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Functional Applications of Electrospun Nanofibers

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1. Introduction

With the rapid development of nanoscience and nanotechnology over the last two decades, great progress has been made not only in preparation and characterization of nanomaterials, but also in their functional applications. As an important one-dimensional nanomaterial, nanofibers have extremely high specific surface area because of their small diameters, and nanofiber membranes are highly porous with excellent pore interconnectivity. These unique characteristics plus the functionalities from the polymers themselves impart nanofibers with many desirable properties for advanced applications.
Several methods have been developed to fabricate nanofibers, such as template (Ikegame et al., 2003), self-assembly (Hong et al., 2003), phase separation (Ma and Zhang, 1999), melt-blowing (Ellison et al., 2007) and electrospinning (Doshi and Reneker, 1995, Lin et al., 2004, Lin et al., 2005a, Fang et al., 2007, Xue et al., 2009, Fang et al., 2010). Electrospinning has been regarded as the most promising approach to produce continuous nanofibers on a large scale and the fiber diameter can be adjusted from nanometers to micrometers (Li and Xia, 2004b).

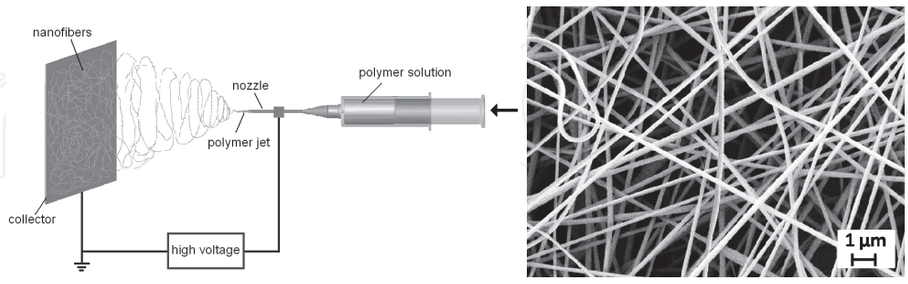

Fig. 1. Schematic for the single needle type electrospinning (Fang et al., 2008) and scanning electron microscopy (SEM) image of a nanofiber membrane.

Technically, electrospinning is a process that uses a strong electrical field to draw a polymer fluid into fine filaments. The basic electrospinning set-up, shown in Fig. 1, consists of a needle nozzle, a high voltage power supply, a container for spinning fluid and an electrode collector. When a viscous fluid is charged with a high voltage, the electrostatic force draws the fluid into a liquid jet. Because of the interaction between the jet and external electric field

and charge repulsion inside the jet, the charged jet undergoes a bending or whipping instability to stretch it thinner. Solvent evaporation from the filaments results in solid fibers (Fig. 1). In most cases, the as-spun fibers deposit randomly on the electrode collector forming a non-woven nanofiber mat. Aligned nanofibers can also be produced using controlled fiber deposition techniques (Theron et al., 2001, Li et al., 2004). Until now, a large number of polymeric and inorganic materials have been electrospun into nanofibers. The nanofibers can have many different morphologies, such as porous-surface nanofibers (Madhugiri et al., 2004, McCann et al., 2005), core-sheath (Sun et al., 2003, Li and Xia, 2004a) and side-by-side structures (Lin et al., 2005b). Electrospun nanofibers have attracted considerable attention because of their unique properties, eases of fabrication and functionalization, and versatility in controlling the fiber diameter and morphology. The extremely fine electrospun nanofibers make them very useful in a wide range of advanced applications.

Although several reviews on nanofibers have been published (Li and Xia, 2004b, Greiner and wendorff, 2007, Thavasi et al., 2008, Cui et al., 2010), new applications are found continuously. In this chapter, we expand on an earlier review on nanofiber applications (Fang et al., 2008) and summarize the recent research advances in the application of electrospun nanofibers. The state-of-the-art applications in functional areas, such as biomedical, energy harvest and storage, and environmental protection are presented in detail. An outlook on the possible future directions is also provided.

2. Biomedical

2.1 Tissue engineering scaffolds

Tissue engineering is an emerging interdisciplinary and multidisciplinary research field which involves the use of living cells, manipulated through their extracellular environment or genetically to develop biological substitutes for implantation into the body and/or to foster remodeling of tissues in some active manners. A basic principle of the tissue engineering is illustrated in Fig. 2. The purpose of tissue engineering is to repair, replace, maintain, or enhance the function of a particular tissue or organ.

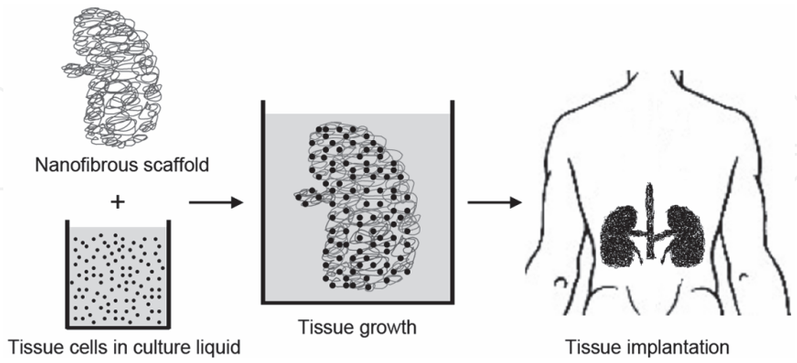

Fig. 2. Illustration of tissue engineering (Fang et al., 2008).

The core technologies intrinsic to this effort can be organized into three areas: cell technology, scaffold construct technology and technologies for *in vivo* integration. The scaffold construct technology focuses on designing, manufacturing and characterizing three-dimensional (3D) scaffolds for cell seeding and *in vitro* or *in vivo* culturing. For a functional

scaffold, a few basic requirements have to be met (Ma, 2004). First, a scaffold should possess a high degree of porosity, with an appropriate pore size distribution. Second, a large surface area is needed. Third, biodegradability is often required, with the degradation rate matching the rate of neo-tissue formation. Fourth, the scaffold must possess the required structural integrity to prevent the pores of the scaffold from collapsing during neo-tissue formation, with the appropriate mechanical properties. Finally the scaffold should be non-toxic to cells and biocompatible, positively interacting with the cells to promote cell adhesion, proliferation, migration, and differentiated cell function. Among all biomedical materials under evaluation, electrospun nanofibrous scaffolds have exhibited great performance in cell attachment, proliferation and penetration, through both *in vitro* and *in vivo* trials.

2.1.1 Blood vessels

Blood vessels vary in sizes, mechanical and biochemical properties, cellar content and ultra-structural organization, depending on their location and specific function. It is required that the vascular grafts engineered should have desired characteristics. Blood vessel replacement, particularly a fine blood vessel (diameter<6 mm), has remained a great challenge.

A comparison of cell growth on an electrospun poly(L-lactide-co-ε-caprolactone) (P(LLA-CL)) nanofibers and a smooth P(LLA-CL) cast film revealed that the function of vascular endothelial cells (ECs) on the P(LLA-CL) cast film, rather than on the electrospun nanofiber mat, was enhanced (Xu et al., 2004). But because the electrospun nanofiber mats can give good support during the initial growth of vascular smooth muscle cells (Mo et al., 2004), smooth film combining with electrospun nanofiber mat could form a good 3D scaffold for blood vessel tissue engineering.

The effect of fiber diameter on endothelial cells culturing was examined using electrospun cellulose acetate (CA) fibers with three different diameter ranges, 0.01-0.2, 0.2-1 and 2-5 μm (Rubenstein et al., 2007). It was interesting to note that the endothelial cells showed a growth preference toward larger fibers. Similar results were also found on poly(ε-caprolactone) (PCL) nanofibers with five different diameters (Balguid et al., 2009), cell penetration increased with the increased fiber diameter and unobstructed cell delivery was observed only on the largest fibers (12.1 μm in diameter).

To mimic the morphological and mechanical characteristics of a native blood vessel scaffold, bilayered electrospun nanofiber architectures were fabricated. A scaffold consisting of a stiff and oriented poly(lactic acid) (PLA) outer nanofiber layer and a pliable and randomly oriented PCL inner nanofiber layer was electrospun. Such a hierarchical scaffold was reported to be able to support the attachment, spread and growth of mouse fibroblasts and human myofibroblasts (Vaz et al., 2005). A composite scaffold incorporating a highly porous poly(ester-urethane)urea (PEUU) inner layer and an external electrospun nanofiber layer was prepared for small diameter vascular grafts (Fig. 3a) (Soletti et al., 2010). The mechanical properties of the bilayered scaffold were comparable with native vessels, and the combination of the two layers enabled better cell integration and growth. Because of the porosity difference in the two layers, high cellular density was found in the inner layer (Fig. 3b).

Surface modification on electrospun nanofibers with natural proteins, such as collagen or gelatin, was found to be an effective way to promote ECs spreading and proliferation. Examples can be found for collagen-grafted PCL (Ma et al., 2005a) and gelatin-grafted polyethylene terephthalate (PET) nanofibers (Ma et al., 2005b). The modified-nanofiber mats

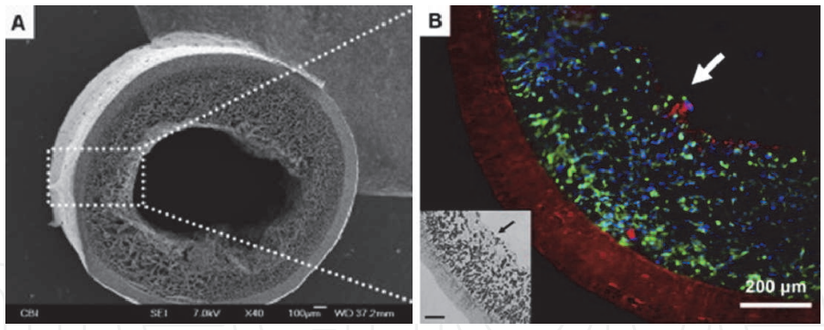

Fig. 3. The cross-sectional images of a double-layered small diameter PU vascular graft before (a) and after (b) cell culturing (Blue, nuclei; green, F-action; red, scaffold) (Soletti et al., 2010).

showed apparent enhancement in the spreading and proliferation of ECs compared with the non-grafted ones. Since a fibroblast growth factor (FGF-2) modulates cell growth, differentiation, migration and survival, the ability to bind FGF-2 to electrospun matrix was improved effectively by coating a bioactive recombinant fragment of perlecan on the surface of electrospun nanofibers (Casper et al., 2007).

To match the mechanical characteristic of natural blood vessel, which has a low-strain mechanical response to blood flow and prevents pulsatile energy from being dissipated as heat, elastin/polymer blend nanofibers were used (Sell et al., 2006). The preliminary cell culture studies showed that cells migrated through the full thickness of the elastin-containing grafts, but failed to migrate into the pure polymer nanofiber control scaffold. To mimic the ratio of collagen and elastin in native blood vessel, electrospun nanofibers of collagen/elastin/synthetic polymer (e.g. poly(lactic-co-glycolic acid) (PLGA), poly-L-lactic acid (PLLA), PCL) (45:15:40 w/w/w) blend were assessed (Lee et al., 2007). The as-spun nanofiber mat showed no cytotoxicity and was dimensionally stable, and its mechanical properties were similar to the native blood vessels.

In vivo assessments of cylindrical electrospun nanofiber constructs from collagen, gelatin, and synthetic biodegradable polymers such as poly(glycolic acid) (PGA), PLA and PGA/PLA copolymer were conducted (Telemeco et al., 2005). When implanted into the interstitial space of rat vastus lateralis muscle, collagen construct was rapidly and densely infiltrated by interstitial and endothelial cells, and functional blood vessels were evident within 7 days, while gelatin and synthetic nanofiber constructs were not infiltrated to any great extent and induced fibrosis.

2.1.2 Bones

Research on engineering bone tissues using electrospun nanofibers began with the work on muscles (Li et al., 2002). Cell growth on PLGA nanofibers indicated that nanofiber structure positively promoted cell-matrix and cell-cell interaction. For bone tissue engineering, nanofibers from PCL have been extensively studied (Yoshimoto et al., 2003, Ekaputra et al., 2009). It was observed that Mesenchymal stem cells (MSCs) penetrated into the PCL matrix accompanied with abundant extracellular matrix after 1 week of seeding, and mineralization and type I collagen occurred at 4 weeks. An *in vivo* experiment was also conducted by implanting a MSCs cultured PCL construct (4 weeks) in the omenta of rats (Shin et al., 2004). After 4 weeks, the constructs maintained the size and shape of the original scaffolds and had a bone-like appearance.

In addition to the pure PCL nanofibers, nanofibers from gelatin/PCL blend (Zhang et al., 2005a) and PCL composite with calcium carbonate nanoparticles and hydroxyapatite (HAp) nanoparticles (Fujihara et al., 2005) for bone scaffolds have been investigated. The addition of 50% gelatin to PCL improved both the fiber mechanical strength and surface wettability, therefore enhancing the cell attachment and growth on the scaffold (Duan et al., 2007). Also, the cells were observed to migrate up to 114 μm inside the scaffold within one week of culture. In contrast, PCL nanofibers containing these inorganic nanoparticles were found with higher osteoblast proliferation and differentiation.

A combination of PCL nanofibers and microfibers was used to develop multilayer scaffolds (Tuzlakoglu et al., 2005, Pham et al., 2006). This multilayer fiber mat contained a thin nanofiber upper layer and an inner microfiber fibrous structure. As the top nanofiber layer assisted cell attachment and spread and the inner microfiber layer provided large pores for cell migration, both cell attachment and migration were improved. Fiber diameter has shown obvious effect on cell culture. Gelatin nanofibers were electrospun with different fiber diameters of 110 and 600 nm for osteoblastic MG63 cell growth. The cells were found to have a similar attachment feature at the first 3 days and with the extended culture time they preferred the coarser fibers. In longer term experiments, the cells differentiated to a greater extent on the scaffolds made from the smaller diameter fibers (Sisson et al., 2010).

Bioactive glass (BG) has also been widely studied for bone regeneration. PCL/BG composite nanofibers considerably improved the differentiation of osteoblast cells as compared to pure PCL nanofibers (Kim et al., 2008a), and a short BG nanofiber/PCL matrix composite scaffold has shown greater mechanical stability and bioactivity than BG power/PCL composite (Jo et al., 2009).

Mechanical stimulation has been applied during bone regeneration, and the results showed that proper stimulation can enhance fracture healing due to the anabolic osteogenic effects (Rath et al., 2008). Mechanical stresses induced by embedded magnetic nanoparticles were applied onto PCL scaffolds to stimulate growth, proliferation and differentiation of preosteoblast MC3T3 cells (Kannarkat et al., 2010). *In vivo* studies (Ko et al., 2008, Schneider et al., 2009b) have also suggested the great potential of electrospun nanofiber scaffold in skeletal tissue engineering because of adequate mechanical properties and osteocondition.

2.1.3 Muscles

Collagen nanofibers were first used to assess the feasibility of culturing smooth muscle cell (Matthews et al., 2002). The cell growth on the collagen nanofibers was promoted and the cells were well integrated into the nanofiber network after 7 days of seeding. Smooth muscle cells also adhered and proliferated well on other polymer nanofiber mats blended with collagen (Stankus et al., 2004, Chen et al., 2010b), the incorporation of collagen into nanofibers was observed to improve fiber elasticity and tensile strength, and increase the cell adhesion.

The fiber surface wettability influences cell attachment. It was reported that when the PS nanofibers were treated with Argon plasma, the fiber wettability was increased significantly. As a result, cell attachment was increased by two folds (Baker et al., 2006). The alignment of nanofibers can induce cell orientation and promote skeletal muscle cell morphologenesis and aligned myotube formation. The cells cultured on the aligned

nanofibers exhibited an alignment factor of 0.74, compared with 0.19 on the randomly orientated scaffold (Baker et al., 2006).
Degradation of smooth muscle cell cultured PGA, PLGA and P(LLA-CL) nanofibers were investigated (Dong et al., 2010b). It has been found that cell culture accelerated the nanofiber scaffold degradation, especially for PGA. P(LLA-CL) nanofibers facilitate long-term (1-3 months) cell growth because of the slowest degradation rate.

2.1.4 Skins

As the largest body tissue, skin functions to prevent outside intrusion and regulate water retention and heat loss. Nanofiber mats from many different types of polymers have been evaluated for their cytocompatibility to fibroblast and/or keratinocytes. In most cases, the electrospun nanofiber mats exhibited good capability of supporting cell attachment and proliferation. Cells seeded on the nanofiber structure tended to maintain phenotypic shape and were guided to grow according to the nanofiber orientation.
Collagen-PCL core-sheath nanofibers were prepared by both one-step coaxial electrospinning and two-step spinning and solution coating process (Zhang et al., 2005b, Zhao et al., 2007). The presence of collagen surface shell on PCL nanofibers was found to support cell proliferation and encourage cell migration inside the scaffold. The collagen coating formed directly from the coaxial-electrospinning had higher cell proliferation efficiency than that from the solution coating method.
Nanofibers of polymer blends were also studied, and showed good cell attachment and proliferation. It was indicated that a small fraction of low molecular weight polyethylene glycol (PEG) in PLLA nanofibers increased the hydrophilicity. As a result, biological reactivity of fibroblast cells was improved (Bhattarai et al., 2006). The fiber wettability could also be improved by co-electrospinning of two different nanofibers (PLGA and chitosan/polyvinyl alcohol (PVA)) into the same fibrous matrix (Duan et al., 2006). The presence of hydrophilic nanofibers (chitosan/PVA) increased the absorption of nutrient fluid during cell culture and thus promoted fibroblast attachment, proliferation, migration and infiltration in the fiber matrix.
The effect of nanofiber alignment on cell adhesion and proliferation was studied (Zhong et al., 2006). When a rabbit conjunctive fibroblast was seeded on an aligned collagen nanofiber mat, lower cell adhesion but higher cell proliferation was observed on the aligned nanofibers, compared with that on the randomly orientated nanofiber mat. It has also been observed that the infiltration of epidermal skin cells was enhanced when aligned PLLA nanofibers were used (Kurpinski et al., 2010).
Cell culture on a 3D nanofiber mat containing large pores, was also studied. A 3D silk fibroin nanofiber matrix was prepared by directly depositing the newly-electrospun silk fibroin nanofibers in a methanol solution (Ki et al., 2007b). This 3D nanofiber matrix supported the cell proliferation inside the fiber matrix quite well. A 3D nanofiber mat was also prepared by adding a chemical blowing agent (BA) into nanofibers via electrospinning, and a post-electrospinning heat-treatment, leading to large pores within the nanofiber mat (Kim and Kim, 2007). These large pores could provide good access to the cells to penetrate inside the nanofiber mat. The relationship between inter-fiber distance and skin tissue regeneration has been investigated on electrospun gelatin scaffolds (Powell and Boyce, 2008). Cell infiltration was found only into the upper regions of the scaffold if the inter-fiber distance was smaller than 5.5 μm, and the distances between 5 to 10 μm have yielded most favorable skin substitute.

2.1.5 Neural tissues

Electrospun nanofibers represent effective guidance substrates for nervous tissue repair. *In vitro* cell culture study of neural stem cells (NSCs) on a PLLA nanofiber scaffold revealed that the nanofiber scaffold not only supported the NSC differentiation and neurite outgrowth, but also promoted NSC adhesion (Yang et al., 2004). Further work using aligned PLLA nanofiber or microfiber scaffolds showed that the directions of NSC elongation and its neurite outgrowth were parallel to the direction of fiber alignment (Yang et al., 2005). The aligned fibers in the scaffold can provide topographical guidance and enhance cell proliferation and neurite outgrowth (Mukhatyar et al., 2011), which has the potential for bridging long peripheral never gaps.

So far, the effects of fiber diameter on cell culturing are still unclear. PLLA nanofibers had higher neural stem cell differentiation than microfibers, but with similar cell orientation (Yang et al., 2005). Among three kinds of PES nanofibers with the diameters of 283, 749 and 1452 nm, cell proliferation and cell spreading increased with the decrease in fiber diameter (Christopherson et al., 2008). In another research on three kinds of PLLA electrospun fibers with different diameters, the neurite length was the shortest on the finest fibers (Wang et al., 2010).

Electrical stimulation has been incorporated during cell growth to improve cell function by preparing conductive nanofibrous scaffolds (Lee et al., 2009b). Polypyrrole (PPy) was grown on random and aligned PLGA nanofibers, and the electrically stimulated nanofibers resulted 40-50% longer neuritis and 40-90% more neurite formation compared to the one without any stimulation.

The feasibility of *in vivo* nerve regeneration using PLGA nanofibers was also investigated (Bini et al., 2004). After implantation of PLGA nanofiber guidance to the right sciatic nerve of rats, no inflammatory response was observed, and 5 out of 11 rats showed successful nerve regeneration one month after implantation. The *in vitro* test also confirmed that nerve stem cells adhered to, and differentiated on, the PLGA nanofiber mats (Bini et al., 2006).

2.1.6 Other tissue scaffolds

In addition to the above mentioned scaffolds, the studies of using nanofibers as scaffold to support other stem cells (Ito et al., 2005), and tissues, such as heart (Zong et al., 2005), cartilage (Matthews et al., 2003), ligament (Lee et al., 2005) and urinary tract (McManus et al., 2007) have been reported.

2.2 Wound healing

Wound healing is a native process of regenerating dermal and epidermal tissues. When an individual is wounded, a set of complex biochemical actions take place in a closely orchestrated cascade to repair the damage. These events can be classified into inflammatory, proliferative, and remodeling phases and epithelialization. Normally, body cannot heal a deep dermal injury. In full thickness burns or deep ulcers, there is no source of cells remaining for regeneration, except from the wound edges. As a result, complete re-epithelialization takes a long time and is complicated with scarring of the base (Marler et al., 1998).

Dressings for wound healing function to protect the wound, exude extra body fluids from the wound area, decontaminate the exogenous microorganism, improve the appearance and sometimes accelerate the healing process. For these functions, a wound dressing material should provide a physical barrier to a wound, but be permeable to moisture and

oxygen. Electrospun nanofiber mat is a good wound dressing candidate because of its unique properties: the highly porous mat structure and well interconnected pores are particularly important for exuding fluid from the wound; the small pores and very high specific surface area not only inhibit the exogenous microorganism invasions, but also assist the control of fluid drainage; in addition, the electrospinning process provides a simple way to add drugs into the nanofibers for any possible medical treatment and antibacterial purposes.

A study on using electrospun polyurethane (PU) mat as wound dressing material revealed that the mat effectively exuded fluid from the wound, without fluid accumulation under the mat, and no wound desiccation occurred neither (Khil et al., 2003). The mat also showed a controlled water loss from evaporation, excellent oxygen permeability, and high fluid drainage ability, besides inhibiting the invasion of exogenous micro organism. Histological test indicated that the rate of epithelialization was increased and the dermis became well organized when the wounds were covered with the electrospun nanofiber mat. Silk nanofiber mats were electrospun with epidermal growth factor to promote wound healing process (Schneider et al., 2009a), and it has been found the functionalized mat increased the wound closure by 90%. An anti-cancer, anti-oxidant and anti-flammatory substance, curcumin, was loaded into PCL (Merrell et al., 2009) and CA (Suwantong et al., 2010) nanofibers for wound dressing. These dressings were superior in supporting human dermal fibroblast attachment and proliferation and exhibited high rate of wound closure.

An open wound healing test using an electrospun collagen nanofiber mat showed that the early-stage healing using collagen nanofiber mat was faster than that of using normal cotton gauze (Rho et al., 2006). In the first week, the wound surface in the cotton group was covered by fibrous tissue debris, below which dense infiltration of polymorphonuclear leukocytes and the proliferation of fibroblasts were formed. By comparison, the surface tissue debris in the collagen nanofiber group disappeared, and prominent proliferation of young capillaries and fibroblasts was found. Later stage healing processes were similar for both groups. PLGA/collagen nanofiber mats also showed an effective wound healing behavior with an active response to human fibroblasts in the early stage (Liu et al., 2010a).

In vivo wound healing of diabetic ulcers was investigated using electrospun block copolymer (PCL-PEG) and PCL. When the nanofibers were chemically modified with a recombinant human epidermal growth factor (rhEGF), the expression of keratinocyte-specific genes and EGF-receptor were enhanced (Choi et al., 2008). Systematic *in vivo* wound healing evaluations have been carried on PVA, PCL, polyacrylonitrile (PAN), poly(vinylidene fluoride-co-hexafluoropropene) (PVdF-HFP), PAN/PEU blend, and wool protein coated PVA and PCL nanofibers (Liu et al., 2008, Liu et al., 2010b). The results showed that wound healing performance was mainly influenced by the porosity, air permeability and surface wettability of the nanofiber mats. A mat with good hydrophilicity and high porosity facilitated the healing at the early stage. However, the fiber diameter and antibacterial activity had a limited effect on the healing efficiency.

Post-surgery tissue adhesion is a widely recognized problem for abdominal surgeries. It not only renders future operations more difficult but also causes other problems such as small bowel obstruction, female infertility, and chronic debilitating pain. An electrospun nanofiber mat containing antibiotic agents has been used as a barrier to prevent the post-surgery abdominal adhesions. It was found that the nanofiber mat eliminated post-surgery abdominal adhesion significantly, thus improving the healing process (Bolgen et al., 2007).

To decontaminate the bacteria invasion, biocides, such as silver (Hong, 2007, Chen and Chiang, 2010) and iodine complex (Ignatova et al., 2007) have been added to the electrospun nanofibers. It was reported that polyvinylpyrrolidone (PVP)-iodine complex (PVP-iodine) gradually released active iodine. Because of the broad-spectrum microbicidal activity of iodine, electrospun PVP-iodine nanofibers had external antibacterial, antimycotic and antiviral applications. Ag ions were incorporated into electrospun nanofibers via adding $AgNO_3$ into the polymer solution for electrospinning. To maintain a long term antibacterial activity and control the release of Ag ions, the Ag was embedded in the form of elementary state by a post-electrospinning treatment. Ag nanoparticles can also be directly incorporated into electrospun nanofibers via the electrospinning process. An Ag/PVA nanofiber mat exhibited excellent antimicrobial ability and good stability in moisture environment, as well as a quick and continuous release with good effectiveness (Hong, 2007).

Besides adding antibacterial additives, antimicrobial nanofibers can also be prepared by directly using antimicrobial polymers. For instance, polyurethanes containing quaternary ammonium groups were electrospun into nanofiber nonwovens, and the nanofibers showed very strong antimicrobial activities against Staphylococcus aureus and Escherichia coli (Kenawy et al., 2002).

2.3 Drug delivery and release control

Controlled release is an efficient process of delivering drugs in medical therapy. It can balance the delivery kinetics, immunize the toxicity and side effects, and improve patient convenience (Yih and Al-Fandi, 2006). In a controlled release system, the active substance is loaded into a carrier or device first, and then released at a predictable rate *in vivo* when administered by an injected or non-injected route.

As a potential drug delivery carrier, electrospun nanofibers have exhibited many advantages. The drug loading is very easy to implement via electrospinning process, and the high applied voltage used in electrospinning process had little influence on the drug activity. The high specific surface area and short diffusion passage length give the nanofiber drug system higher overall release rate than the bulk material (e.g. film). The release profile can be finely controlled by modulation of nanofiber morphology, porosity and composition.

Nanofibers for drug release systems mainly come from biodegradable polymers and hydrophilic polymers. Model drugs that have been studied include water soluble (Kenawy et al., 2002), poor-water soluble (Verreck et al., 2003a) and water insoluble drugs (Zeng et al., 2003). The release of macromolecules, such as DNA (Luu et al., 2003) and bioactive proteins (Zeng et al., 2005), from nanofibers was also investigated.

In most cases, water soluble drugs, including DNA and proteins, exhibited an early-stage burst (Zong et al., 2002). For some applications, preventing post-surgery induced adhesion for instance, and such an early burst release will be an ideal profile because most infections occur within the first few hours after surgery. A recent study also found that when a poorly water soluble drug was loaded into PVP nanofibers (Yu et al., 2009a), 84.9% of the drug can be released in the first 20 seconds when the drug-to-PVP ratio was kept as 1:4, which can be used for fast drug delivery systems. However, for a long-lasting release process, it would be essential to maintain the release at an even and stable pace, and any early burst release should be avoided. For a water insoluble drug, the drug release from hydrophobic nanofibers into buffer solution is difficult. However, when an enzyme capable of degrading nanofibers exists in the buffer solution, the drug can be released at a constant rate because of

the degradation of nanofibers (Zeng et al., 2003). For example, when rifampin was encapsulated in PLA nanofibers, no drug release was detected from the nanofibers. However, when the buffer solution contained proteinase K, the drug release took place nearly in zero-order kinetics, and no early burst release happened. Similarly, initial burst release did not occur for poor-water soluble drugs, but the release from a non-biodegradable nanofiber could follow different kinetics (Verreck et al., 2003b). In another example, blending a hydrophilic but water-insoluble polymer (PEG-g-CHN) with PLGA could assist in the release of a poor-water soluble drug Iburprofen (Jiang et al., 2004). However, when a water soluble polymer was used, the poorly soluble drug was released accompanied with dissolving of the nanofibers, leading to a low burst release (Yang et al., 2007).

The early burst release can be reduced when the drug is encapsulated within the nanofiber matrix. When an amphiphilic block copolymer, PEG-b-PLA was added into Mefoxin/PLGA nanofibers, the cumulative amount of the released drug at earlier time points was reduced and the drug release was prolonged (Kim et al., 2004c). The reason for the reduced burst release was attributed to the encapsulation of some drug molecules within the hydrophilic block of the PEG-b-PLA. Amphiphilic block copolymer also assisted the dispersion and encapsulation of water-soluble drug into nanofibers when the polymer solution used an oleophilic solvent, such as chloroform, during electrospinning (Xu et al., 2005). In this case, a water-in-oil emulation can be electrospun into uniform nanofibers, and drug molecules are trapped by hydrophilic chains. The swelling of the hydrophilic chains during releasing assists the diffusion of drug from nanofibers to the buffer.

Coating nanofibers with a shell could be an effective way to control the release profile. When a thin layer of hydrophobic polymer, such as poly (p-xylylene) (PPX), was coated on PVA nanofibers loaded with bovine serum albumin (BSA)/luciferase, the early burst release of the enzyme was prevented (Zeng et al., 2005). Fluorination treatment (Im et al., 2010b) on PVA nanofibers introduced functional C-F groups and made the fiber surface hydrophobic, which dramatically decreased the initial drug burst and prolonged the total release time.

The polymer shell can also be directly applied via a coaxial co-electrospinning process, and the nanofibers produced are normally named "core-sheath" bicomponent nanofibers. In this case, even a pure drug can be entrapped into nanofiber as the core, and the release profile was less dependent on the solubility of drug released (Jiang et al., 2005, Huang et al., 2009). A research has compared the release behavior of two drug-loaded PLLA nanofibers prepared using blend and coaxial electrospinning (He et al., 2009). It was found that the blend fibers still showed an early burst release, while the threads made of core-sheath fibers provided a stable release of growth factor and other therapeutic drugs. In addition, the early burst release can also be lowered via encapsulating drugs into nanomaterial, followed by incorporating the drug-loaded nanomaterials into nanofibers. For example, halloysite nanotubes loaded with tetracycline hydrochloride were incorporated into PLGA nanofibers and showed greatly reduced initial burst release (Qi et al., 2010).

3. Environmental protection

Current environmental problems are caused by human activities in the last 150 years. They are having serious negative impacts on us and this is likely to continue for a very long time. Effective solutions are urgently needed to protect our environment. Due to their high specific surface area, electrospun nanofibers are expected to be used to collect pollutants via physical blocking or chemical adsorption.

3.1 Filtration

Filtration has been widely used in both households and industries for removing solid substances from air or liquid. In military, they are used in uniform garments and isolating bags, to decontaminate aerosol dusts, bacteria and even virus. Respirator is another example that requires efficient filtration ability. Similar function is also needed for some fabrics used in the medical area. For a fiber-based filter, the removal of particles is determined by different mechanisms. Large particles are blocked on the filter surface due to the sieve effect. Particles that are smaller than the surface-pores could still be collected by the fibers, through a mechanism such as interception, impaction, or static electrical attraction. Very fine particles could also be captured by the Brownian motion effect. The filtration efficiency is normally influenced by the filter physical structure (fiber fineness, matrix structure, thickness, pore size), fiber surface electronic properties, and its surface chemical characteristic (e.g. surface free energy). The particle collecting capability is also related to the size range of particles being collected. Besides the filtration efficiency, other properties such as pressure drop and flux resistance are also important factors to be evaluated for a filter media.

Electrospun nanofibers for filtration application have a long history. A company in US (Donaldson) has produced electrospun nanofiber-based filter products for industry, consumer and defense applications for more than 20 years, and its Ultra-web® nanofiber filter has been developed for nonwoven and filtration industry for a wide range of applications. Recently another company (AMSOIL) has also developed a nanofiber-based fuel filter for automobile applications. DuPont has electrospun fabric products for HVAC, automotive and liquid filtration, bedding protection and apparel applications.

Electrospun nanofiber mat provides dramatic increases in filtration efficiency at relatively small decreases in permeability. In comparison with conventional filter fibers at the same pressure drop, nanofibers with a diameter finer than half a micron have a much higher capability to collect the fine particles, because the slip flow around the nanofibers increases the diffusion, interception and inertial impaction efficiencies (Kosmider and Scott, 2002).

Both experimental measurements and theoretical calculations revealed that electrospun nanofiber mats were extremely efficient at trapping airborne particles (0.5~200 μm) (Gibson et al., 2001). A comparison study between a nylon-6 electrospun mat (thickness 100 μm, pore size 0.24 μm) and a commercial high efficiency particulate air (HEPA) filter (thickness 500 μm, pore size 1.7 μm) using 300 nm test particles indicated that the thin nanofiber mat had a slightly higher filtration efficiency (99.993%) than the HEPA filter (99.97%) (Barhate and Ramakrishna, 2007).

Besides solid particles, tiny liquid droplets within a liquid-liquid immiscible system could also be removed by a nanofiber mat (liquid-liquid coalescence filtration). PS nanofibers were electrospun from a recycled expanded-polystyrene (EPS), and mixed with micro glass fibers to form a filter media for removal of water droplets from a water-in-oil emulsion (Shin et al., 2005). The addition of small amount of PS nanofibers was reported to significantly improve the capture efficiency (from 68% to 88%), but the pressure drop of the filters was increased considerably.

Nanofibers were used as a supporting scaffold in ultrafiltration (UF) for oil/water emulsion separation. The reported UF mat has a three-layered composite structure consisting of a nonporous hydrophilic top layer, a crosslinked PVA electrospun nanofibrous mid-layer and a conventional nonwoven microfibrous substrate (Yoon et al., 2006, Tang et al., 2009). The electrospun nanofibrous substrate provided a well interconnected porous network with a

large specific surface area. The UF filter has a high flux rate and excellent organic solute rejection capability.

Long term filtration performance can be extended by using chemical (Qin and Wang, 2008) or physical (Homaeigohar et al., 2010) crosslinking treatments to stabilize the porous structure of nanofibrous mat. It was recently reported that filters made of multiple thin nanofiber layers had a much better filtration performance than single thick layer nanofiber mat in terms of the pressure drop during filtration (Zhang et al., 2010b).

3.2 Metal ion adsorption and recovery

The elevated level of metal ions has become a serious pollution in water resources, and gives a long term risk to human health and natural environment. These positively charged ions can be removed by many different methods, and among them adsorption through chemical and physical affinity is the most effective and economic one. In this case, electrospun nanofibers have great potential in collecting metal ions from a solution because of their high specific surface area, high porosity and controllable surface functionality.

Polymers with functional groups which have affinity to metal ions were directly electrospun into nanofibers for metal ion adsorption. Electrospun wool keratin/silk fibroin blend nanofibers were initially used to chelate absorb Cu(II) ions from water (Ki et al., 2007a). Wool protein has large number of hydrophilic amino acids with high affinity to metal ions, and the blend nanofibers showed a Cu(II) adsorption capability of 2.8 μg/mg with high recycling efficiency.

Two approaches have been used to improve the adsorption of metal ions on electrospun nanofibers: introducing functional materials to fiber surface using surface chemistry or coating techniques and increasing surface area to improve adsorption capability. For example, amidino diethylenediamine chelating groups was incorporated into PAN nanofiber using heterogeneous reaction with diethylenetriamine (Kampalanonwat and Supaphol, 2010), and the modified fibers had a pH dependent adsorption capacities of 150.6, 155.5, 116.5 and 60.6 mg/g for Cu(II), Ag(I), Fe(II) and Pb(II), respectively. The Cu(II) and Pb(II) adsorption capacities of amidoxime-modified PAN nanofibers were 52.70 and 263.45 mg/g (Saeed et al., 2008). Boehmite nanoparticles were incorporated into polycaprolactone and nylon-6 nanofibers for Cd(II) collection (Hota et al., 2008). In a latest research (Wu et al., 2010b), PVA/SiO_2 composite nanofibers were prepared and functionalized by mercapto groups. The specific surface area of the nanofibers was higher than 290 m^2/g and the nanofibers exhibited the highest Cu(II) adsorption capacity of 489.12 mg/g.

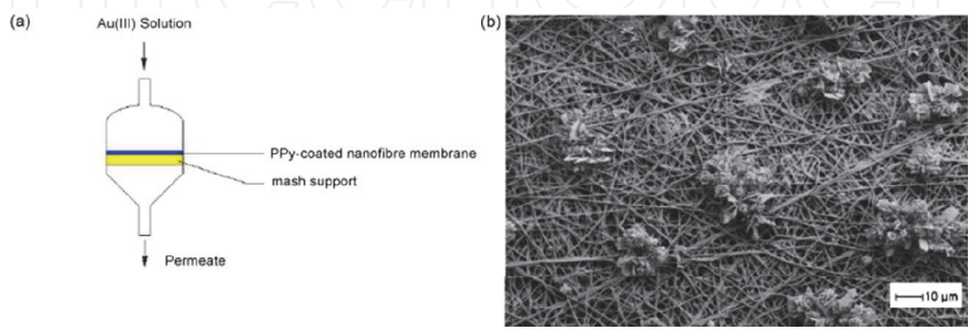

Fig. 4. (a) Apparatus for mat-based Au recovering, (b) SEM image of the PPy-coated nanofibers with aqueous $[Au(III)Cl_4]^-$ solution permeated (Wang et al., 2007).

Apart from the adsorption mechanism, directly converting metal ions into metal element on nanofibers was used for recovering precious metals. Wang et al (Wang et al., 2007) reported a simple and interesting method to grow polypyrrole on nanofiber surface using vapor-phase polymerization. A thin layer of PPy coating on the nanofibers had very little effect on the permeability of the nanofiber membrane, but showed a high efficiency to recover gold ions. The gold ions were converted into micron-sized gold particles (Fig. 4).

4. Catalyst and enzyme carriers

A carrier for catalyst in chemistry and biology is used to preserve high catalysis activity, increase the stability, and simplify the reaction process. An inert porous material with a large surface area and high permeability to reactants could be a promising candidate for efficient catalyst carriers. Using an electrospun nanofiber mat as catalyst carrier, the extremely large surface could provide a huge number of active sites, thus enhancing the catalytic capability. The well-interconnected small pores in the nanofiber mat warrant effective interactions between the reactant and catalyst, which is valuable for continuous-flow chemical reactions or biological processes. The catalyst can also be grafted onto the electrospun nanofiber surface via coating or surface modification.

4.1 Catalysts

Palladium (Pd)-loaded poly(acrylonitrile-acrylic acid) (PAN-AA) nanofibers were prepared by electrospinning a $PdCl_2$-containing PAN-AA solution into nanofibers and subsequently reducing the $PdCl_2$ embedded into Pd nanoparticles. The static catalytic activity of the Pd-loaded nanofibers for selective hydrogenation of dehydrolinalol was measured, to be about 4.5 times higher than that of Pd/Al_2O_3 catalyst (Demir et al., 2004). In a similar work, Pd-loaded PAN-AA nanofibers were confirmed to have high activity and good recycling property for hydrogenation of a-olefin at room temperature. The yield of the hexene to hexane catalyzed by the Pd/PAN-AA nanofibers was 4.7 times higher than that of Pd/γ-Al_2O_3 (Yu and Liu, 2007).

When a molecular catalyst was incorporated into nanofibers, the catalyst could leak out of the nanofibers during the catalysis reaction (Stasiak et al., 2007). Surface coating such as catalyst-loaded nanofiber with a thin layer of polymer considerably retained the catalyst in the nanofibers and the catalyst efficiency was improved at the same time. The catalysis performance was influenced by the type of shell polymer and coating thickness.

TiO_2 is a widely used catalytic material in commercial market. Electrospun PVA-platinum (Pt)/TiO_2 nanofibers were prepared for photocatalytic degradation of solid-state PVA (He and Gong, 2003). Compared with TiO_2 nanoparticles, electrospun TiO_2 nanofibers showed higher photocatalytic activities in terms of photocurrent generation by a factor of 3 because of the mesoporosity and nanoparticle alignment, which caused efficient charge separation through interparticle charge transfer along the nanofiber framework (Choi et al., 2010c). Fiber diameter was reported to play an important role in determining the photocatalytic activity of TiO_2 nanofibers, and the diameter of 200 nm was found to be optimal in photocatalytic performance (Li et al., 2010).

Doping has been used to further increase the photocatalytic activity of TiO_2 nanofibers. Materials such as Pt (Formo et al., 2009), gold (Pan and Dong, 2009), SnO_2 (Wang et al., 2009a) and vanadium (Zhang et al., 2010c) have been used to dope TiO_2 nanofibers for heterostructure using different approaches and enhanced photocatalytic behavior was

achieved. SnO_2 with different morphologies and densities was formed on TiO_2 nanorods (Fig. 5a-d). These SnO_2/TiO_2 heterostructures were demonstrated to have high photocatalytic degradation efficiency and the photocatalytic performance was dependent on the SnO_2 morphology (Fig. 5e).

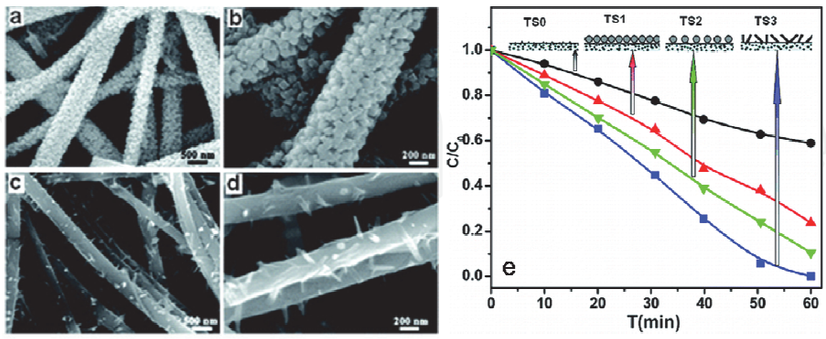

Fig. 5. SEM images of different SnO_2 morphologies on TiO_2 nanofibers (a-d) and the SnO_2 morphology dependent photocatalytic degradation behavior of Rhodamin B (e) (Wang et al., 2009a).

Apart from TiO_2 nanofibers, other inorganic nanofibers (such as ZnO (Lin et al., 2009) and $LaCoO_3$ (Dong et al., 2010a)) have also been investigated as catalysts. For example, ZnO based hierarchical nanofibers has been prepared by growing radically oriented ZnO nanowires on electrospun PLLA nanofibers to make flexible catalyst for continuous-flow photocatalytic water purification (Sugunan et al., 2010).

4.2 Enzymes

Chemical reactions using enzymes as catalysts have high selectivity and require mild reaction conditions. For easy separation from the reaction solution, enzymes are normally immobilized with a carrier. The immobilization efficiency mainly depends on the porous structure and enzyme-matrix interaction. To immobilize enzyme on electrospun nanofibers, many approaches have been used, including grafting enzyme on fiber surface, physical adsorption, and incorporating enzyme into nanofiber via electrospinning followed by crosslinking reaction.

To graft enzymes on nanofiber surface, the polymer used should possess reactive groups for chemical bonding (Wang and Hsieh, 2004, Wang et al., 2006b, Stoilova et al., 2010a). In some studies, polymer blends containing at least one reactive polymer were used (Jia et al., 2002, Kim et al., 2005a, Kim and Park, 2006). The immobilized enzymes normally showed a slightly reduced activity in aqueous environment compared with the un-immobilized native counterpart, but the activity in non-aqueous solution was much higher. For example, α-chymotrypsin was used as a model enzyme to bond chemically on the surface of electrospun PS nanofibers. The enzyme was measured to cover over 27.4% monolayer of the nanofiber surface, and the apparent hydrolytic activity of the enzyme-loaded was 65% of the native enzyme, while the activity in non-aqueous solution was over 3 orders of magnitude higher than that of its native enzyme under the same condition. In another study using PAN nanofibers to immobilize lipase, the tensile strength of the nanofiber mat was improved after lipase immobilization, and the immobilized lipase retained >90% of its initial reactivity after being stored in buffer at 30 °C for 20 days, whereas the free lipase lost 80% of its initial

reactivity. Also the immobilized lipase still retained 70% of its specific activity after 10 repeated reaction cycles (Li et al., 2007). In addition, the immobilized enzyme also showed improved pH and thermal stabilities (Huang et al., 2007). Ethylenediamine was used to modify PAN nanofiber mat to introduce active and hydrophilic groups, followed by a chitosan coating for improvement of biocompatibility (Stoilova et al., 2010b).

Enzymes were incorporated into nanofibers via electrospinning, and subsequent crosslinking the enzymes incorporated effectively prevented their leaching. In the presence of PEO or PVA, casein and lipase were electrospun into ultra-thin fibers. After crosslinking with 4,4'-methylenebis(phenyl diisocyanate) (MDI), the fibers became insoluble, and the lipase en- capsulated exhibited 6 times higher hydrolysis activity towards olive oil than that of the films cast from the same solution (Xie and Hsieh, 2003). The crosslinked enzymes in nanofibers showed very high activity and stability. For example, the immobilized α-chymotrypsin in a shaken buffer solution maintained the same activity for more than two weeks (Herricks et al., 2005).

In addition to chemical bonding, the enzymes were also applied onto nanofibers simply via physical adsorption (Huang et al., 2006, Wang et al., 2006c). Polyacrylonitriles-2-methacryloyloxyethyl phosphoryl choline (PANCMPC) nanofiber was reported to have high biocompatibility with enzymes because of the formation of phospholipid micro-environment on the nanofiber surface. Lipase on the nanofibers showed a high immobilization rate, strong specific activity and good activity retention.

5. Sensors

Sensors have been widely used to detect chemicals for environment protection, industrial process control, medical diagnosis, safety, security and defense applications. A good sensor should have a small dimension, low fabrication cost and multiple functions, besides the high sensitivity, selectivity and reliability (Hall, 1998). High sensitivity and fast response require the sensor device having a large specific surface area and highly porous structure. Several approaches have been used to impart nanofibers with a sensing capability, such as using a polymeric sensing material to electrospin nanofibers, incorporating sensing molecules into nanofibers, or applying sensing material on nanofiber surface via coating/grafting technique.

Electrospun PAA nanofibers have been grafted with pyrene methanol (PM) as the sensing material to detect metal ions Fe^{3+} and Hg^{2+}, and an explosive 2,4-dinitrotuloene (DNT) in water (Wang et al., 2001, Wang et al., 2002a). Due to the quenching effect of these chemicals to the pyrene moieties, the fluorescent intensity of nanofibers had a linear response to the concentration of quenchers, and the nanofibers showed high sensitivities. Similarly, a PM-grafted poly(methyl methacrylate) PMMA nanofibers showed an order of magnitude higher sensitivity to target analyte DNT than its cast film counterpart (Wang et al., 2002b). Explosive 2,4,6-trinitrotoluene (TNT) vapor can be accurately detected using electrospun PAN nanofibers that were coated with a thin layer of conjugated polymer, poly(triphenylamine-alt-biphenylene vinylene) (TPA-PBPV) (Deng et al., 2009).

Fluorescence optical sensors were also prepared by a layer-by-layer electrostatic assembly technique to apply a conjugated polymer onto nanofiber surface for detection of methyl viologen and cytochrome c in aqueous solution (Wang et al., 2004) and porphyrin-doped silica nanofibers were used to trace TNT vapor (Tao et al., 2007). All those nanofiber sensors showed high sensitivity and rapid response. Besides fluorescent properties, conjugated

polymer embedded electrospun nanofibers were also reported to be able to sense volatile organic compounds (VOCs) based on optical absorption properties (Yoon et al., 2007).

A gas sensor using a specific absorption interaction between ammonia and poly(acrylic acid) (PAA) nanofibers was reported. The weight difference induced by the gas absorption was measured by a quartz crystal microbalance (QCM). This sensor was capable of detecting ppb level NH_3 in air, and the sensitivity was four times higher than that of the PAA cast film (Ding et al., 2005). The absorption of gas also leads to changes in FTIR absorption. PAN nanofibers containing metal oxide nanoparticles, such as iron oxide and zinc oxide, have been used to detect carbon dioxide (Luoh and Hahn, 2006). The addition of metal oxide nanoparticles enhanced the gas adsorption and thus improved the sensitivity. In a electrospun carbon nanofiber gas sensor (Im et al., 2010a), carbon black was blended into the fibers to increase the conductivity, and a porous structure was introduced to the fiber surface by etching under a basic condition. The sensory ability for NO and CO gases was reported to be improved dramatically, and the enhanced sensitivity was attributed to higher surface area and improved electrical conductivity due to the formation of carbon black network. It has been found that electrospun SnO_2 fibers with a smaller grain size showed much better sensitivity to CO and NO_2 gases. This was probably because the fibers containing smaller grains had higher resistance, which was the result of larger number of grain-grain interconnections (Park et al., 2011).

Electrical conductivity is an important property for sensor devices. Conducting nanofibers can be produced from semi-conducting oxides, conducting polymers and non-conductive polymers. Pure oxide nanofibers are normally produced by electrospinning a solution containing oxide sol-gel and polymer, followed by calcining treatment to remove the polymer. The detection of gas molecules using oxide nanofibers is based on the conductivity changes due to the doping effect of analyst gases to the oxide. A few oxide nanofibers have been assessed for detecting different gases, such as MoO_3 (Gouma, 2003) nanofibers for ammonia, WO_3 nanofibers for ammonia (Wang et al., 2006a) and NO_2 (Sawicka et al., 2005), TiO_2 nanofibers for NO_2 and H_2 (Kim et al., 2006). These sensors exhibited improved sensitivity, faster response and lower detection limit than that of sol-gel based films

Conducting polymer is another interesting sensor material. Electrospun polyaniline (PANi)/PS nanofibers containing glucose oxidase have been demonstrated to have a high sensitivity to glucose (Aussawasathien et al., 2005). PANi/PVP nanofibers also exhibited sensing ability to NO_2 (Bishop and Gouma, 2005). Organic/inorganic semiconductor Schottky nanodiode was fabricated by PANi nanofibers and inorganic n-doped semiconductor. The device has a rapid response and supersensitive to ammonia (Pinto et al., 2006). Poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS) has also been blended into PVP nanofibers for chemical vapor detection (Choi et al., 2010a).

Besides the conducting and semi-conducting materials, insulating polymers were also used to fabricate electrical sensors. In this case, ions or conductive nano-fillers were added to improve the conductivity. When PEO nanofibers were doped with $LiClO_4$, the mat showed low conductivity and was sensitive to moisture, and the nanofiber mat was reported to have much higher sensitivity than its film-type counterpart (Aussawasathien et al., 2005). Carbon nanotubes/poly(vinylidene fluoride) (PVdF) composite nanofibers showed an increased straining sensing ability (as measured by voltage across the sensor), 35 times higher than that of the film counterpart (Laxminarayana and Jalili, 2005). In addition, electrospun nanofibers incorporated with carbon black showed sensitivity to VOCs (Kessick and Tepper, 2006). When the carbon black concentration was near the percolation threshold, the

composite fibers changed their resistance in volatile organic compounds. Using different polymer matrices, the sensor can be used to detect toluene, trichloroethylene, methanol, and dichloropentane vapors.

Humidity sensor is a very important device for environment tests. KCl doped ZnO (Qi et al., 2009b) and TiO_2 (Qi et al., 2009a) nanofibers have shown higher humidity sensitivity with faster response and recovery time compared to pure ZnO and TiO_2 nanofibers. $BaTiO_3$ nanofibers also exhibited excellent humidity sensing behavior because its complex impedance varied around three orders of magnitude in the whole humidity range (He et al., 2010).

6. Energy harvest and storage

Energy is essential for our modern civilization. The rapidly growing global energy demand has not only sped up the consumption of non-renewable fossil fuels, but also threatened regional stability. In addition to reduce the energy consumption using highly efficient technology, converting other energies into electrical power can considerably assist in alleviating the energy crisis. In this direction, nanotechnology is providing new solutions to solve the problems. It has been found that nanofibrous materials can have significantly higher energy conversion and storage efficiency than their bulk counterparts.

6.1 Solar cells

Solar cells utilize unlimited solar energy for power generation and have been considered as a major solution to current energy crisis. So far, single crystal and polycrystalline silicon based solar cells are dominating the commercial solar cell market. Dye-sensitized solar cells (DSSCs) and organic solar cells are still under development.

Conventional DSSCs have a dye-anchored mesoporous TiO_2 nanoparticle thin layer sandwiched between two conducting glass plates in the presence of an electrolyte. Since electrospun nanofibers are one-dimensional material with better electrical conductivity and higher specific surface area than nanoparticles, and large pore size in nanofibrous mat allows increased penetration of viscous polymer gel electrolyte, nanofibers have shown great application potential in DSSCs.

By using a thin layer of TiO_2 nanofibers as working electrode in DSSC, the photocurrent generation using polymer gel electrolytes was over 90% of liquid electrolyte (Song et al., 2004). DSSC devices (Priya et al., 2008) using polymer electrolytes based on electrospun PVdF-HFP nanofibers could achieve higher conversion efficiency and better long-term stability than conventional liquid electrolyte ones.

The largest problem of using inorganic nanofibrous layers in DSSC is the poor adhesion with conductive substrate. The nanofiber layers are easily separated after calcination due to different thermal expansion coefficients. Many approaches have been tested to address this issue. A TiO_2 nanoparticle layer was coated on conductive glass before nanofiber deposition to increase the adhesion between the glass and the TiO_2 layer (Onozuka et al., 2006). Hot pressing pre-treatment was applied on ZnO/PVA composite nanofiber mat before calcination (Kim et al., 2007b). A self-relaxation layer (Zhang et al., 2009) was also spontaneously formed during electrospinning to release the interfacial tensile stress generated in calcination.

To increase the short-circuit current, the electrospun TiO_2 electrode was treated with $TiCl_4$ aqueous solution to form an additional rutile TiO_2 layer on the fiber surface. Such a rutile

TiO_2 layer increased the fraction volume of active TiO_2 and inter-fiber connection, resulting in an increased photocurrent (Song et al., 2004, Lee et al., 2009a). Another method to improve charge generation and transport was through materials doping. Quantum dots (QDs) were decorated onto TiO_2 nanofibers to yield multiple carrier generation due to the quantum confinement effect (Sudhagar et al., 2009). The electron diffusion coefficient and mobility of the niobium-doped anatase TiO_2 nanofibers were an order of magnitude higher than those of the un-doped fibers (Archana et al., 2010).

Another advantage of electrospun nanofibers is that they can be used to form a transparent mat for counter electrode. This effort has become more and more urgent because of the rapidly growing price of tin and indium, which are typically used for making conductive glass. Copper nanofiber thin layers were prepared using electrospinning for transparent electrode in DSSC (Wu et al., 2010a). The resulted fibers had ultrahigh aspect ratios of up to 100,000 and fused crossing points with ultra-low junction resistance. The fibrous mat exhibited great flexibility and stretchability as well. Electrospun carbon nanofibers were also explored as counter electrode material and an energy conversion efficiency of 5.5% was achieved in the resultant solar cell (Joshi et al., 2010). The carbon nanofiber based DSSC had lower fill factor and overall performance, because of the higher total series resistance (15.5 $\Omega \cdot cm^2$) than that (4.8 $\Omega \cdot cm^2$) of Pt based traditional conductive substrate.

6.2 Fuel cells

Fuel cells are electrochemical devices capable of converting hydrogen or hydrogen-rich fuels into electrical current by a metal catalyst. There are many kinds of fuel cells, such as proton exchange mat (PEM) fuel cells, direct methanol fuel cells, alkaline fuel cells and solid oxide fuel cells (Sundmacher, 2010). PEM fuel cells are the most important one among them because of high power density and low operating temperature.

Pt nanoparticle catalyst is a main component in fuel cells. The price of Pt has driven up the cell cost and limited the commercialization. Electrospun materials have been prepared as alternative catalyst with high catalytic efficiency, good durability and affordable cost. Binary PtRh and PtRu nanowires were synthesized by electrospinning, and they had better catalytic performance than commercial nanoparticle catalyst because of the one-dimensional features (Kim et al., 2008c). Pt nanowires also showed higher catalytic activities in a polymer electrolyte membrane fuel cell (Kim et al., 2009).

Instead of direct use as catalyst, catalyst supporting material is another important application area for electrospun nanofibers. Pt clusters were electrodeposited on a carbon nanofiber mat for methanol oxidation, and the catalytic peak current of the composite catalyst reached 420 mA/mg compared with 185 mA/mg of a commercial Pt catalyst (Li et al., 2008b). Pt nanoparticles were immobilized on polyimide-based nanofibers using a hydrolysis process (Xuyen et al., 2009), and Pt nanoparticles were also loaded on the carbon nanotube containing polyamic acid nanofibers to achieve high catalytic current with long term stability (Nguyen et al., 2009).

Proton exchange mat is the essential element of PEM fuel cells and normally made of a Nafion film for proton conduction. Because pure Nafion is not suitable for electrospinning due to its low viscosity in solution, it is normally mixed with other polymers to make blend nanofibers. Blend Nafion/PEO nanofibers were embedded in an inert polymer matrix to make a proton conducting mat (Lee et al., 2009c), and a high proton conductivity of 0.06-0.08 S/cm at 15 °C in water and low water swelling of 12-23 wt% at 25 °C were achieved. Besides blend electrospinning, Nafion surface coating on polymeric nanofibers (Lin et al., 2010,

Molla and Compan, 2011a, Molla and Compan, 2011b) is another efficient way to obtain better fuel cell performance and reduce Nafion consumption.

6.3 Mechanical energy harvesters

Piezoelectric material can directly convert mechanical energies into electrical power and has shown great potential in powering low energy consumption devices. Piezoelectric power generators, also called nanogenerators in some literatures, are becoming an important source for renewable energy (Wang and Song, 2006, Wang, 2008). These nanogenerators are normally made of aligned inorganic nanowires and their preparation required preciously controlled conditions (Lu et al., 2009, Huang et al., 2010).

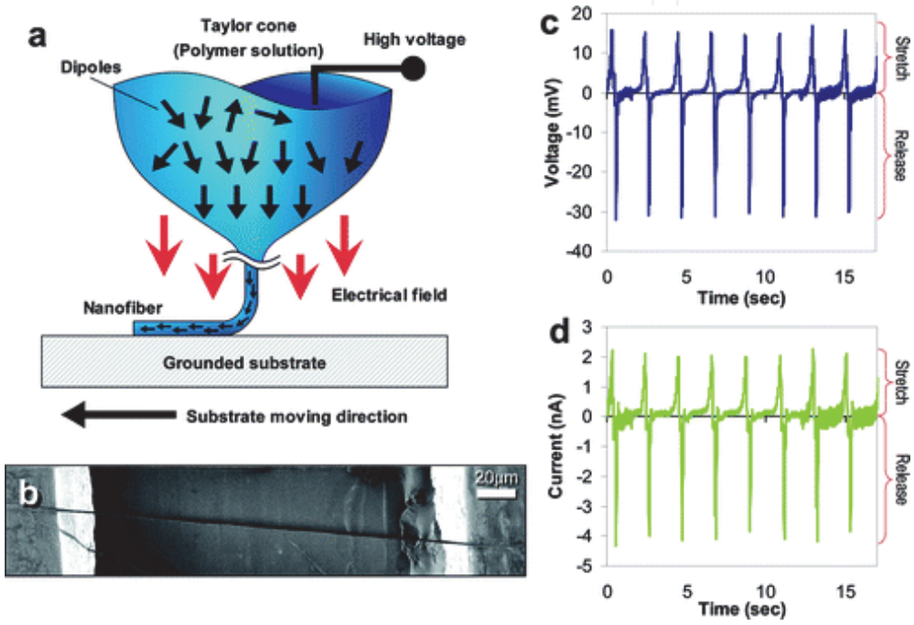

Fig. 6. (a) Scheme of near-field electrospinning process; (b) SEM image of a single PVdF nanofiber power generator; (c) and (d) voltage and current outputs from the generator under applied strain at 2 Hz (Chang et al., 2010).

Electrospinning can process different piezoelectric materials into nanofibrous structure and electrospun piezoelectric nanofibers have been demonstrated to have energy scavenging capability. PVdF nanofiber was directly deposited across two metal electrodes without extra poling treatment to make single fiber nanogenerator using a near field electrospinning technique (Fig. 6a and b) (Chang et al., 2010). Voltage (5-30 mV) and current (0.5-3 nA) outputs were generated when the fiber underwent repeated extensive deformation at 2 Hz (Fig. 6c and d). Rigid lead-zirconate-titanate (PZT) material has been made into electrospun nanofibers with highly improved flexibility for fabricating flexible power generator after a soft polymer packaging (Chen et al., 2010a). The output voltage and power under repeated stress application were 1.63 V and 0.03 μW, respectively. Aligned PVdF nanofibers were collected using a normal electrospinning process and the following poling treatment was used to improve piezo-responsiveness (Hansen et al., 2010). A hybrid nano system combining this fiber based power generator and a flexible enzymatic biofuel cell was demonstrated as a self-powered UV light sensor.

6.4 Lithium ion batteries

Lithium ion batteries are compact and rechargeable electrical energy storage devices. They have very high energy density. Like most other chemical batteries, porous structure is an essential requirement for the battery. A sponge-like electrode has high discharge current and capacity, and a porous separator between the electrodes can effectively stop the short circuit, but allows the exchange of ions freely. Solid electrolytes used in lithium ion battery are typically composed of a gel or porous host to retain the liquid electrolyte inside (Arora and Zhang, 2004). To have high ion conductivity, the host material, also called separator, should have high permeability to ions. A porous mat with well interconnected pores, suitable mechanical strength and high electrochemical stability could be a potential candidate.

Perfluoro polymers have been widely studied in polymer electrolyte because of their chemical and mechanical stability. An electrospun PVdF polymer electrolyte showed high uptake to electrolyte solution (320%—350%) and high ion conductivity (1.7×10^{-3} S/cm at 0 °C). The fibrous electrolyte also had high electrochemical stability of more than 5 V. The prototype cell (MCMB/PVdF based electrolyte/$LiCoO_2$) exhibited a very stable charge-discharge behavior (Kim et al., 2004b). When a thin layer of polyethylene (PE) was plasma polymerized onto PVdF nanofiber surface, a role of shutter by melting of the PE layer grafted was rendered to the nanofiber mat and improved the safety of battery (Choi et al., 2004). It was also found that the formation of interconnected web structure via heat treatment improved both the mechanical properties and dimensional stability of nanofiber mats (Choi et al., 2004, Gao et al., 2006).

Nanofiber mats from other types of polymers, such as PAN (Choi et al., 2005), were also studied as lithium battery separator. The electrospun PAN mat showed high ion conductivity and electrochemical stability. The prototype cell based on the electrospun PAN electrolyte separator with 1 M LiPF6-EC/DMC exhibited an initial discharge capacity of 145 mAh/g, and 94.1% of the initial discharge capacity after 150 cycles at a charge/discharge rate of 0.5 C/0.5 C. To improve ionic conductivity, charge-discharge capability and stability, SiO_2 nanoparticles (Kim et al., 2008b), PMMA (Ding et al., 2009) and PAN (Raghavan et al., 2010) were blended with PVdF-HFP nanofibers for making composite polymer electrolyte.

Besides being used as a separator, some electrospun nanofiber mats have been used as battery electrodes. For example, a carbonated electrospun nanofiber mat was used as anode in lithium ion battery, and the batteries showed a large reversible capacity of 450 mAh/g (Ahn et al., 2006). Some recent researches are focusing on improving battery performance by incorporating different inorganic nanomaterials into carbon nanofibers as electrodes. A anode material made of Fe_3O_4/C composite nanofibers had much better electrochemical performance with a high reversible capability of 1007 mAh/g at the 80th cycle and excellent rate capability (Wang et al., 2008). A Sn/C composite were encapsulated into hollow carbon nanofibers as an anode material for lithium batteries (Yu et al., 2009b) with a high reversible capacity of 737 mAh/g after 200 cycles at 0.5 C (480 mAh/g at 5 °C).

Also, $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (Ding et al., 2008), vanadium oxide (Mai et al., 2010) and $LiFePO_4$/carbon composite nanofibers (Lee et al., 2010) have been investigated as cathode material for lithium ion batteries.

6.5 Supercapacitors

As an electrochemical device with a high power density and super high charging-discharging rate, supercapacitors (also known as double-layer capacitor) have been demonstrated with great potential in different emerging applications, such as power back-up for laptop or mobile

phone and power source for hybrid electric vehicle. For a supercapacitor with high capacitive behavior, electrodes made of porous carbon materials are extremely important, and electrospinning technique has been used to prepare carbon nanofibrous mats with high specific surface area and controllable pore size for this purpose. Activated carbon nanofibers prepare from a PAN/DMF solution have shown a maximum specific capacitance of 173 F/g (Kim and Yang, 2003). The polybenzimidazole (PBI) based carbon nanofibers had specific surface areas ranging from 500 to 1220 m^2/g, and the fabricated double-layer capacitor exhibited specific capacitance between 35 ~ 202 F/g (Kim et al., 2004a).

The capacitance of electrospun nanofiber based supercapacitor can be enhanced by using composite carbon electrodes. $ZnCl_2$ (Kim et al., 2007a), carbon nanotubes (Guo et al., 2009) and nickel (Li et al., 2009), have been blended into procurer solutions for electrospinning and then carbonization. The $ZnCl_2$/C composite nanofibers exhibited a capacitance of 140 F/g with a specific surface area of 55 m^2/g when the carbon nanofibers were doped with 5 wt% $ZnCl_2$. The specific capacitance of an electrical double-layer capacitor with electrodes made of carbon nanotubes embedded carbon nanofiber reached as high as 310 F/g.

In a recent publication (Niu et al., 2011), bicomponent electrospinning was applied to prepare side-by-side nanofibers with PAN on one side and a thermoplastic polymer, PVP on the other side. The resultant carbon fibers after pyrolysis showed improved inter carbon fiber connections and crystallization. The capacitance of the electrochemical cell (Fig. 7a) made of these inter-bonded carbon nanofibers was much higher than that of the carbon nanofibers from polymer blends (Fig.7 b and c).

Apart from carbon, other inorganic nanofiber electrodes have also been examined for supercapacitor applications. For example, RuO_2 has been deposited on a Pt nanofiber mat to function as hybrid electrode and the supercapacitor exhibited a specific capacitance of 409.4 F/g with a capacity loss of only 21.4% from 10 to 1000mV/s (Choi et al., 2010b). Electrospun V_2O_5 nanofiber based supercapacitor had the highest specific capacitance of 190 F/g in an aqueous electrolyte and 250 F/g in an organic electrolyte when the nanofibers were annealed at 400 °C (Wee et al., 2010).

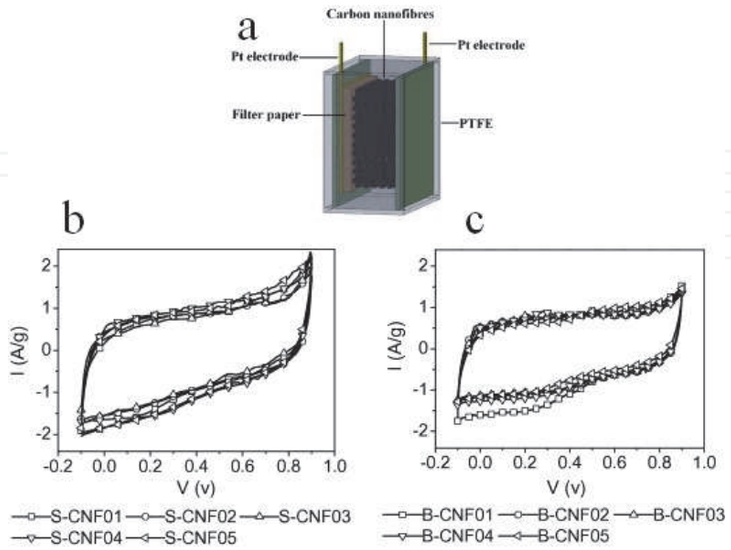

Fig. 7. (a) Illustration of electrochemical cell and the cyclic voltammetry curves of side-by-side (b) and blend (c) carbon nanofibers (Niu et al., 2011).

6.6 Hydrogen storage

Hydrogen has been widely known as an ideal alternative energy to solve energy crisis and global warming. Because high-pressure and cryogenic storage systems can't satisfy the criteria for on-board storage, the key issue for the current hydrogen energy research is hydrogen storage.

It has been reported that carbonaceous materials, such as active carbon, carbon nanotubes and graphite, are able to store hydrogen because of their large specific surface area, high pore volume and light weight. The hydrogen-storage capabilities of electrospun carbon fibers carbonated from different starting polymers (PAN (Kim et al., 2005b), PVdF (Hong et al., 2007), PANi (Srinivasan et al., 2010) and polycarbosilane (PCS) (Rose et al., 2010)) have also been assessed. Carbon nanofiber can be a better hydrogen storage material than other carbon materials because it has an optimized pore structure with controlled pore size (Im et al., 2009b).

To increase graphitization during carbonation, Fe (III) acetylacetonate was used as catalyst to prepare graphite nanofibers and the resulted nanofiber (surface areas of 60-253 m^2/g) had the H-storage capacity of 0.14-1.01 wt%. To increase the specific surface area of carbon nanofibers, different inorganic materials (normally metal (Im et al., 2009a) and metal oxides (Im et al., 2008a)) were mixed into polymer solutions for electrospinning. The resultant carbon nanofiber could have a specific surface area of 2900 m^2/g with an H-storage capacity of 3 wt%. Even though the hydrogen adsorption ability increases with the increasing the specific surface area, pore volume is also very important. It has been concluded that the most effect pore width is in the range from 0.6 to 0.7 nm (Im et al., 2008b), which is slightly larger than hydrogen molecule (0.4059 nm).

Exciting results have been obtained more recently. PANi fibers were prepared by electrospinning and showed a reversible hydrogen storage capacity of 3-10 wt% at different temperatures (Srinivasan et al., 2010). Highly porous carbide-derived carbon fibers with a specific surface area of 3116 m^2/g were prepared after pyrolysis and chlorination of electrospun polyacrbosilane fibers (Rose et al., 2010). The fibers have shown a very high hydrogen storage capability of 3.86 wt% at a low pressure (17 bar).

7. Other applications

Early studies on electrospun nanofibers also included reinforcement of polymers. As electrospun nanofiber mats have a large specific surface area and an irregular pore structure, mechanical interlocking among the nanofibers should occur. When a thin electrospun nylon-4, 6 nanofiber mat was added to epoxy, the composite showed transparency to visible light, and both the stiffness and strength were increased considerably compared with the pure epoxy film (Bergshoef and Vancso, 1999). Recently, polysulfone (PSF) (Li et al., 2008a) and polyetherketone cardo (PEK-C) (Zhang et al., 2010a) nanofibers were used to improve the toughness of carbon fiber/epoxy composite. When carbon nanofibers were dispersed into the PEK-C nanofiber phase, a synergistic effect to enhance the toughness and other mechanical properties was also observed (Zhang et al., 2011).

Electrospun polybenzimidazole (PBI) nanofibers have been used as fillers to reinforce epoxy and rubber (Kim and Eneker, 1999). An epoxy containing 15 wt% electrospun PBI nanofibers was found to have higher fracture toughness and modulus than the one containing 17 wt% PBI whiskers. Also the Young's modulus and tear strength of styrene-butadiene rubber

(SBR) containing the PBI nanofibers were higher than those of pure SBR. In addition, electrospun nylon PA 6 nanofibers were used to improve the mechanical properties of a BISGMA/TEGDMA dental restorative composite resins (Fong, 2004).

Electrospun nanofibers showed excellent capability to absorb sound. A leading nanofiber technology company, Elmarco, recently patented an electrospun nanofiber material that had unique sound absorption characteristics, with only about one-third of the weight of conventional sound absorption materials. It was able to absorb sounds across a wide range of frequencies, especially those below 1000 Hz.

Electrospun nanofibers have also shown application potential in field-effect transistor (FET). EFT behavior has been observed in camphor sulfonic-acid-doped electrospun PANi/PEO nanofibers (Pinto et al., 2003). Saturation channel currents were found at low-source-drain voltage with a hole mobility in the depletion regime of 1.4×10^{-4} cm^2/Vs. Electrospun nanofiber mat has also been demonstrated with the application ability for ultrafast identification of latent fingerprints (Yang et al., 2011).

8. Concluding remarks

The application areas of electrospun nanofibers have been expanding in recent years. Most studies in this area have been conducted on fibers produced on a very small scale, using a needle based electrospinning system. It is expected large-scale nanofiber production will be further improved by commercial technology providers (e.g. Elmarco and eSpin) and research efforts (Niu et al., 2009, Wang et al., 2009b) to provide large amount of high quality nanofibers and reduce the application cost.

So far, almost all of the applications are based on using nanofiber nonwoven mat. It is expected that more sophisticated structures made from nanofiber assemblies, i.e. nanofiber yarns (Ali et al., 2010) and fabrics, will be further developed for novel applications.

Further developments in melt electrospinning technology are needed to expand the range of polymers available for producing nanofibers, and to avoid the use of organic solvents for environmentally friendly nanofiber production. It is also worth noting that other non-electrospinning technologies, such as the melt-blowing and micro-fiber technologies used in the fiber/textile industry, have the potential of producing submicron fibers. Hybrid technologies are being developed also to mass produce nanofibers.

Based on the history and current achievements in electrospinning, electrospun nanofibers are expected to play more and more important role in many important application areas, such as renewable energy and environmental protection. Much work remains to realize the full application potential of nanofiber materials.

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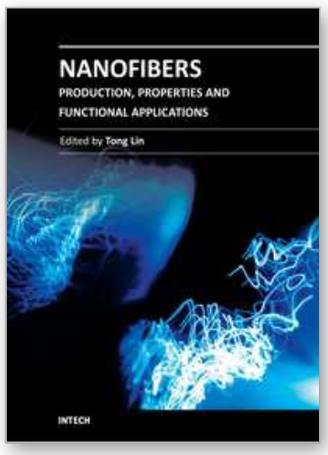

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As an important one-dimensional nanomaterial, nanofibers have extremely high specific surface area because of their small diameters, and nanofiber membranes are highly porous with excellent pore interconnectivity. These unique characteristics plus the functionalities from the materials themselves impart nanofibers with a number of novel properties for advanced applications. This book is a compilation of contributions made by experts who specialize in nanofibers. It provides an up-to-date coverage of in nanofiber preparation, properties and functional applications. I am deeply appreciative of all the authors and have no doubt that their contribution will be a useful resource for anyone associated with the discipline of nanofibers.

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