dipped into the electrospinning solution such that a small droplet sits on the surface of the tip. When a high voltage is applied, bundles of aligned fibers are formed between the tip and the grounded electrode. The jet ejected from the Taylor cone is pulled toward the ground electrode without any bending. The jet is stretched between the tip and the grounded collector. As the solvent evaporates, the dried and stretched jet forms bundles of aligned fiber arrays between the tip and the collector. The fibers are later transferred onto silicon wafer and thermally annealed to obtain aligned inorganic fibers.

1.3.5 Composite Fibers

The potential of using one-dimensional structures such as fibers, tubes, whiskers, and needles for functional applications is well established and proven by several groups [5, 8, 9, 13, 27, 33, 34, 72–74]. The high surface area and aspect ratio of these 1D structures are known to greatly influence their mechanical, electrical, and thermal transport characteristics. Hence, researchers have identified them as the building blocks for nanoscale/microscale devices. Electrospinning not only enables the control of fiber assembly, fiber size, and geometry but also increases the structural complexity of fiber composites.

One-dimensional composite structures in the form of fibers are fabricated by combining two or more materials with an aim of improving the functionality and material properties of the matrix material. As an example, carbon nanotubes (CNTs) are often incorporated within the inorganic matrix to improve the mechanical strength, stiffness, and resistance to corrosion of the composite [35, 38]. A straightforward technique to produce composite fibers is based on incorporating inorganic fillers into the solgel solution prior to electrospinning. The fibers with inorganic fillers are then thermally annealed to obtain hybrid fibers.

Wen et al. [43] dispersed SiO_2 nanoparticles within the precursor solgel solution of SiO_2. Hybrid fibers are obtained after electrospinning and thermal treatment. In a similar study, Aryal et al. [38] dispersed multi-walled carbon nanotubes (MWCNT) in the precursor solgel solution of TiO_2. The solution mixture is electrospun, and the fibers are thermally annealed to obtain MWCNT-reinforced TiO_2 fibers. Zhu et al. [75] used the same method to prepare CNT-reinforced TiO_2 fibers for

lithium-ion battery applications. They showed that these composites displayed improvement in capacity retention.

The solgel and electrospinning technique that is used for fabrication of single-phase ceramic fibers can also be extended to process composite ceramic fibers. In this approach, precursor solutions of two different materials are separately prepared and added into a polymer solution, which is electrospun to obtain the precursor fibers. These fibers are then annealed to yield the composite ceramic fibers [18, 38, 76].

Zhang et al. [76] used this technique to produce CeO_2–ZrO_2 composite fibers. Briefly, precursors of CeO_2 and ZrO_2 are separately dissolved in solvents. The polymer solution is prepared by dissolving PVP in ethanol. Then, both solutions with precursors are mixed in the polymer solution. This composite solution is electrospun, and the fibers are subsequently annealed to obtain composite ceramic fibers. In our recent study [13], we also used this approach to prepare $BaTiO_3$/$CoFe_2O_4$ composite fibers.

Figure 1.7 shows TEM images of $BaTiO_3$/$CoFe_2O_4$ composite fibers which display magnetoelectric properties. Li et al. [72] used coaxial electrospinning to prepare porous TiO_2–carbon nanofibers and used these fibers as anode materials in Li-ion batteries. Briefly, poly(methyl methacrylate) (PMMA) solution is fed into the core capillary of the spinneret, while polystyrene (PS) along with TiO_2 precursors is fed into the shell capillary of the spinneret. The PMMA phase within the core–shell fibers served as the sacrificial component and played a role in producing the pores, while PS in the fiber served as the carbon source. Thus, porous TiO_2–carbon fibers are produced after thermally annealing the precursor fibers. These porous TiO_2–carbon fibers exhibit excellent electrochemical performance.

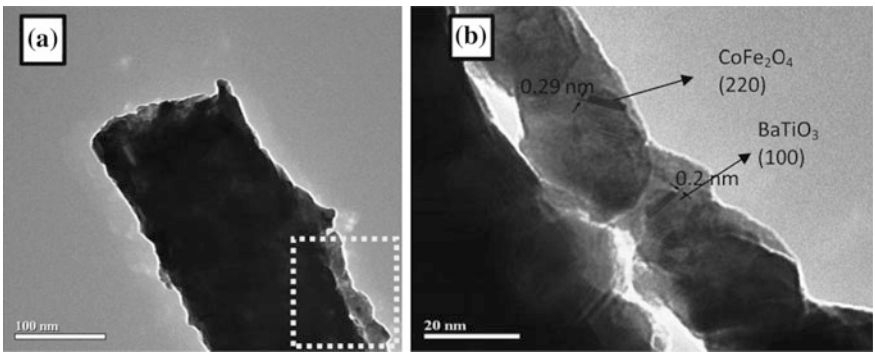

Fig. 1.7 **a** TEM image of $BaTiO_3$/$CoFe_2O_4$ composite fiber and **b** high magnification TEM image of a selected region (reproduced from Ref. [13] with kind permission of © 2014 Royal Society of Chemistry)

1.3.6 Hierarchical Structures Based on Ceramic Fibers

Recently, researchers have focused their interests on fabricating inorganic fibers based on complex architectures as these fibers are capable of demonstrating improved functionality [39]. For example, hierarchical structures based on inorganic ceramic or metal oxide fibers give superior photoelectrochemical performance, optical and electrical properties compared to their bulk counterparts and neat fibers [16, 39, 43]. In general, electrospinning can be used in two different ways to fabricate hybrid fibers or hierarchical structures based on ceramic fibers. In one technique, nanostructures grown on the fiber surface rely on hydrothermal treatment of the inorganic fibers in an aqueous solution.

Kanjwal et al. [39] dispersed ZnO nanoparticles in a precursor Co_3O_4 solgel solution. This colloidal solution is electrospun and then thermally annealed to obtain Co_3O_4 fibers dispersed with ZnO particles. An aqueous solution containing bis-hexamethylene triamine and zinc nitrate hexahydrate is prepared, and the annealed fibers are hydrothermally treated in this solution to grow ZnO nanostructures. Figure 1.8 shows the SEM image of Co_3O_4 fibers with ZnO nanostructures uniformly deposited on its surface.

Similar technique is used by Dai et al. [22] to grow K_xMnO_2 nanoplates on the surface of TiO_2 fibers. In their study, porous TiO_2 nanofibers using solgel combined with electrospinning technique are first prepared. Following this, the porous TiO_2 fibers are immersed in sulfuric acid with $KMnO_4$. This leads to the deposition of K_xMnO_2 plates on the surface of the fibers. It is further shown that the density can be controlled by adjusting the concentration of $KMnO_4$ in sulfuric acid and by adjusting the soaking time. Athauda et al. [77] used a similar approach to fabricate TiO_2 fibers. Dense ZnO nanorods are then grown on the surface of TiO_2 fibers by hydrothermal methods. First, TiO_2 fibers are dipped in ZnO seed solution, and then dip coated in a growth solution consisting of zinc nitrate hexahydrate and hexamethylenetetramine. The SEM image of the fabricated hybrid fibers is shown in Fig. 1.9.

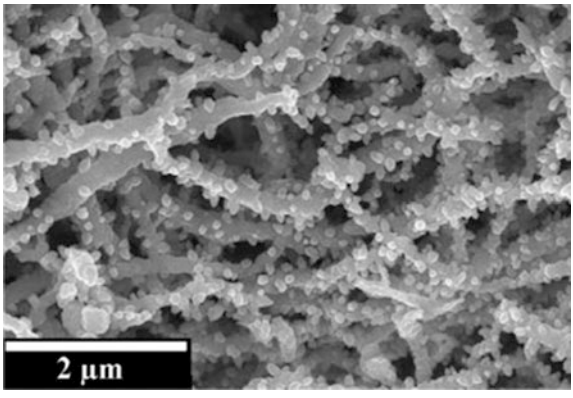

Fig. 1.8 SEM image of Co_3O_4 fibers with ZnO nanostructures deposited on its surface (reproduced from Ref. [39] with kind permission of © 2011 Elsevier.)

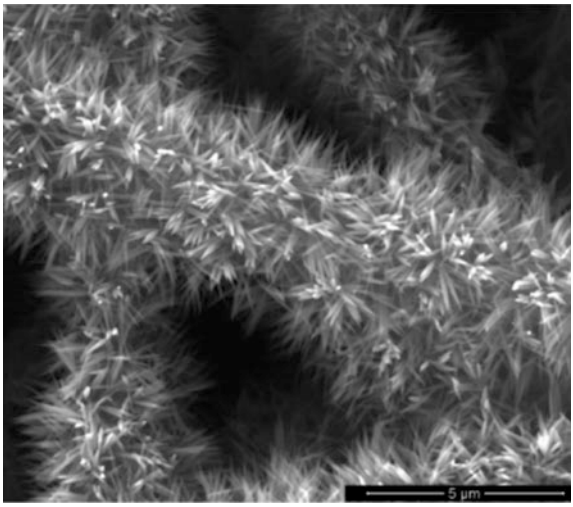

Fig. 1.9 SEM image of TiO_2–ZnO hierarchical structures. ZnO nanorods are grown on the surface of TiO_2 fibers (reproduced from Ref. [77] with kind permission of © 2012 American Chemical Society)

Another technique to fabricate hierarchical structures depends on the generation of nanostructures on the surface of the inorganic fibers. Here, desired metal salts can be introduced directly into the solgel solution and electrospun to obtain composite fibers. Following this step, the composite fibers can be thermally treated to grow metallic nanostructures on the surface of the fibers. Ostermann et al. [36] showed that electrospinning polymer solution containing a mixture of precursors led to the formation of composite metal oxide fibers. By controlling the annealing temperature and time, V_2O_5 nanorods can be grown on the surface of TiO_2 fibers. In the first step, the precursors of both V_2O_5 and TiO_2 are mixed in PVP solution. This solution is then electrospun to obtain PVP fibers with precursors of V_2O_5 and TiO_2. During annealing, both V_2O_5 and TiO_2 phases begin to crystallize. But their difference in crystallization results in phase separation, forming a unique morphology [36] which can be tailored by controlling the concentration of TiO_2 precursor in the electrospinning solution and annealing temperature. Thinner and more uniform V_2O_5 nanorods are grown on TiO_2 fiber surface when a lower annealing temperature is used.

In another study, Zhang et al. [78] produced hierarchical structures by first fabricating carbon fibers produced by electrospinning poly(amic acid) fibers which are thermally imidized and carbonized in a tube furnace. Then, a low-temperature chemical bath deposition process is utilized to grow $Ni(OH)_2$ nanoplatelets on the surface of the fibers. $Ni(NO_3)_2{\cdot}6H_2O$ and small quantity of urea are dissolved in deionized water and ethyl alcohol solution. The carbon fibers are treated in this solution to grow $Ni(OH)_2$ nanoplatelets on their surfaces. Figure 1.10 shows a SEM image of the obtained carbon fibers with $Ni(OH)_2$ nanoplatelets.

Recent studies have also demonstrated the use of electrospinning as a straightforward technique to produce carbon fibers that are decorated with metal oxide particles [35]. Lee et al. [35] showed that single nozzle electrospinning could be

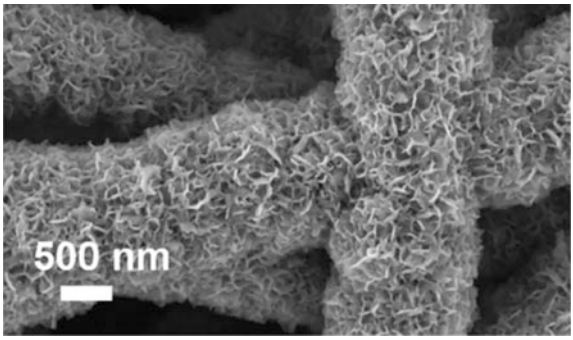

Fig. 1.10 SEM image of carbon fibers/$Ni(OH)_2$ hybrid fibers (reproduced from Ref. [78] with kind permission of © 2015 American Chocal Society)

used to produce such hybrid fibers. The electrospinning solution prepared consisted of 4 components, viz. polyacrylonitrile (PAN), PVP, precursor solution of $ZnAc_2$, and precursor solution of $SnCl_4$. Due to the differences in the viscosities of PAN and PVP, and their immiscibility, the lower viscosity of PVP forms the continuous phase while the higher viscosity solution of PAN forms the droplets, which leads to the formation of core–shell fibers [35]. When this solution is electrospun, electrical forces act on the outer continuous phase while the inner phase only experiences shear force that is applied on its surface due to the flow of the outer continuous phase. Figure 1.11 shows the TEM image of the PAN–PVP core–shell fibers. Inorganic precursors along with PVP formed the shell and the PAN formed the core in the core–shell structures. Thermally annealing these fibers carbonized the PAN in the core region and led to the formation of ZnO and SnO_2 nanoparticles on the surface of the fibers. It is further shown that the concentration of the nanoparticles

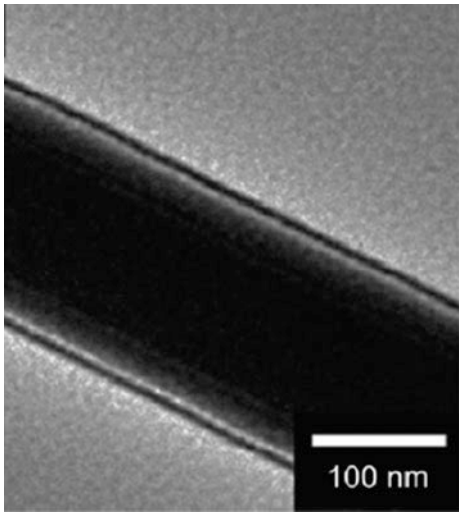

Fig. 1.11 TEM image of PAN–PVP core–shell fiber (reproduced from Ref. [35] with kind permission of © 2011 American Chocal Society)

on the surface of the fibers can be controlled by adjusting the concentration of the precursors in the initial solgel solutions.

1.4 Applications of Inorganic Fibers

Electrospinning is a simple straightforward fabrication technique that can be used to produce inorganic nanofibers with controlled size and structures. Therefore, these electrospun inorganic fibers have found applications in many fields including energy harvesting, filtration, sensors, electrocatalysis, super-hydrophobic and super-hydrophilic surfaces, and biomedical fields. Some common applications of these metal oxide fibers are discussed in this section.

1.4.1 Filtration

Recent interest among researchers is to develop membranes to filter specific molecules and a wide range of contaminants from aqueous solutions or from air medium [31, 79–81]. Electrospun fibrous membranes are most sought after because of their efficient filtration performance, high surface area to volume ratio, and their superior ability to trap contaminants. The function of these membranes is to allow only certain specific molecules to pass through it and block others including the contaminants. Dai et al. [22] fabricated hierarchical structures using electrospinning and demonstrated their use for water filtration applications. In their study, TiO_2 nanofibrous membranes are first fabricated and then K_xMnO_2 nanoplatelets grown on the surface of the fibers. These hierarchical structures are shown to remove Congo red molecules efficiently from an aqueous medium. The mechanical integrity and stability of the membranes are also proven since shear flow of solution has not damaged the K_xMnO_2 nanoplatelets on the surface of the fibers [22].

Electrospun membranes are also widely used for air filtration and personal healthcare applications. Membranes based on nanofibers have shown some promising applications as filters that are capable of intercepting Escherichia coli, severe acute respiratory syndrome (SARS) virus, and influenza A (H1N1) virus [82–84]. The membranes based on fibers can also be used as N95 respirator mask if the channels and the size of the structural elements match the size of the particulates that are to be captured [85]. The efficiency of the filter can be improved if the size of the fibers within the membranes is reduced to nanoscale dimensions. It is argued that fibers of finer diameters have better filtration performance with no change in permeability compared to micron size fibers [85]. The membrane based on electrospun fibers not only has high permeability but also is capable of capturing dust particles due to its small pore size. The dust particles can later be removed by reversing the air flow through it or by other mechanical methods. Although electrospun membranes based on polymers are widely used for air filtration

applications, their applications are limited due to the low thermal stability of the polymers. Hence, they cannot be used as high-temperature filter membranes. However, membranes based on inorganic materials owing to their chemical and thermal stability can function at high temperatures and are being increasingly used for such filtration applications. The functionality of the inorganic membranes can be further improved by addressing their brittleness.

Mao et al. [79] used a solgel combined with electrospinning technique to fabricate a new class of flexible silica fibrous membranes that can be used at high temperatures. The thermal stability of these membranes is demonstrated using thermogravimetric analysis. Their results show no weight loss of the inorganic membrane in the range 100–900 °C. They also studied the effect of annealing temperature on the mechanical strength and flexibility. The results show that membranes obtained using lower annealing temperatures have better flexibility compared to those fabricated at higher annealing temperatures. The formation of quartz crystals is attributed to the better flexibility seen for the membranes that are fabricated at lower annealing temperatures [79]. The filtration efficiency of these membranes is tested by feeding neutralized NaCl aerosol through the filters and is over 99.7%. The working principle is by trapping the NaCl aerosol particles in the top layers of the membranes.

In a similar study, Yang et al. [81] fabricated flexible inorganic membranes based on silica nanofibers using solgel combined with electrospinning. Following this, polymerized fluorinated polybenzoxazine layer is incorporated on the surface of the fabricated silica membranes by dipping the membranes in solvent containing the monomers. They showed that these membranes are highly flexible and can potentially be used for high-temperature filtration applications. In another study [80], Wang et al. used electrospinning to fabricate flexible alumina fibers and demonstrated its ability for filtration applications. The filtration efficiency is tested by passing neutrally charged dioctyl phthalate (DOP) aerosols through the membrane and noting the concentration of the aerosol before and after filtration. These membranes have filtration efficiency of 99.8%.

1.4.2 Sensors

Semiconducting metal oxides such as SnO_2, In_2O_3, ZnO, and TiO_2 have been frequently used as gas sensors due to their ability to detect molecules of gases [17, 35, 60, 86]. Typically, a mesoporous layer of 1–10 μm thickness acts as an active sensing layer. This layer consists of sintered and interconnected nanometer-sized particles. The sensing mechanisms are based on the diffusion-reaction mechanisms. The gas molecules diffuse into the layer and interact with some of the pre-adsorbed O-adions that are present on the surface of the nanoparticles. This is known to affect the charge transfer interaction between nanoparticles and the gas adsorbates, which in turn affects the electrical resistance of the sensing layer. By monitoring the electrical resistance, the changes in the surrounding gas composition can be traced.

Thus, having a porous sensing layer improves the sensitivity as it enables gas penetration and exchange. Conventional techniques used to prepare the porous layers limit their gas sensing abilities due to the difficulty for the gas to diffuse into the inner regions of the layers.

Electrospinning is extensively explored to develop novel structures and fibers that can be used as sensors. One-dimensional structures, e.g., fibers, wires, rods, and tubes, which are obtained using electrospinning, are shown to have distinct properties compared to their bulk counterparts [17, 35, 60, 86]. These 1D fibers are shown to demonstrate improved chemical sensing behavior compared to the conventional thin-film sensors. This is attributed to the large surface to volume ratio of the 1D structures. Due to its high sensing abilities, they are capable of sensing very low concentration of gases such as NO_x and Cl_2. Lim et al. [17] used solgel combined with electrospinning technique to fabricate mesoporous indium acetate (In_2O_3) fibers and demonstrated its ability to detect CO in air. The high surface area of the fibers presented large quantity of sites on its surface for CO adsorption and reaction.

Similarly, other studies [12, 86, 87] have developed electrospun nanofiber membranes based on TiO_2 and SnO_2 for gas sensing applications. In these studies, when the sensing membranes are exposed to traces of gases in air, their electrical resistance is seen to change. This resistance is monitored to detect any changes in gases. The usual practice is to evaluate the sensitivity of the fabricated materials at elevated temperatures. Heating the material thermally activates the process on the surface region of the material to quicken the response and recovery. Lee et al. [35] in their study fabricated hybrid fibers by depositing metal oxides on the surface of the carbon fibers. They showed that these metal oxides decorated carbon fibers that can be used as chemical sensors. These materials demonstrated excellent sensitivity and are reported to be 10–100 times more sensitive compared to carbon nanotubes. This is attributed to the presence of metal oxide nanoparticles present on the surface of the fibers that help increase the surface area of the material.

1.4.3 Photocatalysis

n-type semiconducting metal oxides are widely used as photocatalyst because of their excellent catalytic properties and abilities to remove pollutants from aqueous solutions or gases. Water purification using such materials relies on a photon-assisted oxidation process. This method abates and mineralizes the organic pollutants with the help of highly reactive hydroxyl radicals. When the semiconducting metal oxides are exposed to photons that have energies similar to or greater than the energy associated with its band gap energy, the electrons from the valence bands jump to the conduction band. This process results in a hole generated at the valence band [88]. The electrons generated by the photon energy and the holes can recombine to release energy. Alternatively, the electrons and holes can interact with electron donors or acceptors that are adsorbed on the surface of the semiconducting

metal oxides. The electrons can react with O_2 molecules that are adsorbed on the surface of the semiconducting metal oxides and reduce them to radical O_2^- anions. By contrast, the holes possessing positive charge can interact with hydroxyl or water molecules to oxidize them into hydroxyl radicals. It is these radicals that act on the organic compounds by decomposing them [88].

It is well established that nanostructures of metal oxides demonstrate superior catalytic properties compared to their bulk counterparts due to the huge surface area associated with the nanostructured materials. Hence, electrospun metal oxide fibers have found great potential for water treatment. These metal oxide fibers can help to degrade the organic pollutants present in the aqueous solutions. Lu et al. [58] used emulsion electrospinning to fabricate porous TiO_2 nanofibers and showed their use for water treatment. The porous TiO_2 fibers have large surface area and a combination of anatase and rutile crystal phases which can improve the efficiency of the photocatalysis due to efficient separation of mixed electrons and holes. Zhan et al. [37] used the core–shell electrospinning setup to produce hollow TiO_2 fibers. Mesopores on the fibers are introduced with the help of pore-directing agent. They showed that these mesoporous TiO_2 fibers exhibited higher photocatalytic behavior toward methylene blue degradation compared to commercial TiO_2 nanoparticles and mesoporous TiO_2 powders. The increased photocatalytic behavior of the mesoporous hollow TiO_2 fibers is attributed to increased surface area. In yet another study, electrospun ZnO nanofibers are shown to degrade polycyclic aromatic hydrocarbons and naphthalene in the presence of UV radiation [59]. Methods to further improve the photocatalytic activities of electrospun metal oxide fibers have been investigated. Typically, the photocatalytic activity can be reduced due to rapid recombination rate of the holes and the excited electrons. This issue can be resolved by doping the metal oxides with other transition metals. The dopants reduce the recombination rate of holes and excited electrons and increase the surface area.

1.4.4 Energy

Nanofibers fabricated using electrospinning owing to their geometry and associated properties have been the focus of interest for applications related to energy storage and energy devices [8, 11, 29]. The high surface area and porous structures of the fibers have been found to be beneficial for energy storage and conversion [31, 42]. Electrospinning is increasingly investigated for fabrication of fibers for energy conservation applications such as fuel cells and solar cells as well as for energy storage applications such as supercapacitors. Electrospun fibers have been used in dye-sensitized solar cells (DSSCs) to enable conversion of light to electricity [24, 46, 89]. Porous metal oxide fibers are deposited on a transparent conducting glass to serve as the photoanodes in DSSCs. A photosensitizing dye is adsorbed on these semiconducting metal oxide fibers. Hence, when the dye absorbs the photons in these solar cells, the photoelectrons move into the conduction band of the

semiconducting metal oxide fibers. These photoelectrons are collected on the photoanode and transferred to the counter electrode via an external circuit. The flow of electrons through the external circuit produces current. Studies demonstrate that the one-dimensional geometry of the fiber increases the energy efficiency due to better charge conduction [8, 29]. Porous metal oxide fibers such as TiO_2 are widely investigated for photoanodes as the high surface area ensures that a larger amount of photosensitizing dye is absorbed.

Further, one-dimensional fibrous structures obtained using electrospinning have fewer grain boundaries compared to sintered nanoparticles, which improves charge conduction and reduces recombination of the charge carriers. Nair et al. [89] fabricated porous TiO_2 fibers using electrospinning and developed DSSCs based on TiO_2 fibers as photoanodes. This DSSC shows an efficiency of $\sim$4.2% and incident photon to electron conversion efficiency of $\sim$50%. The DSSC gives a current density of 8 mA/cm^2 and an open-circuit voltage of 0.81 V.

Fuel cell is another area in which electrospun fibers are used to convert chemical energy into electrical energy. Among all types of fuel cells, direct methanol fuel cells (DMFCs) are widely investigated due to their low operating temperature and high power density [11, 26, 28]. Within these fuel cells, catalysts of platinum nanoparticles are loaded onto the supporting material. Studies demonstrate that the type of supporting material used has a great influence on the catalytic activity of the platinum nanoparticles. The criterion for selecting the supporting material for DMFCs is that the supporting material should have large surface area, stable, and electrically conductive. Electrospinning has been widely used to fabricate fibers as supporting materials in DMFCs. The 1D geometry of the fibers ensures the stability of the supporting material and plays a role in improving the performance of the resulting electrodes. Electrospun fibers based on carbon materials due to their ease in fabrication, low cost, and good electrical conductivity are used as catalyst support in DMFCs.

Li et al. [25] have used electrospinning to produce polyacrylonitrile (PAN) fibers which are thermally treated to convert to carbon fibrous mats. Then, a multi-cycle CV method is employed to deposit platinum clusters onto these mats. These platinum-loaded carbon fibrous mats are used in DMFC and shown to improve the catalytic peak current to 420 mA/mg. Thus, 1D carbon fibrous mats improve the performance of the catalyst.

1.5 Conclusions and Future Perspective

Development of novel materials with controlled structures and geometries is shown to be the candidate of choice for applications such as energy devices, sensors, filtration, and photocatalysis. One-dimensional structures in the form of fibers have immense significance in these applications. Of all the fabrication techniques,

electrospinning is attractive for fabrication of 1D fibers and provides the flexibility to control the compositions of the fibers. This technique can also be used to fabricate ceramic or metal oxide fibers from precursor polymers and affords an opportunity to fabricate binary and multi-component ceramic oxide fibers.

In this chapter, we review the various techniques based on electrospinning to fabricate ceramic or metal oxide nanofibers with various morphologies, structures, and geometries. Typically, the ceramic or metal oxide fibers obtained using electrospinning are polycrystalline. This is in contrast to the inorganic fibers fabricated using conventional techniques such as CVD where the material can be grown to consist of one single crystalline phase. The domain size in electrospinning can in some cases match the size of the fibers. This can provide additional functionality to the fibers as they demonstrate improved sensitivity. Hollow or porous fibers obtained using electrospinning have been widely used as electrodes in solar cells. It is also shown that the energy conversion efficiency of these fibers is significantly higher compared to other nanomaterials.

Similarly, ceramic and metal oxide fibers obtained using electrospinning are also shown to have better photocatalytic performance compared to other nanostructures produced using conventional techniques. It is illustrated that the geometry and morphology of obtained fibers can be tailored by controlling the processing variables. Thus, the performance of inorganic fibers can be easily altered based on the processing conditions. Modification of these one-dimensional inorganic fibers into hybrid or hierarchical fibrous structures can further improve its application in energy devices. The hybrid or hierarchical fibrous structures can improve light absorbance and carrier collection efficiency compared to neat ceramic or metal oxide fibers. Such fibers can be assembled and potentially important for future smart nanoscale electronic devices.

Although these inorganic fibers have many proven functional applications, their brittleness is one technical issue that must be resolved. Obtaining flexible ceramic or metal oxide fibers can improve their applications in filtration where the filters should possess high mechanical robustness. Recent studies have successfully fabricated hybrid inorganic fibers and demonstrated the membranes to be flexible. Other studies have shown that by adding polymer to ceramic or metal oxide particles as a binder, the resulting membrane can be dimensionally stable and flexible. This approach can be extended to electrospinning. Polymer-ceramic core–shell fibers can be fabricated by coaxial electrospinning, and these fibers can be used for photocatalytic applications.

Acknowledgements We would like to acknowledge the support of SUTD-MIT International Design Centre (Project No: IDG31400101). We also thank the financial support of SUTD start-up grant (Grant No. SRG-EPD-2013-055).

References

1. Liu SX, Hu LF, Xu XJ et al (2015) Nickel cobaltite nanostructures for photoelectric and catalytic applications. Small 11(34):4267–4283
2. Sharma J, Imae T (2009) Recent advances in fabrication of anisotropic metallic nanostructures. J Nanosci Nanotechnol 9(1):19–40
3. Ye XZ, Qi LM (2011) Two-dimensionally patterned nanostructures based on monolayer colloidal crystals: controllable fabrication, assembly, and applications. Nano Today 6(6):608–631
4. Cozzoli PD, Pellegrino T, Manna L (2006) Synthesis, properties and perspectives of hybrid nanocrystal structures. Chem Soc Rev 35(11):1195–1208
5. Law M, Goldberger J, Yang PD (2004) Semiconductor nanowires and nanotubes. Annu Rev Mater Res 34:83–122
6. Moriarty P (2001) Nanostructured materials. Rep Prog Phys 64(3):297–381
7. Wang ZY, Zhou L, Lou XW (2012) Metal oxide hollow nanostructures for lithium-ion batteries. Adv Mater 24(14):1903–1911
8. Barth S, Hernandez-Ramirez F, Holmes JD et al (2010) Synthesis and applications of one-dimensional semiconductors. Prog Mater Sci 55(6):563–627
9. Kim FS, Ren GQ, Jenekhe SA (2011) One-dimensional nanostructures of pi-conjugated molecular systems: assembly, properties, and applications from photovoltaics, sensors, and nanophotonics to nanoelectronics. Chem Mater 23(3):682–732
10. Kim Y, Shanmugam S (2013) Polyoxometalate-reduced graphene oxide hybrid catalyst: synthesis, structure, and electrochemical properties. ACS Appl Mater Interfaces 5(22):12197–12204
11. Dong ZX, Kennedy SJ, Wu YQ (2011) Electrospinning materials for energy-related applications and devices. J Power Sources 196(11):4886–4904
12. Kim ID, Jeon EK, Choi SH et al (2010) Electrospun SnO_2 nanofiber mats with thermo-compression step for gas sensing applications. J Electroceram 25(2–4):159–167
13. Baji A, Mai Y-W, Yimnirun R et al (2014) Electrospun barium titanate/cobalt ferrite composite fibers with improved magnetoelectric performance. RSC Adv 4(98):55217–55223
14. Baji A, Mai Y-W, Li Q et al (2011) Electrospinning induced ferroelectricity in poly (vinylidene fluoride) fibers. Nanoscale 3(8):3068–3071
15. Baji A, Mai Y-W, Wong SC et al (2010) Electrospinning of polymer nanofibers: effects on oriented morphology, structures and tensile properties. Compos Sci Technol 70(5):703–718
16. Kumar PS, Nizar SAS, Sundaramurthy J et al (2011) Tunable hierarchical TiO_2 nanostructures by controlled annealing of electrospun fibers: formation mechanism, morphology, crystallographic phase and photoelectrochemical performance analysis. J Mater Chem 21 (26):9784–9790
17. Lim SK, Hwang SH, Chang D et al (2010) Preparation of mesoporous In_2O_3 nanofibers by electrospinning and their application as a CO gas sensor. Sens Actuators, B 149(1):28–33
18. Wang Y, Huang HB, Gao JX et al (2014) TiO_2–SiO_2 composite fibers with tunable interconnected porous hierarchy fabricated by single-spinneret electrospinning toward enhanced photocatalytic activity. J Mater Chem A 2(31):12442–12448
19. Baji A, Zhou LM, Mai Y-W et al (2015) On the Adhesion performance of a single electrospun fiber. Appl Phys A-Mater 118(1):51–56
20. Li CR, Zhang XQ, Dong WJ et al (2012) High photocatalytic activity material based on high-porosity ZnO/CeO_2 nanofibers. Mater Lett 80:145–147
21. Baji A, Mai Y-W, Du XS et al (2012) Improved tensile strength and ferroelectric phase content of self-assembled polyvinylidene fluoride fiber yarns. Macromol Mater Eng 297 (3):209–213
22. Dai YQ, Lu XF, McKiernan M et al (2010) Hierarchical nanostructures of K-birnessite nanoplates on anatase nanofibers and their application for decoloration of dye solution. J Mater Chem 20(16):3157–3162

23. Lu BA, Li XD, Wang TH et al (2013) WO_3 nanoparticles decorated on both sidewalls of highly porous TiO_2 nanotubes to improve UV and visible-light photocatalysis. J Mater Chem A 1(12):3900–3906
24. Jo SM, Song MY, Ahn YR et al (2005) Nanofibril formation of electrospun TiO_2 fibers and its application to dye-sensitized solar cells. J Macromol Sci Pure 42(11):1529–1540
25. Li MY, Han GY, Yang BS (2008) Fabrication of the catalytic electrodes for methanol oxidation on electrospinning-derived carbon fibrous mats. Electrochem Commun 10(6):880–883
26. Agarwal S, Greiner A, Wendorff JH (2013) Functional materials by electrospinning of polymers. Prog Polym Sci 38(6):963–991
27. Baji A, Mai Y-W, Li Q et al (2011) Nanoscale investigation of ferroelectric properties in electrospun barium titanate/polyvinylidene fluoride composite fibers using piezoresponse force microscopy. Compos Sci Technol 71(11):1435–1440
28. Wang XH, Richey FW, Wujcik KH et al (2014) Ultra-low platinum loadings in polymer electrolyte membrane fuel cell electrodes fabricated via simultaneous electrospinning/electrospraying method. J Power Sources 264:42–48
29. Cavaliere S, Subianto S, Savych I et al (2011) Electrospinning: designed architectures for energy conversion and storage devices. Energy Environ Sci 4(12):4761–4785
30. Sahay R, Kumar PS, Sridhar R et al (2012) Electrospun composite nanofibers and their multifaceted applications. J Mater Chem 22(26):12953–12971
31. Thavasi V, Singh G, Ramakrishna S (2008) Electrospun nanofibers in energy and environmental applications. Energy Environ Sci 1(2):205–221
32. Larsen G, Velarde-Ortiz R, Minchow K et al (2003) A method for making inorganic and hybrid (organic/inorganic) fibers and vesicles with diameters in the submicrometer and micrometer range via sol-gel chemistry and electrically forced liquid jets. J Am Chem Soc 125(5):1154–1155
33. Li D, Xia YN (2003) Fabrication of titania nanofibers by electrospinning. Nano Lett 3 (4):555–560
34. Baji A, Mai YW, Li QA et al (2011) One-dimensional multiferroic bismuth ferrite fibers obtained by electrospinning techniques. Nanotechnology 22(23):235702
35. Lee JS, Kwon OS, Park SJ et al (2011) Fabrication of ultrafine metal-oxide-decorated carbon nanofibers for DMMP sensor application. ACS Nano 5(10):7992–8001
36. Ostermann R, Li D, Yin YD et al (2006) V_2O_5 nanorods on TiO_2 nanofibers: a new class of hierarchical nanostructures enabled by electrospinning and calcination. Nano Lett 6(6):1297–1302
37. Zhan SH, Chen DR, Jiao XL et al (2006) Long TiO_2 hollow fibers with mesoporous walls: sol–gel combined electrospun fabrication and photocatalytic properties. J Phys Chem B 110 (23):11199–11204
38. Aryal S, Kim CK, Kim KW et al (2008) Multi-walled carbon nanotubes/TiO_2 composite nanofiber by electrospinning. Mater Sci Eng, C 28(1):75–79
39. Kanjwal MA, Sheikh FA, Barakat NAM et al (2011) Co_3O_4–ZnO hierarchical nanostructures by electrospinning and hydrothermal methods. Appl Surf Sci 257(18):7975–7981
40. Isobe T, Kameshima Y, Nakajima A et al (2006) Extrusion method using nylon 66 fibers for the preparation of porous alumina ceramics with oriented pores. J Eur Ceram Soc 26 (12):2213–2217
41. Jang YS, Jank M, Maier V et al (2010) SiC ceramic micropatterns from polycarbosilanes. J Eur Ceram Soc 30(13):2773–2779
42. Lu XF, Wang C, Wei Y (2009) One-dimensional composite nanomaterials: synthesis by electrospinning and their applications. Small 5(21):2349–2370
43. Wen SP, Liu L, Zhang LF et al (2010) Hierarchical electrospun SiO_2 nanofibers containing SiO_2 nanoparticles with controllable surface-roughness and/or porosity. Mater Lett 64 (13):1517–1520
44. Danks AE, Hall SR, Schnepp Z (2016) The evolution of 'sol-gel' chemistry as a technique for materials synthesis. Mater Horiz 3(2):91–112

45. Anjusree GS, Bhupathi A, Balakrishnan A et al (2013) Fabricating fiber, rice and leaf-shaped TiO_2 by tuning the chemistry between TiO_2 and the polymer during electrospinning. RSC Adv 3(37):16720–16727
46. Chen HY, Zhang TL, Fan J et al (2013) Electrospun hierarchical TiO_2 nanorods with high porosity for efficient dye-sensitized solar cells. ACS Appl Mater Interfaces 5(18):9205–9211
47. Nuansing W, Ninmuang S, Jarernboon W et al (2006) Structural characterization and morphology of electrospun TiO_2 nanofibers. Mater Sci Eng, B 131(1–3):147–155
48. He ZY, Liu Q, Hou HL et al (2015) Tailored electrospinning of WO_3 nanobelts as efficient ultraviolet photodetectors with photo-dark current ratios up to 1000. ACS Appl Mater Interfaces 7(20):10878–10885
49. Leng JY, Xu XJ, Lv N et al (2011) Synthesis and gas-sensing characteristics of WO_3 nanofibers via electrospinning. J Colloid Interface Sci 356(1):54–57
50. Chen ZX, Zhang Z, Tsai CC et al (2015) Electrospun mullite fibers from the sol-gel precursor. J Sol–Gel Sci Technol 74(1):208–219
51. Guo AR, Liu JC, Dong X et al (2013) Preparation of porous silica ceramics from silica spinning solution and introduced silica particles by electrospinning. Mater Lett 95:74–77
52. Newsome TE, Olesik SV (2014) Electrospinning silica/polyvinylpyrrolidone composite nanofibers. J Appl Poly Sci 131(21)
53. Ding T, Tian Y, Liang K et al (2011) Anisotropic oxygen plasma etching of colloidal particles in electrospun fibers. Chem Commun 47(8):2429–2431
54. Zhang CL, Yu SH (2014) Nanoparticles meet electrospinning: recent advances and future prospects. Chem Soc Rev 43(13):4423–4448
55. Lu XF, Zhao YY, Wang C (2005) Fabrication of PbS nanoparticles in polymer-fiber matrices by electrospinning. Adv Mater 17(20):2485–2488
56. Bai J, Li YX, Yang ST et al (2007) Synthesis of AgCl/PAN composite nanofibres using an electrospinning method. Nanotechnology 18(30):305601
57. Bognitzki M, Becker M, Graeser M et al (2006) Preparation of sub-micrometer copper fibers via electrospinning. Adv Mater 18(18):2384–2386
58. Lu BA, Zhu CQ, Zhang ZX et al (2012) Preparation of highly porous TiO_2 nanotubes and their catalytic applications. J Mater Chem 22(4):1375–1379
59. Singh P, Mondal K, Sharma A (2013) Reusable electrospun mesoporous ZnO nanofiber mats for photocatalytic degradation of polycyclic aromatic hydrocarbon dyes in wastewater. J Colloid Interface Sci 394:208–215
60. Wang PP, Qi Q, Xuan RF et al (2013) A facile method for enhancing the sensing performance of zinc oxide nanofibers gas sensors. RSC Adv 3(43):19853–19856
61. Xia YJ, Song JL, Yuan DN et al (2015) Synthesis and characterization of one-dimensional metal oxides: TiO_2, CeO_2, Y_2O_3-stabilized ZrO_2 and $SrTiO_3$. Ceram Int 41(1):533–545
62. Liu BT, Peng LL (2013) Facile formation of mixed phase porous TiO_2 nanotubes and enhanced visible-light photocatalytic activity. J Alloy Compd 571:145–152
63. Choi SH, Ankonina G, Youn DY et al (2009) Hollow ZnO nanofibers fabricated using electrospun polymer templates and their electronic transport properties. ACS Nano 3 (9):2623–2631
64. Choi SJ, Chattopadhyay S, Kim JJ et al (2016) Coaxial electrospinning of WO_3 nanotubes functionalized with bio-inspired Pd catalysts and their superior hydrogen sensing performance. Nanoscale 8(17):9159–9166
65. Liu RL, Liu HQ, Liu JS et al (2012) Fabrication of patterned inorganic nanofibers by electrospinning. Prog Chem 24(8):1484–1496
66. Zhang J, Choi SW, Kim SS (2011) Micro- and nano-scale hollow TiO_2 fibers by coaxial electrospinning: preparation and gas sensing. J Solid State Chem 184(11):3008–3013
67. Zhang ZY, Li XH, Wang CH et al (2009) ZnO hollow nanofibers: fabrication from facile single capillary electrospinning and applications in gas sensors. J Phys Chem C 113 (45):19397–19403
68. Li D, Wang YL, Xia YN (2003) Electrospinning of polymeric and ceramic nanofibers as uniaxially aligned arrays. Nano Lett 3(8):1167–1171

69. Chang JY, Domnner M, Chang C et al (2012) Piezoelectric nanofibers for energy scavenging applications. Nano Energy 1(3):356–371
70. Baji A, Mai Y-W, Wong SC (2011) Effect of fiber diameter on the deformation behavior of self-assembled carbon nanotube reinforced electrospun polyamide 6,6 fibers. Mater Sci Eng, A 528(21):6565–6572
71. Wu H, Lin DD, Zhang R et al (2007) Oriented nanofibers by a newly modified electrospinning method. J Am Ceram Soc 90(2):632–634
72. Li XY, Chen YM, Zhou LM et al (2014) Exceptional electrochemical performance of porous TiO_2-carbon nanofibers for lithium ion battery anodes. J Mater Chem A 2(11):3875–3880
73. Li XY, Chen YM, Wang HT et al (2016) Inserting sn nanoparticles into the pores of TiO_2-x-c nanofibers by lithiation. Adv Funct Mater 26(3):376–383
74. Li XY, Chen YM, Huang HT et al (2016) Electrospun carbon-based nanostructured electrodes for advanced energy storage-A review. Energy Storage Mater 5:58–92
75. Zhu PN, Wu YZ, Reddy MV et al (2012) Long term cycling studies of electrospun TiO_2 nanostructures and their composites with MWCNTs for rechargeable Li-ion batteries. RSC Adv 2(2):531–537
76. Zhang YF, Li JY, Li Q et al (2007) Preparation of CeO_2–ZrO_2 ceramic fibers by electrospinning. J Colloid Interface Sci 307(2):567–571
77. Athauda TJ, Neff JG, Sutherlin L et al (2012) Systematic study of the structure-property relationships of branched hierarchical TiO_2/ZnO nanostructures. ACS Appl Mater Interfaces 4 (12):6916–6925
78. Zhang LS, Ding QW, Huang YP et al (2015) Flexible hybrid membranes with $Ni(OH)_2$ nanoplatelets vertically grown on electrospun carbon nanofibers for high-performance supercapacitors. ACS Appl Mater Interfaces 7(40):22669–22677
79. Mao X, Si Y, Chen YC et al (2012) Silica nanofibrous membranes with robust flexibility and thermal stability for high-efficiency fine particulate filtration. RSC Adv 2(32):12216–12223
80. Wang Y, Li W, Xia YG et al (2014) Electrospun flexible self-standing gamma-alumina fibrous membranes and their potential as high-efficiency fine particulate filtration media. J Mater Chem A 2(36):15124–15131
81. Yang LP, Raza A, Si Y et al (2012) Synthesis of superhydrophobic silica nanofibrous membranes with robust thermal stability and flexibility via in situ polymerization. Nanoscale 4(20):6581–6587
82. Yoon K, Hsiao BS, Chu B (2008) Functional nanofibers for environmental applications. J Mater Chem 18(44):5326–5334
83. Ding B, Wang MR, Wang XF et al (2010) Electrospun nanomaterials for ultrasensitive sensors. Mater Today 13(11):16–27
84. Hung CH, Leung WWF (2011) Filtration of nano-aerosol using nanofiber filter under low Peclet number and transitional flow regime. Sep Purif Technol 79(1):34–42
85. Wang XF, Ding B, Sun G et al (2013) Electro-spinning/netting: a strategy for the fabrication of three-dimensional polymer nano-fiber/nets. Prog Mater Sci 58(8):1173–1243
86. Landau O, Rothschild A, Zussman E (2009) Processing-microstructure-properties correlation of ultrasensitive gas sensors produced by electrospinning. Chem Mater 21(1):9–11
87. Kim ID, Rothschild A, Lee BH et al (2006) Ultrasensitive chemiresistors based on electrospun TiO_2 nanofibers. Nano Lett 6(9):2009–2013
88. Malwal D, Gopinath P (2016) Fabrication and applications of ceramic nanofibers in water remediation: a review. Crit Rev Env Sci Technol 46(5):500–534
89. Nair AS, Jose R, Shengyuan Y et al (2011) A simple recipe for an efficient TiO_2 nanofiber-based dye-sensitized solar cell. J Colloid Interface Sci 353(1):39–45