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Applications of electrospun nanofibers in the biomedical field

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Electrospinning is a technology that has been widely used as a novel method for the generation of nano scale fibres. Electrospun fibres are used in a wide range of applications from electronics to textile. The viability and popularity of this technology can be evidenced by its ease of use and the simplicity of the science behind building the electrospinning machine. The generated fibres have a high surface area- to- volume ratio, the fibrous mats are highly porous and display excellent mechanical properties when compared to other materials of the same scale. In the past decade, this technology has taken off with the use of biocompatible and biodegradable polymers. This review is a summary of the different ways in which electrospinning can be used in the biomedical field. This article analyzes the recent advances of this technology in tissue engineering, drug delivery and in enzyme immobilisation, which once again showcases the versatility of the electrospinning procedure.

Electrospun nanofibres are generated using an external electric field to induce instability in a drop of polymer fluid or solution causing the droplet to elongate and whip, reducing the diameter of the polymer fiber. The complete electrospinning unit was first designed by Cooley and Morton in 1902. They used various collectors to explain the effect of the external electric field on fluids. During the 1930's Formals introduced a cellulose acetate polymer into the electric field created by two electrodes with opposite charge. Formals placed the positive electrode into the solution with the polymer. When the positively charged polymer left the needle it was drawn by the electromechanical stress towards the negatively charged collector. The jet continues to accelerate and thin due to the tensile stress. The solution evaporated from the charged jets to become fibres which were collected [1, 2].

The basic electrospinning unit requires the following: (1) High voltage power supply, (2) micro-volume syringe pump, (3) syringe and a small diameter needle and (4) metal collector. Similar to Formals's experimental setup the positive electrode of the power supply is connected to the needle and the negative is grounded to the collector. A schematic diagram of the electrospinning unit and generated nanofibres can be seen in figure 1.

There are many applications of the electrospinning technology in the biomedical field. The reasons are quite evident such as the simplicity of the procedure in generating the large surface area- to- volume ratio of the material and the mechanical stability of the fibres that allows for its use in the biomedical field. Research has however been centered around three main issues: (1) the generation of scaffolds for tissue engineering; (2), drug delivery mechanisms; and (3) enzyme immobilization for faster reaction rates in biological reactions. There have been many articles published that highlight the importance of the biomedical applications of electrospinning such as a review by Agrewal et al. [3], and Laurencin et al. They have also reviewed the recent patents on electrospun biomedical nanostructures [4]. The current available techniques for nanofiber synthesis and the use of nanofibers in tissue engineering and drug-delivery applications are reviewed by Vasita et al. [5]. This article, similar to its predecessors, will once again try to highlight and review the recent techniques using the electrospinning technology in the biomedical field.

Many biocompatible polymers have been used to generate nanofibres; these polymers can be either biodegradable or non-biodegradable. Non biodegradable polymers or polymers that have a longer degradation time than biodegradable polymers offer better structural and mechanical support such as with polymers like PHBV (Poly-hydroxy butyrate valerate) and PLLA (Poly-L-lactic acid). However, these materials interfere with tissue turnover and remodelling [6]. Polymers that are degradable in vivo due to enzymatic and hydrolytic activities do not interfere with cellular activities and allow for the cell proliferation and spaces or holes created by the degraded fibres allow ECM (extracellular matrix) to infiltrate and provide nutrition for the proliferating cells. Therefore, non- biodegradable

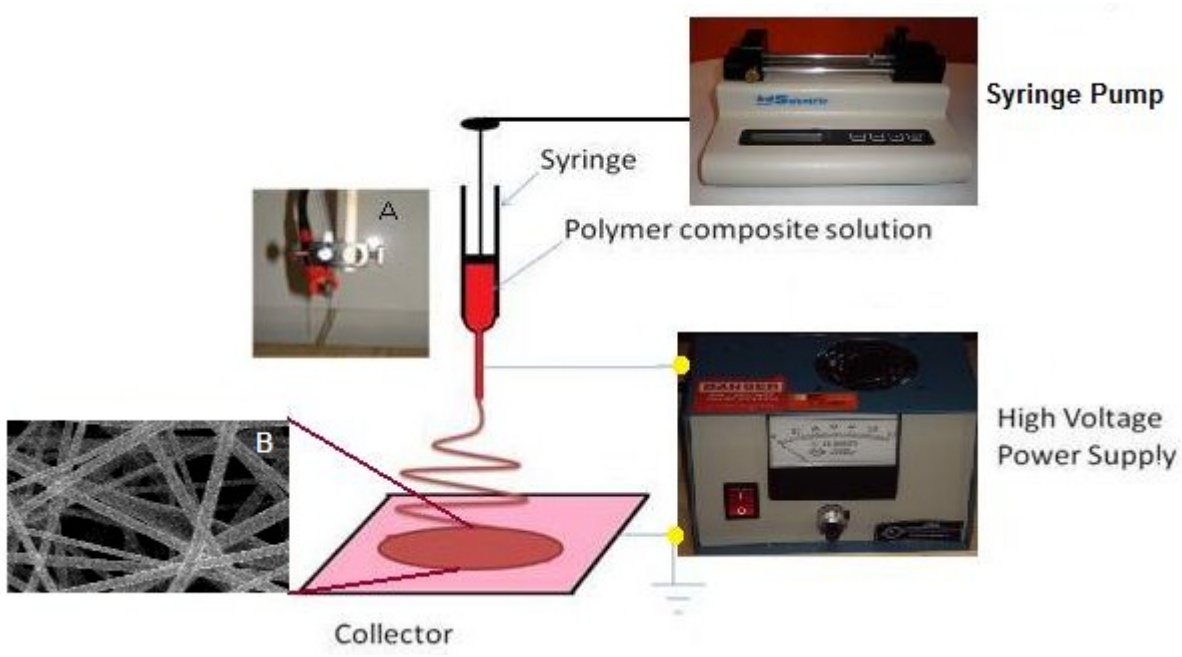

Figure 1: Schematic diagram of the complete electrospinning setup. A) Needle connected to the high voltage power supply. B) Nanofibrous mats

polymers can be effectively used for enzyme immobilization and filtration systems in procedures like dialysis, whereas biodegradable polymers can be used in tissue engineering and drug delivery systems [6, 7].

BIOMEDICAL APPLICATION

Drug Delivery Methods

One of the main areas of research in biomedical application is drug delivery where the electrospun fibers help to encapsulate the therapeutic agent in the fibers. In addition, electrospun fibers maintain the integrity and bioactivity of the drug molecules due to the mild processing parameters. Localized inoculation of medicines in wound treatment using electrospun fibers as delivery vehicles can significantly reduce the systemic absorption of the drug and prevent/reduce any side effects from the drugs. In addition, the efficacy of the drug would also improve due to localization of the treatment [8]. The release of the drug is then dependent on the degradation of the polymer fibers and thus can be properly controlled. The core shell electrospun fibers have usually been used in drug delivery applications. This is due to the fiber's ability to encapsulate the drug molecules until they are needed in the hollow core. These fibers protect the drug and also prevent other molecules such as enzymes and growth factors from denaturing during processing [9-11]. In this manner the therapeutic agents remain unaltered and encapsulated until needed at the site of action.

Yang et al. used lysozyme as a model protein and studied the bioreactivity and structural integrity of PDLLA (Poly-D,L-lactic acid, poly DL lactide) ultrafine nanofibers. Scanning electron microscope SEM analysis showed that fibers had the core shell structure, which were highly porous and bead free [12]. This core sheath structure can be seen in the figure 2.

Many compounds for therapeutic use can be encapsulated within the nanofibers for drug delivery. Complexities arise in this process due to the processing parameters which are somewhat more complicated than for simple encapsulation methods, by controlling the mode of encapsulation and the architecture of electrospun fibers, to achieve appropriate drug release patterns as summarized below. [8].

The medicine can be encapsulated using two different methods. The simplest method is by blending whereby the drug molecules are "blended" or mixed with the polymer and electrospun together to form the encapsulated fibers. Cui et al. found that larger diameter fibers displayed zero order kinetics in drug release, which means that the rate of release of the drug will be is constant [13]. In this method the molecules are located on the surface of the fibers and the process would be easy to execute. The second method used to generate encapsulated drug delivery systems (as mentioned previously) is the core shell structure created using the coaxial spinneret. Studies using these fibers by Yang et al. have shown that the drug is released with an initial burst and then stabilizes to a constant rate [14]. In

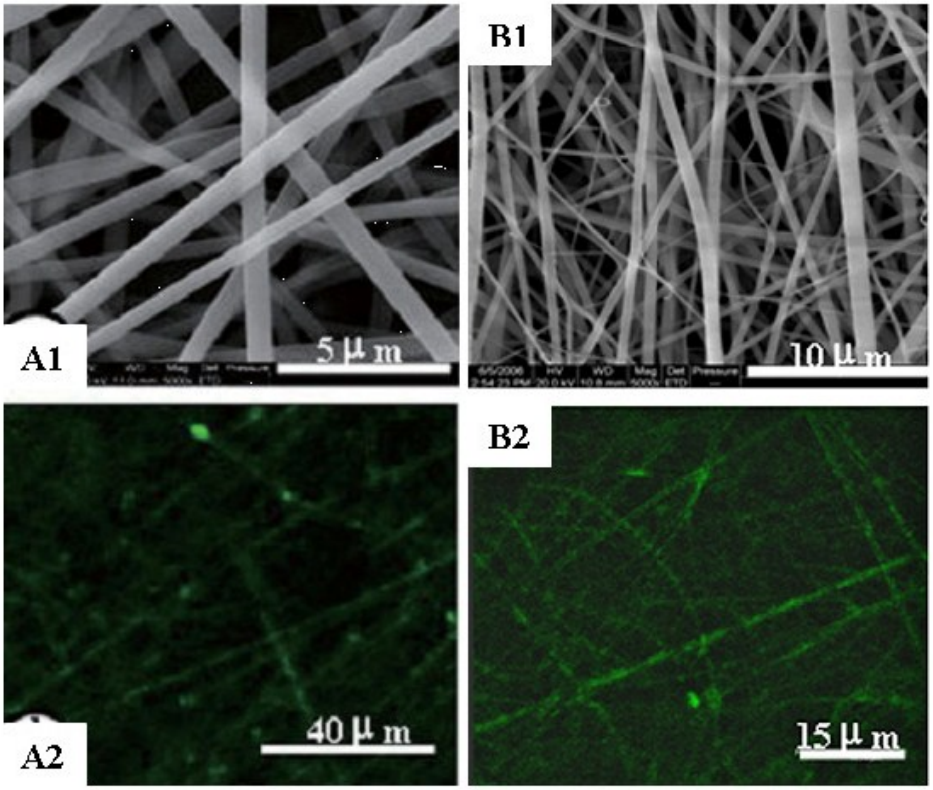

Figure 2: SEM images (a1) and LCSM images (a2) of PDLLA electrospun core-shell fiber containing 5% Bovine serum albumin (BSA); SEM images (b1) and LCSM images (b2) of PDLLA electrospun core-shell fiber containing 5% lysozyme. Reproduced from Cui et al. [8] by permission.

addition, medically active agent can be coated to the surface of the fibers. In this method the drug molecules can be adsorbed or cross linked to the fibers via physical and chemical bonds. [9] For example, in a study by Zhai et al. Methylene Blue (MB) was used to load the electrospun fibers using an ionic link. This study demonstrated that the drug releasing rate of the electrospun fiber fiber mesh can be controlled by varying pH value or temperature [9].

The high surface area of the nanofibers overcomes the loading limitations that are normally encountered in normal drug delivery methods. In addition, the surface area of the nanofibers can be further increased when the fiber created has porous rather than a smooth surface. Dayal et al. created porous fibers using iPMMA as it can be seen in the following figure 3. The pores increase the surface area and provide larger number of binding sites for drug loading.

These pores can be created by the selective removal of materials that are blended together or by phase separation and modifying the electrospinning techniques. Dayal et al. have shown that there is a competition between the rate of phase separation and solvent evaporation which, causes the pores to form in the fibers. The size of these pores depends on the surface energy [15].

Chen et al. used Heparin (which prevents cell proliferation in fibroblasts, mesangial cells and vascular smooth muscle cells) encapsulated it in Poly(L-lactide-co-ε-caprolactone) (P(LLA-CL)). Fibroblast proliferation is a major issue in surgical wound healing which leads to premature wound closure. They used the coaxial spinneret to generate core shell fibers of relatively even diameter fibers in

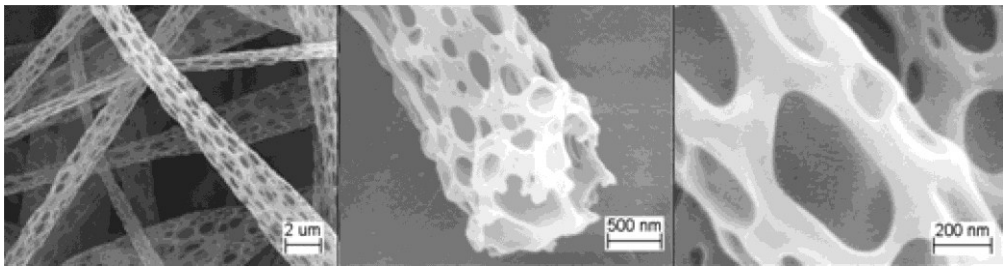

Figure 3: Porous nanofibres of iPMMA solution using electrospinning. Reproduced from Dayal et al. [15] by permission.

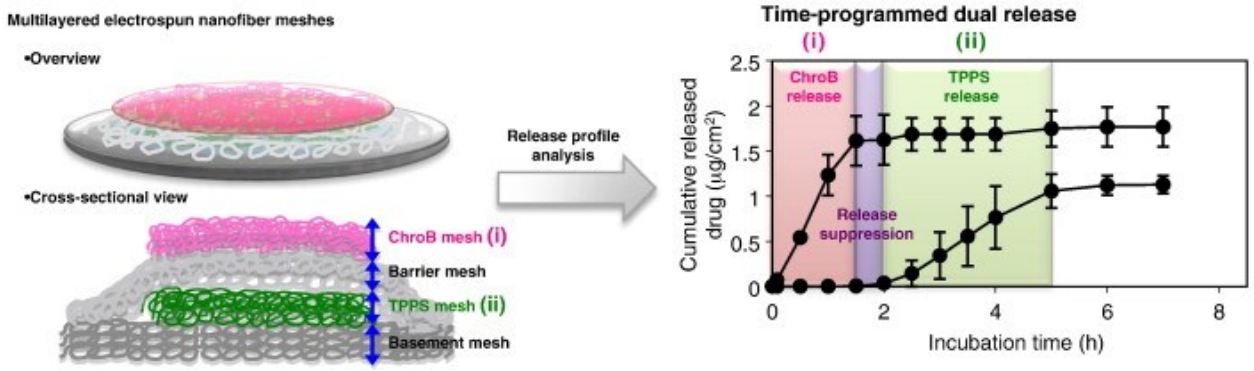

Figure 4: Multilayer encapsulated therapeutic agents for slow time release (i) encapsulated electrospun TPPS drug, (ii) Mesh to control the rate of release of the second drug ChorB (iii) and (iv) base for attachment. Reproduced from Okuda et al. [11] by permission.

the range of 413 nm. When compared with the control fiber without any heparin it was found that the drug encapsulated fibers hindered cell growth after 48 hrs [10].

Okuda et al. have created a novel method of slowly releasing a combination of drugs using multilayered drug loaded nanofibers. The polymer used was PLCL and this was loaded with two drugs 5,10,15,20-tetraphenyl-21H,23H-porphinetetrasulfonic acid disulfuric acid (TPPS) and chromazurol B (ChorB) and the drug release profile was investigated. Figure 4 illustrates this technique.

They found that the drug release can be controlled by varying the electrospinning parameters such as the mesh size and fiber diameter. These forms of drug therapies can be used in sequential treatment of diseases such as AIDS and some forms of cancer [11].

Tissue Engineering

Electrospinning is a very efficient method for tissue scaffold manufacturing to produce a nonwoven mesh of micron-sized to submicron-sized fibers. Many researchers have generated various types of scaffolds for human tissue and organ regeneration, including bone, dentin, collagen, liver, cartilage, and skin. Both natural and synthetic polymer electrospun nanofibers have been used in making these scaffolds. These electrospun nanofibers are used to repair, replace and enhance the properties of the tissues. The electrospun nanofibers, which are used in the scaffold, need to be well designed and must have uniformity of dimension. In addition, other requirements such as high porosity (good pore size distribution), large surface area, biodegradability, the ability to maintain structural integrity with tissue, good mechanical properties, non toxicity to cell and biocompatibility are also important in tissue engineering while using electrospinning [16].

In the body support is usually provided by the ECM (extracellular matrix), made up of polymers of fibrous proteins such as collagen and glycosaminoglycans (GAGs) which are proteoglycans or a form of polymers made of carbohydrates. The electrospun mats that are highly porous behave similar to the extracellular matrix in the body [17]. Therefore, scaffolds composed of polymers that are conducive to cellular attachment and present in the natural ECM (e.g., collagen) would further enhance the nanofiber efficiency. The collagen exhibits favorable tensile mechanical properties at the level of single fiber, but its poor bulk properties limit its ability to be used as sole material in making scaffolds for biomedical applications. In addition, the production of the collagen fibers by electrospinning is not economically advantageous. Hence, many researchers have synthesized collagen fibers with other biodegradable polymers. These composite materials have good mechanical properties and enhance the reactivity of collagen to the cells. PLLA nanofibers have been synthesized with collagen (less than 10%) for bone applications due to their biocompatibility. The pure PLLA scaffold may lack the specific functionality that would promote the interactions between cells and scaffold [18, 19]. There are many electrospun polymer fibers effectively applied in tissue engineering. Some of these polymers especially those applied in tissue engineering are listed in Table 1.

In tissue engineering applications, core/shell nanofibers are used due to their versatility not only for the encapsulation of biologically relevant molecules and nano composites but also for modifying the surfaces of electrospun fibers. The electrical and mechanical properties of the nanofibers are very important in the tissue engineering. Conductive electrospun nanofiberous scaffolds have been fabricated using biodegradable poly (lactic acid) (PLA) mixed with single wall carbon nanotubes (SWNT). The SWNT incorporated nanofiber scaffolds allow cells to grow with no hostile influence on cell proliferation. Zhang and research group synthesized collagen surface coated poly (ε-caprolactone (PCL) by coaxial electrospinning and studied functionalized PCL nanofibers cell-scaffold interactions by using the human dermal fibroblasts as the sample cells for skin tissue engineering [20]. The PCL/Gelatin core shell

Table 1: List of polymer fibres which are used in biomedical applications.

	Polymer	Solvent	Fibre Diameter	Ref.
	Drug Delivery System:			
1	(a) Poly(ε-caprolactone) (shell)+ Poly(ethylene glycol) (core)	2,2,2-trifluoroethanol (b) Water	200-350 nm	[41]
2	(a) Poly(ε-caprolactone) and poly(ethylene glycol) (shell) Dextran (core)	Chloroform and DMF , Water	1-5 μm	[42]
3	Poly(ε-caprolactone) (shell) Poly(ethylene glycol) (core)	Chloroform and DMF, Water	500-700 nm	[43]
4	Poly(ε-caprolactone-co-ethyl ethylene phosphate)	DCM and PBS	~ 4 μm	[44]
5	Poly(D,L-lactic-co-glycolic acid), PEG-b-PLA, and PLA	DMF	260-350 nm	[45]
6	Poly(D,L-lactic-co-glycolic acid)	DCM	1-10 μm	[46]
7	Poly(L-lactide-co-glycolide) and PEG-PLLA	Chloroform	690-1350 nm	[47]
	General Tissue Engineering:			
8	Poly(ε-caprolactone)	Chloroform and methanol	2-10 nm	[48]
9	Poly(ε-caprolactone) (core)+ Zein (shell)	Chloroform and DMF	500-900 nm	[49]
10	Poly(ε-caprolactone) (core) + Collagen (shell)	2,2,2-trifluoroethanol	500 nm	[50]
11	Poly(D,L-lactic-co-glycolic acid) and PLGA-b-PEG-NH2	DMF and THF	400 -1000 nm	[51]
12	Poly(D,L-lactide-co-glycolide)	DMF and THF	500-800 nm	[52]
13	Poly(ethylene glycol-co-lactide)	DMF and acetone	1-4 mm	[53]
14	Poly(ethylene-co-vinyl alcohol)	2-propanol and water	0.2-8.0 mm	[54]
15	Collagen	HFP	180-250 nm	[55]
16	Gelatin	2,2,2-trifluoroethanol	0.29-9.10 mm	[56]
17	Fibrinogen	HFP	120-610 μm	[57]
18	Poly(glycolic acid) and chitin	HFP	130-380 nm	[37]
	Vascular Tissue Engineering			
19	Poly(ε-caprolactone)	Chloroform and DMF	0.2-1 nm	[58]
20	Poly(L-lactide-co-ε-caprolactone)	Acetone	200-800 nm	[59,60, 61]
21	Poly(propylene carbonate)	Chloroform	5 μm	[62]
22	Poly(L-lactic acid) and hydroxylapatite	DCM and 1,4-dioxane	300 nm	[63]
23	Chitin	HFP	0.163-8.77 nm	[64]

fibers prepared by Zhao et al. have high mechanical stability and bioactivity. Gelatin has the capability of stimulating cell adhesion, proliferation and differentiation and it can be directly incorporated via electrostatic interactions [21].

3,3-dithiobis(propanoicdihydrazide)-modified Hyaluronic acid (HA-DTPH) and poly(ethylene glycol) diacrylate (PEGDA) cross linked fiber system synthesized by double syringe electrospinning method are being used for soft-tissue scaffold materials in 3D cell cultures [22]. Multi-layering and mixing electrospinning using four different biopolymers or synthetic polymers such as type-I-collagen, polymerizable styrenated gelatin (ST-gelatin), segmented polyurethane (SPU), and poly (ethylene oxide) (PEO) were synthesized by Kidoa Ki et al. Multilayered ST-gelatin, SPU and type-I-collagen fiber mats have been used in tissue-engineered matrices, scaffolds, and devices [23].

Fugihara and group synthesized PCL/$CaCO_3$ nano composite fibers for guided bone regeneration (GBR) membranes and achieved high mechanical stability of fiber films by using multiple layer PCL and PCL/$CaCO_3$ composite nanofiberous membranes. These calcium rich GBR membranes are favored in vivo condition to enhance osteoconductivity at bone defects [24,25]. Lee et al. prepared PCL/Collagen electrospun fibers and investigated whether orientation of electrospun PCL/collagen nanofibers affects morphology, adhesion, proliferation, differentiation, and organization of human skeletal muscle cells [16]. Mey et al. also synthesized fully aligned PCL and PCL/collagen electrospun fibers. Collagen is the prevalent structural protein of the extracellular matrix and it enhances the biological effects of PCL [26]. Polymerization of acrylic acid surface modified biodegradable synthetic polymers, i.e., poly (glycolic acid) (PGA), poly (L-lactic acid) (PLLA) and poly (lactic-co-glycolic acid) (PLGA) are being actively utilized for the fabrication of tissue scaffolds or as delivery vehicles [27]. Li et al. prepared composite electrospun nanofiberous membranes. They studied in-vitro degradation properties, pH value, molecular weight and mechanical properties of the composites. The tensile strength and Young's modulus of composite membranes were still higher than those of electrospun PLGA membranes during degradation. The cell-culture experiment results indicated that the electrospun PLGA-chitosan/PVA composite membranes could facilitate the adhesion of human embryo skin fibroblasts [28]. Ramakrishna et al. prepared PLLA membranes by electrospinning. The PLLA scaffold was intended for neural tissue engineering and its suitability evaluated in vitro using neural stem cells (NSCs) [29]. Chew and group prepared the PCL and poly (ethyl ethylene phosphate) (PCLEEP) electrospun nanofibers. They were able to isolate a suitable

candidate for the production biodegradable protein-encapsulated fibers [30]. Zong and his medical group prepared PLGA and PLGA/PEG-PLA polymer blend (85:15 by weight) nanofibers and tested these fibers in–vivo in animals without medication. Under these conditions, through adjustment of hydrophilicity, the adhesion properties were significantly improved [31]. They also prepared electrospun scaffolds consisting of four different compositions: PLA, PLGA (LA/GA=50/50) copolymer, PLA-b-PEG-b-PLA triblock copolymer and lactide. The role of high molecular weight (HMW) PLA was to provide the overall mechanical strength, the purpose of the PLGA was to grossly tune the degradation rate, the lactide was used to finely set the degradation rate and the PLA-b-PEG-b-PLA copolymer was used to control the hydrophilicity [32].

The aligned collagen scaffold produced by electrospinning with a rotational wheel collector exhibits a distinct fiber alignment when compared to the random fibrous mats generated without the use of the rotating wheel collector. The aligned collagen nanofiberous scaffolds can be very useful in engineering different specific tissues or organs where the elongated proliferation patterns of the cells coincides with the cell morphology [33]. Yang's research group fabricated electrospun PLLA/HA (hydroxyapatite) hybrid membrane, which was used for bone tissue regeneration. To achieve the purpose, laboratory synthesized HA nanoparticles were carefully dispersed in PLLA polymer and nano sized PLLA/HA hybrid fibers were electrospun through well-controlled spinneret to fabricate desirable hybrid membrane. They investigated structural and mechanical properties and in vitro degradation of the PLLA/HA hybrid membrane [34].

As a biodegradable polymer, PHBV, was conjugated with type-I collagen as an electrospun nanofiberous scaffold in order to produce a nanofiberous mat. This biodegradable scaffold was highly mechanically stable and can be used as an animal cell adhesive material (PVHB-Col). In in-vitro experiments, it was determined that the NIH3T3 fibroblast cells showed significantly better adherence and proliferation on the PHBV-Col nanofiberous scaffold than did the PHBV control scaffold [35]. Yuan et al. successfully prepared nanofiberous PLGA/chitosan membranes by using a dual source and dual-power electrospinning. They successfully used different power supplies and different syringe pumps with variable number of syringes with altered compositions. The enhanced structural and mechanical properties and the cyto-compatibilities of the hybrid nanofiberous PLGA/chitosan membranes were studied because of the introduction of large amounts of hydrophilic chitosan (from 32.3 to 86.5%) into the membranes. The cyto-compatibility study suggested that interactions between endometrial stromal fibroblasts (hESFs) and PLGA/chitosan hybrid membranes and the hybrid nanofiberous PLGA/chitosan membrane, with suitable chitosan amount (from 32.3 to 86.5%) is an efficient scaffold for skin tissue engineering [36].

The increasing use of biodegradable polymers in medicine has attracted polymer scientists since this material exhibits unique properties for specific uses in the field. Electrospun hexanoyl chitosan (H-chitosan), PLA and H-chitosan/PLA fibers prepared from corresponding solutions in chloroform, dichloromethane and tetrahydrofuran were shown to have good mechanical properties and many applications in tissue engineering [37]. The biodegradable and biocompatible polymers, PLA, poly (glycolic acid) (PGA), and their copolymers have extensive applications in surgical sutures, drug delivery and scaffolds for tissue generation. Chitin has good biocompatibility and biodegradableility and has various biofunctionalities including antithrombogenic, hemostatic immunity enhancing, and wound healing properties. Park and his group synthesized nanostructured scaffolds of PGA/chitin blends and investigated hydrolytic degradation behavior of PGA/chitin blend nanofibers in vitro. They examined the effect of PGA/chitin scaffolds on the cell attachment and spreading of normal human epidermal fibroblasts (NHEF) [38]. Pham et al. prepared the multi-layer electrospun PCL microfiber scaffolds with a 300 sec nanofiber layer (i.e. the electrospinning process was run for 300 seconds). This fiber exhibited reduced cellular infiltration under both static and flow culture conditions tested here. The optimization to get a balance between the nanofibers and microfibers in these multilayer structures has tremendous potential for 3D tissue engineering applications [39]. Wang prepared the 3D poly (D, L-lactide-co-glycolide)/hydroxyapatite (PLGA/HAp) composite fibrous scaffolds to develop recombinant human bone morphogenetic protein-2 (rhBMP-2). The PLGA/HAp composite scaffolds developed in this study exhibits even morphology with homogeneous dispersion of HAp nanoparticles inside PLGA matrix within the scaffold. In vitro test show that the BMP-2 protein successfully maintained its integrity and natural conformations after undergoing the electrospinning process. Cell culture experiments showed that the encapsulation of HAp could enhance cell attachment to scaffolds and reduce lower cytotoxicity [40].

Catalysis

Electrospun materials from stable polymers or ceramic fibers are ideal candidates for catalytic supports as they can provide a large surface area and a high porosity for most catalytic interaction. Researchers have studied the immobilization of catalysts with high efficiency and high active surface area that is created by the electrospinning method. The electrospun TiO_2 catalysts have a high efficiency and high active surface area. Doh et al. have immobilized photocatalytic TiO_2 (236 nm thick) on nanofibers using electrospinning for application in the degradation of dye pollutants. They coated the photocatalytic TiO_2 particles on the TiO_2 nanofibers to enhance degradation efficiency of dye pollutants and proposed that the composite TiO_2 nanofibers and nanoparticles are suitable for the

degradation of organic pollutants [65]. Metal oxide electrospun nanofibers are usually prepared with a precursor metal salt solution with the help of a proper polymer, followed by calcination to decompose the polymer completely and turn metal salt into metal oxide [65].

Liu et al. prepared ZnO nanofiber and nano particles by using a novel electrospinning system. In this process Zn acetate acts as a precursor, N, N-dimethylformamide (DMF)/acetone as a solvent, and cellulose acetate (CA) as a fiber template. ZnO nanoparticles smaller than 40 nm in diameter are obtained by direct calcination of ZnAc/CA composite nanofibers. They obtained ZnO nanofibers with diameter less than 23 nm with the calcination of Zn $(OH)_2$/cellulose composite nanofibers. The photocatalytic activity of ZnO nanofibers is evaluated and compared with that of ZnO nanoparticles by measuring the photo-degradation of the dye molecules such as Rhodamine B and acid fuchsin under visible light irradiation. These ZnO nanofibers mats are highly efficient photocatalysts and can be potentially used in the treatment of waste water [66].

Transition-metal particles have a wide range of application in catalysis, such as solar energy absorption, and magnetic materials. Erman et al. prepared the catalytic palladium (Pd) nanoparticles with electrospun copolymers of poly-acrylonitrile and poly(acrylic acid) (PAN-AA) mats. Electrospun nanofiberous mats from homogeneous solutions of PAN-AA and $PdCl_2$ in DMF. Palladium cations were reduced to Pd metal when the fibrous mats were treated in an aqueous hydrazine solution at room temperature. The catalytic activity of the Pd nanoparticles in electrospun mats were examined by selective hydrogenation of dehydrolinalol in toluene at 90 °C. Electrospun fibers with Pd particles have 4.5 times higher catalytic activity than the currently using Pd/Al_2O_3 catalyst [67]. Hou et al. reported that the Pd-NP-carrying carbonized electrospun nanofibers (Pd-NP/CENFs) were used as catalysts for a C–C coupling reaction. The Pd-NP/CENFs were prepared via a carbonizing process of electrospun composite nanofibers based on PAN and Pd acetate. The Pd nano particles were partially embedded into the nanofibers. These nanostructures create a stronger bond between the Pd-NPs and the nanofibers. Therefore, the Pd-NP/CENF catalysts are expected to have advantages like having the1D nanofiber making it easy for the catalyst to separate from a reaction mixture. In addition, the firm bindings between the metal nanoparticles and the supporting nanofibers make the catalyst leaching-resistant for good retrieval and reusability [68].

Wei et al. prepared porous silica nanofibers containing catalytic silver nanoparticles synthesized by sol-gel chemistry and electrospinning techniques. Tetraethyl orthosilicate (TEOS), poly-[3-(trimethoxysily)propyl methacrylate] (PMCM), and silver nitrate ($AgNO_3$) were used as precursors for the production of silica-PMCM hybrid fibers. Calcinations of the hybrid fibers at high temperatures resulted in porous silica fibers due to the thermal decomposition of PMCM polymer and conversion of $AgNO_3$ to silver nanoparticles. From the silver-catalyzed reduction of MB dye with sodium boron hydride as reducing agent silver nanoparticles in the silica fibers exhibited good catalytic properties [69]. Wendroff et al. presented a novel concept for the immobilization of catalysts. They prepared naphthalene-oligostyrene conjugates using this approach. Low molecular weight oligostyrenes can be coelectrospun with high molecular weight polystyrene (150-300 kDa) to provide nanofibers where the oligostyrenes are well dispersed within the fibers. The naphthalene-polystyrene conjugates with defined molecular weight are readily prepared using nitroxide-mediated radical polymerization (NMP). Due to the high surface area of the nanofibers and the well dispersed catalytic active moieties within the fibers, this system should behave as a highly active immobilized catalyst system [70].

Hatton and Rutledge prepared functionalized oxime nanofibers via electrospinning by the dispersion of polyacrylamidoxime (PANOx) blended with PAN. The oxime groups of the enzymes are nucleophilic and capable of hydrolyzing esters. The effect of the fiber size on reaction rate indicates that intra-fiber diffusion resistance may limit the accessibility of the catalytic sites in the fibers and affect the overall catalytic activity [71]. Xia et al. used the surface of anatase TiO_2 nanofibers with Pt nanoparticles and then Pt nano wires to develop a heterogeneous catalyst. These nanofibers were prepared in the form of a nonwoven mats by electrospinning with a solution containing both poly-(vinyl pyrrolidone (PVP) and titanium tetraisopropoxide, followed by calcination in air at 510 °C. The fiber mat was then immersed in a polyol reduction bath of ethylene glycol (EG) solution containing H_2PtCl_6 and PVP to coat the surface of TiO_2 fibers with Pt nanoparticles of 2-5 nm. The Pt nanoparticles coated on anatase nanofibers could also serve as seeds for the growth of Pt nanowires up to 125 nm in length as shown in Figure 5. The resultant fiber membranes proved to have excellent catalytic activities for the hydrogenation of methyl red, the efficiency of which improved as the coverage of the Pt nano particle increased [72].

Electrospun carbon fibrous mats (CFMs) have a remarkable porous structure, close contact between the nanofibers and a high surface area-to-volume ratio. If a catalyst particle is deposited on the CFMs, it can satisfy the requirements of reactant access, proton access and electronic continuity for DMFCs. Yang et al. described the fabrication of the catalytic electrodes Pt/CFM, and evaluated their performance for electrocatalytic oxidation of methanol. The CFMs were fabricated and the platinum particles deposited on the carbon fibers by multi-cycle CV method. The platinum supports on CFMs exhibit high performance in their electrocatalytic activity and their stability towards the oxidation of methanol [73]. The generated polyvinyl alcohol (PVA)–Pt/TiO_2 composite fibers with diameters 150–350 nm by electrospinning. It was found that the PVA fiber could be degraded by photo catalytic oxidation under UV irradiation. The rate of degradation under UV-C irradiation is

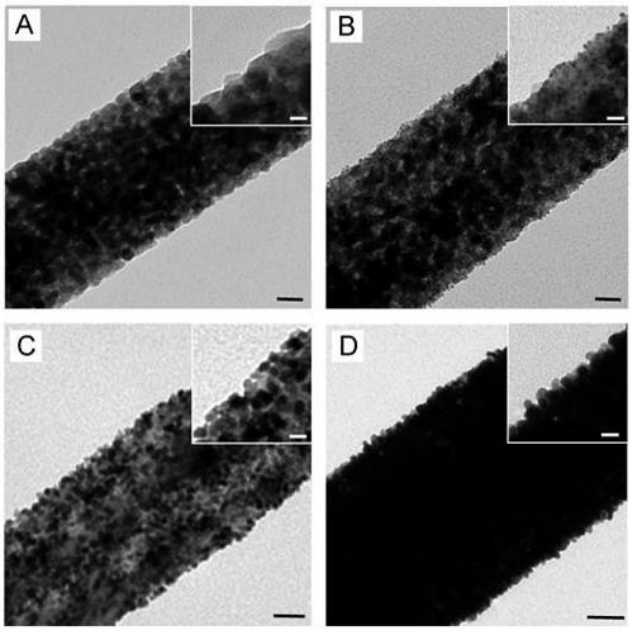

Figure 5: Titanium oxide nanowires surface modified by the Platinum nanoparticles. Reproduced from Formo et al. [72] by permission.

approximately double of that under UV-A irradiation. Based on the relationship between the weight loss and the reaction conditions, it is supposed that the direct oxidation pathway by direct electron transfer from reaction substrates to the active site on the photocatalyst surface is the most probable mechanism for the destruction of solid-phase PVA in PVA–Pt/TiO2 composite fiber under UV irradiation [74]. Ebert et al. studied the immobilization of Pd nanoparticles on electrospun nanofibers of poly-(amideimide) (PAI). The PAI nanofiberous mats collected during spinning were further catalytically activated by a thermal treatment in air to yield fixed nanosized catalyst on the surface of the nanofibers. The catalytic activity of these nanofiberous mats was tested in the hydrogenation of methyl-*cis*-9-octadecenoate (methyl oleate), a model compound for the industrial process of edible oil hydrogenation [75].

CONCLUSION

In biomedical applications and enzyme immobilization, the electrospun nanofibres have a wide range of applications, from tissue engineering to enzyme immobilization. These applications are made possible due to the inherent characteristics of the nanofibres such as its high porosity and high surface area-to-volume ratio. Although there are other methods of generating nano scale materials, such as drawing, template synthesis, phase separation, self-assembly. Only the electrospinning process has the flexibility and ease of fiber production in both in the lab and in the production plant.

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