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Electrospun Nanofibers: From Rational Design, Fabrication to Electrochemical Sensing Applications

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1. Introduction

Electrospinning is a convenient and versatile technique to prepare continuous fibers with diameters ranging from tens nanometers to several micrometers [1]. In early works, electrospinning was limited to the fabrication of nanofibers from organic polymers due to the stringent requirement on the viscoelastic behavior of the electrospinning solution [2]. Recent efforts have greatly expanded the application scope of electrospinning technique. Various one-dimensional (1D) nanomaterials can be prepared by electrospinning besides the common polymer fibers, such as polymer fibers loaded with nanoparticles and functional molecules, ceramics fibers and metal/metal oxide fibers. Additionally, with the development of electrospinning method and setup, electrospun fibers have not been limited to the morphology of solid interior and smooth surface. Fibers with novel secondary structures, such as core/sheath, hollow and porous, can also be prepared if appropriate processing parameters or new designs of setups are employed.

Due to the small diameter, extremely long length, high surface area and complex pore structures, electrospun fibers have being attracted extensive research interests for their applications in biomedical field [1, 3, 4], such as tissue engineering, drug delivery and wound healing, as well as energy and environmental engineering [5, 6]. The relatively large specific surface area and high porosity make electrospun nanomaterials attract significant attentions in developing ultrasensitive sensors [7-9]. Various electrospun nanomaterial-based sensors have been designed, including resistive sensor, electrochemical sensor, fluorescent sensor, acoustic wave sensor, colorimetric sensor, photoelectric sensor, etc. Among these read-out modes, electrochemical read-out, featured with high sensitivity and selectivity, inexpensive equipment and easy miniaturization, has attracted remarkable attentions in the ultrasensitive detection. In this chapter, we focus on the synthesis of nanofibers with different composition,

and the design and preparation of electrospun nanofibers with novel secondary structures. Following this, the application of electrospun nanomaterials in constructing electrochemical sensors and their analytical performance is discussed.

2. General process of electrospinning

The basic setup for electrospinning consists of three major components: a high voltage power supply, a spinneret, and a collector (a counter electrode) (Fig. 1). In the process of electrospinning, the applied voltage causes a cone-shaped deformation of the drop of polymer solution (Taylor cone). Once the strength of electric field exceeds a threshold value, the electrostatic force on the deformed polymer drop can overcome the surface tension and thus a liquid jet is formed. This electrified jet then moves toward counter electrode, leading to the formation of a long and thin thread. As the liquid jet is continuously elongated and the solvent is evaporated, solid fibers with diameters as small as tens nanometers are deposited on the colletor.
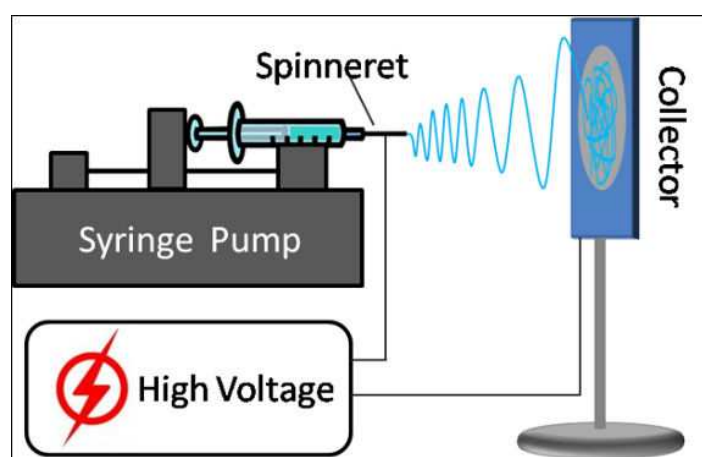

Figure 1. Schematic illustration of the basic setup of electrospinning.

In spite of the simple setup, there are a number of parameters that can greatly affect the morphology and diameter of electrospun fibers, including: (1) the intrinsic properties of solution such as the type of polymer, concentration, conductivity, and solvent volatility; and (2) the processing parameters such as the strength of the applied electric field, solution flow rate, and the distance between spinneret and collector [2, 10, 11]. In addition, the humidity and temperature of the surroundings may also play an important role in determining the morphology and diameter of electrospun fibers. Numerous experimental investigations and theoretical models have drawn some general relationships between these parameters and fiber morphology. For example, the higher applied voltage will lead to a larger fiber diameter, but this trend is not monotonic; the higher polymer concentration (higher viscosity) or faster flow rate usually results in the larger nanofiber diameters. In contrast, the increase of solution conductivity can significantly reduce the fiber diameter. These results are instructive to some extent in experiment design and predicting the resultant fiber morphology. However,

empirical knowledge is crucial because the ideal values of these parameters vary considerably with the polymer/solvent system.

3. Fabrication of nanofibers by electrospinning

Electrospinning has been proved to be a versatile method to prepare 1D nanomaterials of polymer, ceramics, metal, and metal oxide. Various functional elements, such as drugs, dyes, DNA, proteins, and nanoparticles, could be incorporated into electrospun nanofibers to form composite nanofibers. Additionally, except for the nanofibers with solid interior and smooth surface, nanofibers with various secondary structures, including core/sheath, hollow, and porous, could be fabricated by electrospinning. In this section, the preparation of electrospun nanofibers with different composition and secondary structures is introduced, and the parameters that control the composition and morphology are highlighted.

3.1. Electrospun nanofibers with different composition

In principle, almost all natural and synthetic polymers can be electrospun into their 1D nanostructures through judicious selection of solution and processing parameters [1]. Besides itself nanofibers, polymers can also be used as template or host to load nanoparticles or functional molecules. The produced composite nanofibers exhibit various electronic, optical, magnetic, and biological properties.

In order to incorporate nanoparticles into electrospun fibers, pre-synthetic Au [12], Fe_3O_4 [13], SiO_2 nanoparticles [14], CdTe quantum dots [15], and Au nanorods (AuNRs) [16] were introduced in polymer solution and then electrospinning was conducted. For example, AuNRs/poly(vinyl alcohol) (PVA) nanofiber was prepared by electrospinning the mixture solution of AuNRs and PVA [16]. The AuNRs were well aligned along the axis direction of the fibers due to the external fields (Fig. 2A). In a one-step method, silver nitrate was dissolved in poly(vinyl pyrrolidone) (PVP)/N, N-dimethylformamide (DMF) [17], or nylon 6/formic acid [18] solution, where DMF and formic acid acted as both a solvent for polymer and a reducing agent for the Ag^+ ion, followed by electrospinning to form Ag nanoparticle-filled composite nanofibers. In addition, the introduction of nanoparticles into polymer nanofibers have also been accomplished by adding appropriate precursors to the electrospinning solution, after that a chemical or physical method was used to reduce the metal precursor. For example, $PdCl_2$ and copolymers of acrylonitrile and acrylic acid (PAN-AA) are dissolved in DMF for electrospinning. And then, the fiber mat was immersed into diluted hydrazine water solution to reduce Pd cations [19]. The as-prepared Pd/PAN-AA composite material showed high catalytic activity toward hydrogenation of dehydrolinalool. Li et al. prepared Ag nanoparticle-loaded PAN nanofibers via electrospinning of PAN/$AgNO_3$-DMF solution followed by UV-irradiation photoreduction [20].

Carbon nanotubes (CNTs), an actively studied nano-object, can also be incorporated into electrospun fibers. The goal of most studies in this direction is to improve the electrical conductivity and mechanical strength of the fibers [21-25]. Some exciting properties were also

observed for CNT-incorporated polymer fibers, such as enhanced thermal stability [21], anisotropic electrical conductivity [24], and the preferential orientation of the CNTs along the fiber axis. These composite fibers can find promising applications in high strength membrane and electronics. Graphene, a single layer of aromatic carbon nanomaterial, has also been used as nanofiller in polymer nanofibers to reinforce the mechanical, electrical, thermal, and optical properties. For example, Bao et al. prepared graphene-poly(vinyl acetate) (PVAc) composite nanofibers by electrospinning [26]. The results indicated that the dispersity of pristine or functionalized graphene greatly influenced the morphology of fibers. When graphene modified by 1-pyrenebutanoic acid succinimidyl ester (G-PBASE) or 4-(2-(pyridin-4-yl)vinlyl) phenyl group (G-dye) was used as nanofillers, uniform and smooth nanofibers were readily obtained (Fig. 2B). In contrast, some micrometer-sized beads were formed when plain graphene oxide (GO) was used due to the poor dispersion of GO in the DMF solvent.

In addition to the nano-objects, drugs, dyes, proteins, DNA, virus, and other compounds can be readily incorporated into electrospinning solutions to produce functional fibers. For example, collagen could be electrospun into fibers from a solution of 1, 1, 1, 3, 3, 3-hexafluoro-2-propanol (HFP) [27, 28], or from a blend with poly(ethylene oxide) (PEO) [29]. Other proteins and enzymes, such as elastin [29], casein [30], α-chymotrypsin [31], bovine serum albumin (BSA) [32, 33], silk fibroin [34], lipase [30, 35], cellulose [36, 37], lysozyme [38, 39], glucose oxidase [40], luciferase [32], alkaline phosphatase and β-galactosidase [41], diisopropylfluorophosphatase [42], and lactate dehydrogenase [43], could only be processed by electrospinning as blends with synthetic polymers. The catalytic activity of encapsulated enzyme is usually lower than that of free enzyme, but more active than that in the cast membrane due to the higher surface area and porous structures of electrospun fibers. In addition, DNA molecules can also be encapsulated in electrospun fibers from blends with polymers [44, 45]. DNA molecules incorporated into electrospun nanofiber could reserve structurally intact and bioactive. More interestingly, virus could be used to fabricate 1D micro- and nanosized diameter fibers by electrospinning [46]. M13 virus was dispersed in HFP solution to form a homogeneous virus suspension, and then was directly electrospun into fibers (Fig. 2C). Due to the toxicity of HFP to the M13 virus, infectibility of M13 virus in HFP solution was dramatically decreased, showing no infectibility. In order to improve processing ability and preserve the intact viral structure and infecting ability, the M13 virus suspension was blended with a water soluble polymer PVP. Uniform fibers with the diameter of 100-200 nm could then be obtained.

For inorganic compounds, it is very difficult to directly process by electrospinning due to the strict requirement of solution viscoelasticity. Only a few types of inorganic fibers could be obtained by carefully selecting metallic precursors and solvents [47-49]. Recent studies demonstrated that the combination of electrospinning and sol-gel process could be used for direct producing inorganic fibers, for example TiO_2/SiO_2 and Al_2O_3 [50], SiO_2 [51], V_2O_5/SiO_2 [52], SiO_2/ZrO_2 [53]. The key point of this method was to control the hydrolysis rate of sol-gel precursors by adjusting the pH value or aging conditions. However, the fibers prepared via direct electrospinning of inorganic sols are usually several hundred nanometers in diameter with poor monodispersity, and only a limited number of materials can be prepared by this

method. In order to reduce the diameter of electrospun fibers, Li and Xia developed a new approach in which polymer was introduced into the sol-gel precursor to control the viscoelastic behavior, at the same time the sol-gel reaction was controlled to take place mainly in the spinning jet rather than in the stock solution [54-56]. In a typical procedure [55], a sol-gel precursor of titanium tetraisopropoxide (Ti(OiPr)$_4$) was mixed with PVP in alcohol solution. After the solution had been electrospun into a thin jet, the metal alkoxide immediately started to hydrolyze by reacting with the moistrure in air to generate a continuous gel network within the polymer matrix. As a result, TiO$_2$/PVP composite nanofibers would be obtained (Fig. 2D). These composite nanofibers could subsequently be converted into TiO$_2$ nanofibers without changing their morphology via calcinations at the elevated temperature (Fig. 2E). The average diameter of these ceramic nanofibers could be controlled in the range of 20-200 nm with relatively narrow size distribution by varying a number of parameters. This method has also been extended to process many other oxide ceramics into nanofibers. Similarly, a great number of metal oxide or sulfide nanofibers have been produced by electrospinning the solutions of appropriate metal precursors and polymers, followed by calcination at elevated temperatures. Electrospun metal oxide nanofibers could be further converted into continuous and thin metal nanofibers in reducing atmosphere, such as Cu [57, 58], Fe, Co, and Ni [59]. Shui and Li prepared long Pt nanowires with a few nanometers in diameter by electrospinning of H$_2$PtCl$_6$/PVP mixture solution and heat treatment [60]. A series of processing parameters were optimized to control the morphology and diameter of the nanowires. Very recently, Greiner's group prepared Au nanowires by electrospinning of highly concentrated aqueous dispersions of gold nanoparticles in the presence of PVA and subsequent annealing at 300-500 ℃ in air [61]. The produced Au nanowires represented solid structures like bulk gold (Fig. 2F). The electrospun metal nanofibers with ultrahigh aspect ratio and ultralow junction resistance are of great interest for foundational research and applications in nanoelectronics, fuel cells, and sensors.

Carbon fibers or nanofibers, which have many noticeable properties in mechanical strength, electrical conductivity, and special surface area, have been considered as one of the most important materials for modern science and technology. Various electrospun polymer nanofibers could be converted into carbon nanofibers, such as polyacrylonitrile (PAN), polyimide (PI), PVA, poly(vinylidene fluoride) (PVDF) and pitch. Inagaki et al. recently composed a review on the preparation of carbon nanofibers from electrospun polymer nanofibers [62]. Carbon precursors and the control of structure and texture in the resultant carbon nanofibers were highlighted.

3.2. Nanofibers with core/sheath structures

Nanofibers with core/sheath structures have many potential applications in microfluidics, photonics, and energy storage. Electrospinning provides a simple method for the large-scale fabrication of such nanofibers. Up to now, several methods have been developed to prepare core/sheath structured nanofibers by electrospinning. For example, in template-directed method, polymer fibers (template) were produced by ordinary electrospinning, and then the as-prepared fibers were coated with the shell component by various chemical and physical methods [63-67]. With the use of conventional single-nozzle electrospinning, it is also possible
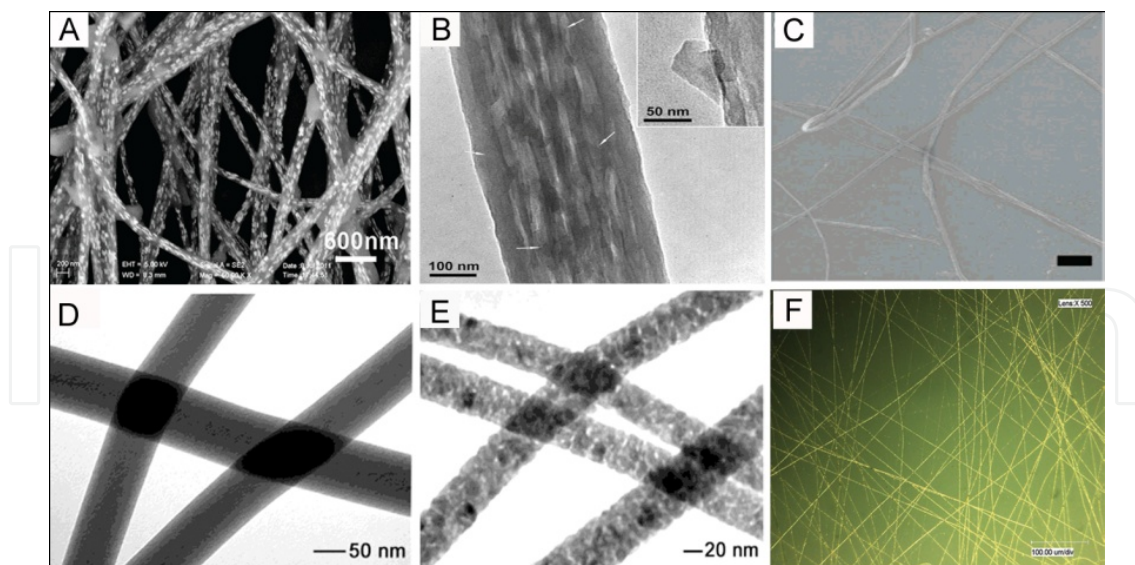
Figure 2. Electrospun nanofibers with different composition. (A) Typical backscattering SEM image of the AuNRs/PVA nanofibers [16]. (B) High-magnification TEM image of G-PBASE/PVAc nanofiber. The arrows indicate the graphene flakes inside the nanofiber. The inset shows an enlarged image of G-PBASE embedded in the sidewall of a PVAc nanofiber [26]. (C) SEM image of electrospun M13 virus-only fibers. (Scale bars: 5 μm) [46]. (D) TEM image of TiO$_2$/PVP composite nanofibers fabricated by electrospinning an ethanol solution that contained 0.03 g/mL PVP and 0.1 g/mL Ti(O*i*Pr)$_4$ [55]. (E) TEM image of TiO$_2$ nanofibers prepared by calcining (D) sample in air at 500 ℃ for 3 h [55]. (F) Optical microscopy image of gold nanowires on a mica slide, scale bar: 100 μm [61].

to prepare core/sheath nanofibers from emulsion or homogeneous polymer solutions. In the case of emulsion electrospinning, a core/sheath jet was formed in the electrospinning process due to the stretching and collapse of emulsion. This method has been used to prepare poly(methyl methacrylate) (PMMA)/PAN [68, 69], protein-methyl cellulose/poly(D, L-lactide) (MC/PDLLA) [39, 70], and PEO/poly(ethylene glycol)-poly(L- lactic acid) (PEG-PLA) (Fig. 3) [71] core/sheath nanofibers, and has the potential to extend to any pair of water-soluble polymer and hydrophobic (or amphiphilic) polymer. In the case of homogeneous solution electrospinning, the formation of core/sheath structure was mainly attributed to the phase separation of polymer blends, different solubility of the two components, and some other rheological factors [72-76]. The type of polymers, the ratios of components and the additives play key roles in the formation of core/sheath structures, rather than co-continuous morphologies. Recently, Jo et al. reported a one-step, single-nozzle electrospinning method for producing core-sheath nanofibers with cross-linked polymeric colloids as core and polymer as sheath (Fig. 4) [77]. Cross-linked PMMA colloids or poly(N-isopropylacrylamide) (PNIPAm) microgels were dispersed in a concentrated polymer solution, e.g. poly(ε-caprolactone) (PCL) in chloroform solution, for electrospinning. In the electrospinning process, fast evaporation of the solvent from the Taylor cone and following solution jet enhanced the phase separation of colloids from the condensed polymer solution, which resulted in a continuous colloidal packing at the inner region of fibers. If a small amount of colloids was used, the beanpod-like morphology of the nanofibers could be obtained; while a larger amount of colloids would lead to the colloids closely packing at the central area of the fibers, and core/sheath fibers consisting of a colloidal core could be produced.
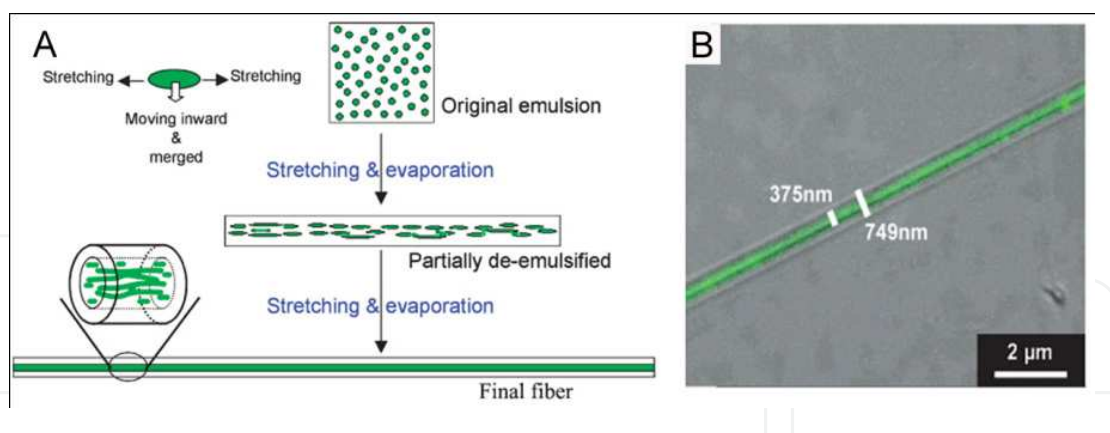
Figure 3. (A) Schematic mechanism for the formation of core/sheath composite fibers during emulsion electrospinning. (B) Confocal laser scanning microscope image of core/sheath structured PEO/PEG-PLA nanofiber prepared from W/O emulsions [71].
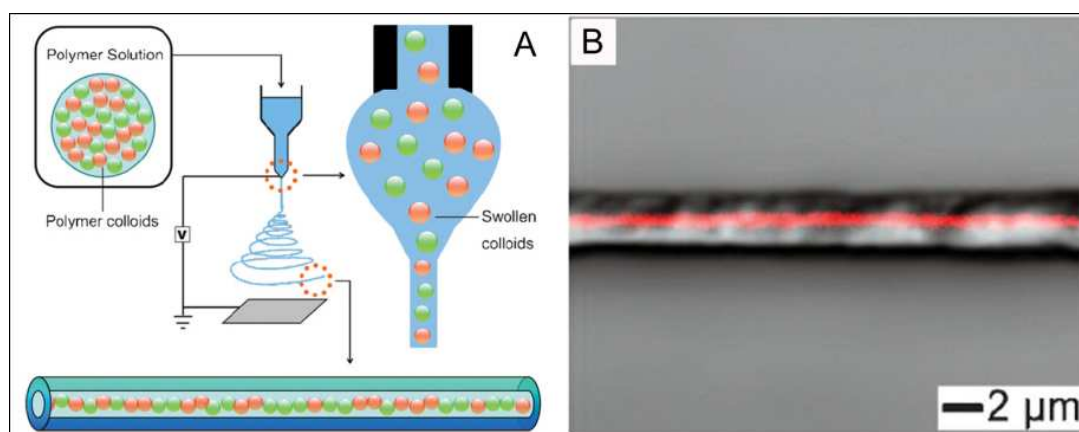

Figure 4. (A) Schematic illustration of the method for producing core/sheath nanofibers that contain an array of colloids in the core. (B) Combination of optical and fluorescent mode images of the core/sheath fiber, consisting of a PCL sheath and PNIPAm microgel particles in the core [77].

Coaxial electrospinning, in which coaxial two spinnerets replaced the single nozzle in the conventional setup for electrospinning, is a more convenient and direct method for the preparation of core/sheath structured nanofibers. Loscertales et al. initially designed a coaxial spinneret to generate steady core/sheath liquid jet from immiscible liquids [78]. However, in their experiment, the liquid jet was broke up to form core/sheath capsules, rather than fibers. Sun and co-workers overcame the instability problem in the coaxial electrospinning process to obtain continuous core/sheath jet, and then core/sheath polymer fibers [79]. The experimental setup for coaxial electrospinning is shown in Fig. 5A. It was proposed that undesirable mixing of the two polymer solutions could be prevented by the low diffusion coefficients relative to the fast stretching and solidification processes taking place in the electrospinning process. Core/sheath fibers with identical polymers PEO/PEO, or two different polymers polysulfone (PSU)/PEO could be obtained using this method. More importantly, non-spinnable solutions, such as poly(dodecylthiophene) (PDT) and $Pd(OAc)_2$, could also be used as core

components to obtain core/sheath structured PDT/PEO (Fig. 5B) and Pd/PLA composite fibers. Yu et al. detailedly studied the coaxial electrospinning process for producing fibers with smaller diameters and core/sheath structure from difficult-to process fluids [80]. They pointed out that the stabilization of the core fluid in the sheath against breakup into droplets were mainly accomplished through two mechanisms: (1) The viscoelastic sheath fluid could delayed or completely suppressed the Rayleigh instability (which resulted in the breakup of fluid jet into droplets) in the core fluid. In the electrospinning process, stretching of the sheath component imparted great elasticity to the interface due to strain hardening, further stabilizing the core fluid. (2) The sheath fluid also reduced the surface forces at the boundary of the core fluid by replacing the relatively high fluid-vapor surface tension typically present in single-fluid electrospinning by a lower fluid-fluid interfacial tension. Additionally, the fast travelling speed of fluids in electrospinning process prevented the two fluids from mixing significantly. Li and Xia also systematiclly investigated the coaxial electrospinning process by using two immiscible liquids of heavy mineral oil and an ethanol solution of PVP and Ti(OiPr)$_4$ as the materials for core and sheath [81]. They argued that rapid stretching of the sheath caused strong viscous stress, which would stretch the oil phase and elongate it along with the sheath solution via the mechanisms of viscous dragging and/or contact friction.
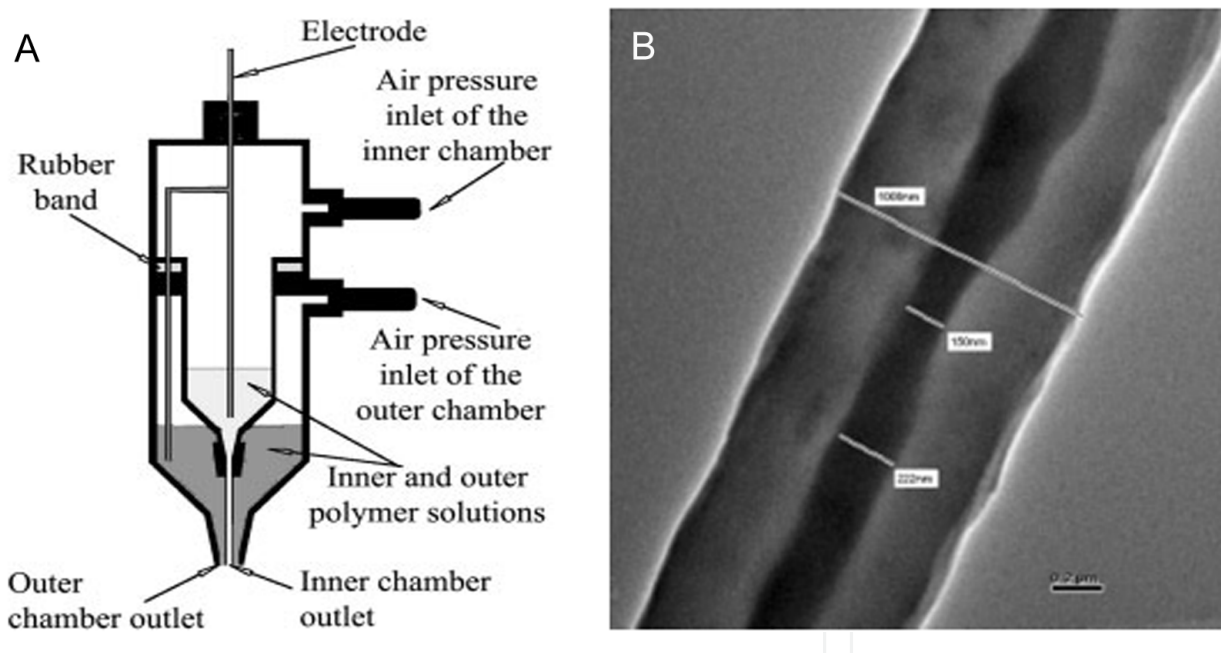

Figure 5. (A) Experimential setup used for coaxial electrospinning of core/sheath nanofibers. (B) TEM image of co-electrospun PEO (shell) and PDT (core) composite nanofibers [79].

With the development of theoretical and experimental aspects, this coaxial electrospinning method has been extended to prepare core/sheath fibers of various composition, such as gelatin/PCL [82, 83], poly(ethylene glycol) (PEG)/PCL [38], PCL/collagen [84], polyurethane/polycarbonate (PU/PC) [85], PCL/PEG [86], PVP/PDLLA [87], polypyrrole (PPy)/PVP [88], poly(lactide-co-glycolide) (PLGA)/chitosan [89], PVP/poly(L-lactide-co-epsilon-caprolactone) (PLCL) [90], dextran/PLCL [91], Alq3/PVP [92], poly(glycerol sebacate) (PGS)/gelatin [93],

poly(lactic acid) (PLA)/chitosan [94], PEO/chitosan [95], poly(L-lactide-co-caprolactone) (PLLACL)/collagen [96], and poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV)/chitosan [97]. Other functional components, for example, FePt nanoparticles [98], Si nanoparticles [99], multi-walled carbon nanotube (MWNT) [100], O_2 indicator (PtOEP) and γ-Fe_3O_4 [101], proteins [102], and drug molecules [103], have also been used as core components to fabricate core/sheath fibers. In combination of coaxial electrospinning and sol-gel process, inorganic fibers with core/sheath structures were also prepared, such as $LiCoO_2$/MgO [104], TiN/VN [105], $CoFe_2O_4$/$Pb(Zr_{0.52}Ti_{0.48})O_3$ [106], and SnO_2/TiO_2 [107].

3.3. Nanofibers with hollow structures

Tubular nanostructures with dimensions in the range of submicrometer to a few nanometers are of great interest for applications in catalysis, fluid transportation, drug release, sensing, and gas storage. Various methods have been demonstrated to fabricate such structures from a broad range of materials. Similar to the preparation of core/sheath nanofibers, electrospun nanofibers have been used as sacrificial templates for preparing tubular fibers. For example, Bognitzki and co-workers designed a method termed tubes by fiber templates (TUFT) process for fabricating nano- and mesotubes [108]. They selected electrospun PLA nanofibers as templates. Polymer, polymer-metal hybrid and metal tubes could be obtained after coating and removing the template fibers. In this template method, various coating techniques have been employed, such as chemical vapor deposition [108, 109], physical vapor deposition [108], sol-gel process [110], electrochemical deposition [111], in-situ polymerization [112], layer-by-layer assembly [113-115], vapor deposition polymerization [116], atomic layer deposition [117], and sputtering [118]. After the formation of core/sheath fibers, the templates could be removed by heat treatment [108-110, 117, 118], or solvent extraction [109, 111-116], to obtain tubular structures. Additionally, nanofibers with hollow interior could be prepared by using electrospun nanofibers as sacrificial templates without post-treatment process. For example, Te and Bi_xTe_{1-x} hollow nanofibers were directly synthesized by galvanic displacement reaction of electrospun Ni nanofibers at room temperature [119]. In general, additional coating and etching steps are required in these template methods, and the quality of the resultant tubes is strongly dependent on the control of each step.

Nanofibers with hollow structures were also prepared by single-nozzle electrospinning, followed by appropriate post-treatment. For example, ceramics or metal oxide tubes have been fabricated by calcining the composite fibers, which were produced by electrospinning the mixture solution of polymer and procursors. $LiNiO_2$ [120], CeO_2 [121], Y_2O_3-ZrO_2 [122], $LaMgAl_{11}O_{19}$ [122, 123], ZnO [124], MgO [125], TiO_2 [126], $BaFe_{12}O_{19}$ [127], SiO_2 [128], α-Fe_3O_4 and Co_3O_4 [129], Fe_2O_3 [130], $CoFe_2O_4$ [131], CuO and Cu [132], and SnO_2 [133] tubes have been prepared by this method. Several groups have systematically investigated the preparation process and proposed the formation mechanism of hollow fibers [120, 121, 129, 130, 133]. Cheng et al. [130] proposed that: In the electrospinning process, the evaporation of solvent would result in the formation of a gel layer on the surface of composite nanofibers, which has an important function to keep fiber texture during heat treatment. During heating, the gas produced by the decomposition of polymer would

diffuse through the fiber surface. Once the rate of gas release was larger than gas diffusion through the fiber surface, the pressure inside the fibers increased to be larger than that outside of the composite fibers; consequently, hollow fibers could be obtained. However, Xia and co-workers argued that polymer template and Kirkendall effect played an important role to build hollow fibers [133]. Vacancies generated by the diffusion of metal precursors to the fiber surface and the decomposition of polymers finally formed the hollow structures. Although the exact mechanism is ambiguous and not consistent, a necessary condition for the formation of tubular structures is that a rigid "skin" must form before the complete removal of polymer. In this method, the concentration of precursor, the ratio of precursor to polymer, the calcination temperature and heating rate significantly influence the morphology of the final products. In another single-nozzle electrospinning method, tetraethyl orthosilicate (TEOS) [134], PEO [135], or mineral oil [136] was introduced into the electrospinning solution to induce phase separation, and finally hollow fibers were obtained. Yu et al. prepared Sn nanoparticle encapsulated multichannel carbon microtubes by single-nozzle electrospinning process of tin octoate-PMMA-PAN in DMF emulsion and subsequent calcinations [137]. Because PAN solution is easier to stretch than PMMA/DMF fluid, thus a core-shell jet was formed and the subsequent formation of core-shell fibers. The as-collected electrospun fibers were stabilized in air at 250 ℃, leading to the thermal degradation of the core components to create SnO_2 nanoparticles encapsulated in porous hollow fibers. After carbonization under an Ar/H_2 atmosphere, the fibers were transformed into multichannel hollow porous carbon microtubes and SnO_2 was reduced to Sn nanoparticles.
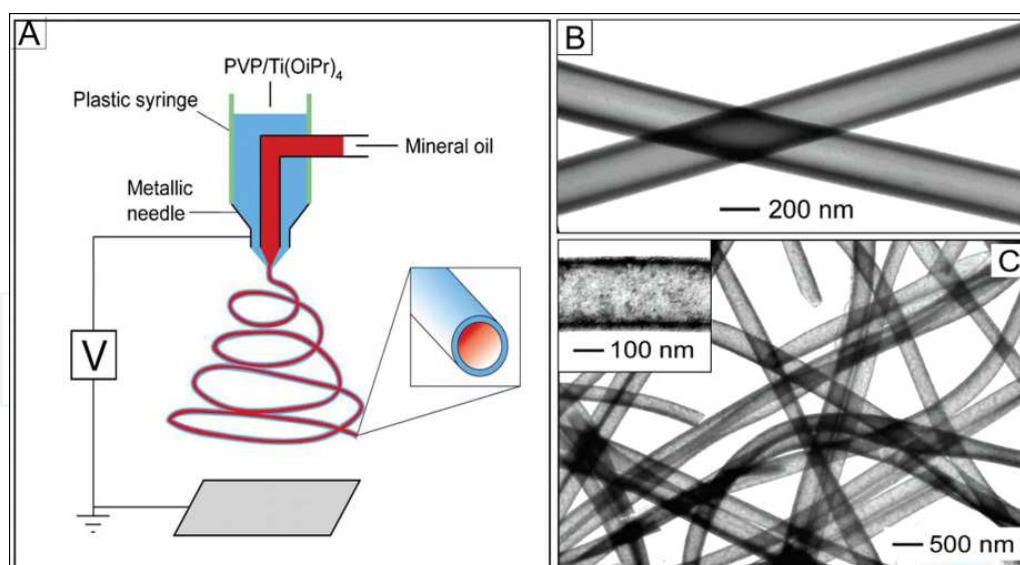

Figure 6. (A) Schematic illustration of the setup for electrospinning nanofibers with a core/sheath structure. The spinneret was fabricated from two coaxial capillaries, through which heavy mineral oil and an ethanol solution containing PVP and Ti(OiPr)$_4$ were simultaneously ejected to form a continuous, coaxial jet. (B) TEM image of two as-spun hollow fibers after the oil cores had been extracted with octane. The walls of these tubes consisted of amorphous TiO_2 and PVP. (C) TEM image of TiO_2 (anatase) hollow fibers that were obtained by calcining the composite nanotubes in air at 500 ℃ [81].

The studies in several groups have demonstrated that electrospinning could be directly utilized to prepare hollow nanofibers. For example, Li and Xia developed a coaxial electrospinning setup to fabricate ceramic hollow fibers by co-electrospinning viscous mineral oil as the core and a mixture ethanol solution of PVP and Ti(OiPr)$_4$ as the shell (Fig. 6A) [81]. The mineral oil was subsequently extracted to form amorphous TiO$_2$/PVP composite tubes (Fig. 6B). After calcination at elevated temperatures in air, hollow TiO$_2$ fibers were obtained (Fig. 6C). The wall thickness and inner diameter of the hollow nanofibers could be varied in the range from tens of nanometers to several hundred nanometers by controlling the processing parameters. The same group also demonstrated that functional nanoparticles (iron oxide, SnO$_2$, Au) or molecular species (dye, octadecyltri-chlorosilane) could be directly incorporated into the hollow interiors by pre-dissolving these functional materials into the core liquid [138]. Using a similar setup, Loscertales and co-workers prepared polymer-free SiO$_2$ and ZrO$_2$ tubes by co-electrospinning an aged inorganic sol and an immiscible (or poorly miscible) liquid such as olive oil or glycerin, followed by selective removal of the inner liquid [139]. Turbostratic carbon nanotubes with inner diameter of 500 nm and wall thickness of 200 nm could also be obtained via coelectrospin-ning of PAN and PMMA with subsequent thermal degradation of the PMMA core and finally carbonization of the PAN shell [140]. Besides the ceramics and carbon tubes, polymeric microtubes were also fabricated in a single step by using the co-electrospin-ning of two polymeric solutions [141]. In this approach, two mechanisms, fast evapora-tion of the shell solvent and contact with a nonsolvent, were responsible for the formation and stabilization of the microtubes. Using the coaxial electrospinning, hollow fibers with various composition have been prepared, such as zeolite [142], SiO$_2$ [143, 144], TiO$_2$ [145], LiNiO$_2$ [146], LiCoO$_2$ [147], BaTiO$_3$ [148], LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$-MgO [149], PMMA [150, 151], PC [151], poly(3-hydroxy butyrate) (PHB) [152], Sn@carbon nanoparticles encapsulated carbon [153], and carbon [154].

Except for the spinneret with two coaxial capillaries, tri-axial spinneret was also designed to fabricate hollow nanostructures. For example, Lallave et al. [155] prepared Alcell lignin hollow nanofibers by tri-axial spinneret co-electrospinning Alcell lignin solutions at room temperature without any added polymer. The outmost sheath flow of ethanol was used to avoid solidification of the Taylor cone. After stabilization and carbonization of the as-spun fibers at elevated temperatures, hollow carbon nanofibers were obtained. Zhao and co-workers developed a multifluidic compound-jet electrospinning technique to fabricate bio-mimic hierarchical multichannel microtubes (Fig. 7a) [156]. They used an ethanol solution of Ti(OiPr)$_4$ and PVP as outer liquid and paraffin oil as inner liquid. After a compound fluidic electrospinning process and removing the organics, TiO$_2$ three-channel tubes were obtained (Fig. 7b, c and d). With the rational design of the spinneret, tubes with two to five channels have been successfully fabricated. Such multichannel structure greatly improved photocatalytic activity of TiO$_2$ for degrading gaseous acetaldehyde due to a cooperative effect of trapping more gaseous molecules inside the channels and multiple reflection of incident light [157].
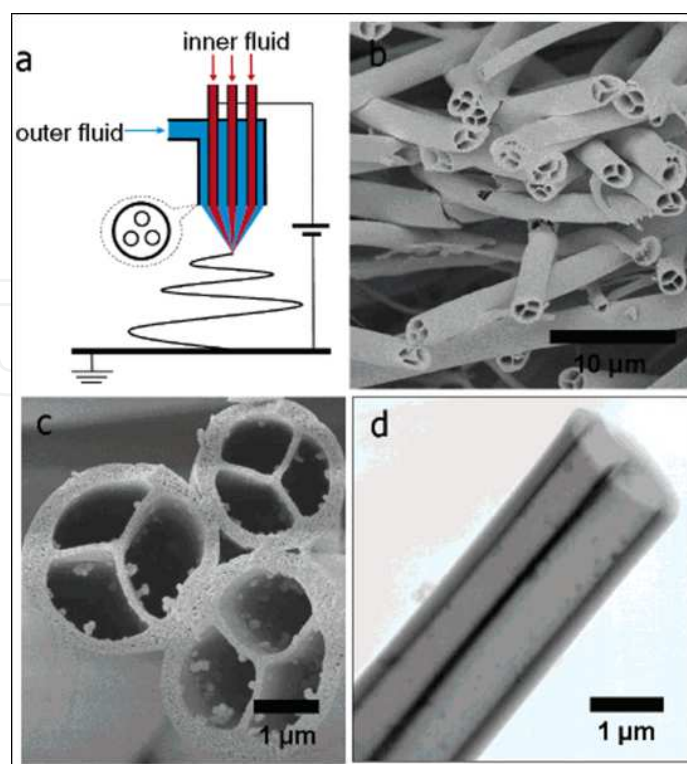
Figure 7. (a) Schematic illustration of the three-channel tube fabrication system. The immiscible inner and outer fluids were paraffin oil (red), and ethanol solution containing Ti(OiPr)$_4$ and PVP (blue). The inset shows the outlet section of the spinneret. (b) Side-view SEM image of sample after the organics have been removed. (c) Magnified SEM image of tubes in which the channels were divided into three independent flabellate parts by a Y-shape inner ridge. (d) TEM image of a three-channel tube; the individual channels of tube are straight and continuous [156].

3.4. Nanofibers with porous structures

Nanofibers with porous structures have excited immense interest because of their ultrahigh surface area, and thus potential applications in filtration, absorption, fuel cell, catalysis, tissue engineering, and sensors. Several methods have been reported for fabricating porous electro-spun nanofibers. In one method, phase separation was utilized to induce the formation of porous nanostructures in the electrospinning process. For example, Bognitzki et al. prepared porous polymer fibers of poly(L-lactic acid) (PLLA), PC, and polyvinylcarbazole by using dichloromethane as solvent [158]. For PLLA fibers, the average pore size is in the order of 100 nm in width and 250 nm in length with the long axis being oriented along the fiber axis (Fig. 8). The fast evaporation of solvent gave rise to local phase separation, and the solvent-rich regions transformed into pores during the electrospinning process. Rabolt's group systemat-ically investigated the influence of polymer/solvent properties on the fiber surface morphology [159]. A variety of solvents (tetrahydrofuran (THF), CS$_2$, toluene, THF/DMF) with different boiling points and vapor pressures were examined to prepare polystyrene (PS) fibers. It was found that a very high density of pores were observed on PS fibers electrospun from THF, while the microtexture and nanopores disappeared as substitution of THF with DMF. This result indicated that the volatility of the solvent significantly influenced the pore formation.

In addition to PS, the polymers including PMMA, PC, and PEO were also investigated. In general, electrospun PMMA fibers from $CHCl_3$ and THF exhibited a nanoporous surface texture. PC fibers electrospun from $CHCl_3$ showed elongated nanopores of about 100-250 nm, while those formed from THF exhibited irregular-shaped micropores with diameters of about 20 μm. However, no nanopores were observed on electrospun PEO fibers under any process-ing conditions. They also investigated the effect of humidity and molecular weight on the surface morphology of electrospun PS fibers from PS/THF solution [160]. They found that increasing humidity caused an increase in the number, diameter, shape, and distribution of the pores, and increasing the molecular weight of PS resulted in larger, less uniform shaped pores. From these systematic studies, they ascribed the formation of porous surface morphol-ogy to the combinative effect of both phase separation and breath figure formation. Dayal and co-workers studied experimentally and theoretically the formation of porous structures from electrospinning of $PMMA/CH_2Cl_2$ and PS/THF systems [161]. They proposed that the porous fibers were favored to form if the polymer/solvent system was partially miscible showing an upper critical solution temperature (UCST) envelope at the electrospinning temperature, especially if the solvent utilized were volatile and sensitive to moisture absorption. The pore size depends on various factors such as surface energy and the solvent evaporation rates. With the use of phase separation mechanism, ultrafine porous cellulose triacetate (CTA) fibers were also prepared by electrospinning CTA dissolved in CH_2Cl_2 or a mixed solvent of CH_2Cl_2/ethanol [162]. Similarly, PS fibers with micro- and nanoporous structures both in the core and/or on the fiber surfaces were prepared in a single process by varying solvent compositions (THF/DMF) and the concentration of PS solutions [163]. Porous polymer fibers of PLLA [164], PAN [165], and cellulose acetate [166] were also prepared by electrospinning with appropriate binary solvent system. The formation of porous structures was mainly due to the spinodal decomposition phase separation occurred during the electrospinning process.
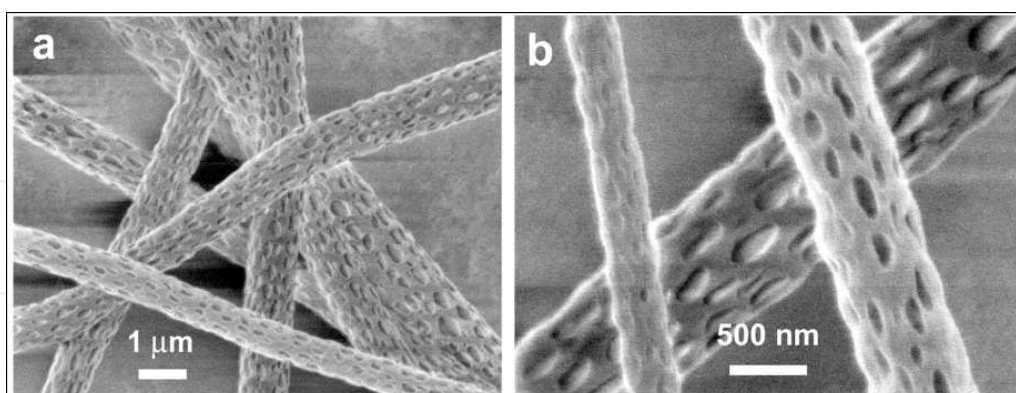

Figure 8. SEM micrographs of porous PLLA fibers obtained via electrospinning of a solution of PLLA in dichlorome-thane. a) Survey; b) Magnification [158].

In another method, porous nanofibers could be prepared by the selective removal of a component from nanofibers made of a composite or blend material. For example, the structural changes for fibers consisting of a PLA/PVP blend were investigated when one of the two components was selectively removed [167]. It was found that porous nanofibers were obtained

after selective removal of PVP by water extraction or PLA by annealing at elevated tempera-tures when equal amount of the two polymers were loaded into the electrospinning solution. However, the fibers remained compact without any alteration of the surface structure after removing the minor component when another component was the major one in the composite fibers. This morphological change was believed to result from the rapid phase separation and rapid solidification in the electrospinning process. Porous inorganic nanofibers of TiO_2 [55, 81], SiO_2 [168-170], SnO_2 [171, 172], $NaYF_4$:Yb_3, Er_3@silica [173], and $ZnCo_2O_4$ [174] have been fabricated by electrospinning the blend solutions of polymer and procursors, followed by selective removal of the polymer component. Porous polymer fibers, such as PEI [175], poly(glycolic acid) (PGA) [176], and PAN [177] were also prepared by electrospinning of a blend solution, followed by thermal degradation or solvent extraction of another component. Salts, such as $GaCl_3$ and $NaHCO_3$, were also introduced into the electospinning solution to induce porous structures after the removal of the salts [178, 179].

Xia's group reported a novel method to produce porous nanofibers by modifying the electro-spinning setup [180]. In this setup, the collector was immersed in a bath of liquid nitrogen. Porous polymer fibers can be obtained through thermally induced phase separation (TIPS) between the solvent-rich and solvent-poor regions in the fiber during electrospinning, followed by removal of solvent in vacuum. PS fibers with ~1 μm in diameter were obtained by using this method (Fig. 9A). Examination of the end of a broken fiber (inset) indicated that the fiber was porous throughout. It should be noted that the fibers prepared by this method had larger diameters than those prepared without the use of a liquid nitrogen bath. The reason is that the fibers were collected with a smaller distance between the spinneret and the liquid nitrogen (10 cm), which greatly weakened the size reduction caused by whipping and solvent evaporation. This method could be extended to prepare porous fibers from a variety of different polymers, such as PAN, PVDF, and PCL (Fig. 9B). Similarly, Pant et al. developed a water-bath electrospinning setup, and highly porous PCL fibers were prepared by electro-spinning from pure PCL, and its blends with methoxy poly(ethylene glycol) (MPEG) [181]. A simultaneous phase separation and dissolution of MPEG from electrospun PCL fibers caused the formation of porous structure during water-bath electrospinning.
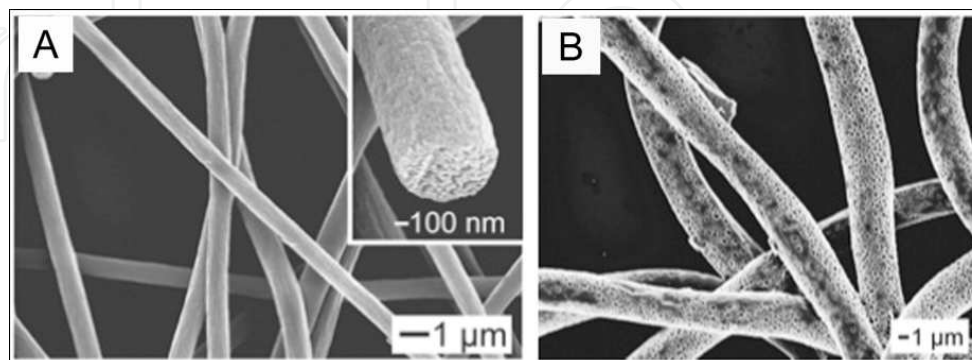

Figure 9. (A) SEM images of PS porous fibers prepared by electrospinning into liquid nitrogen, followed by drying in vacuum. The inset is a SEM micrograph of the broken end of a fiber at a higher magnification, showing that the fiber was porous throughout. (B) PCL fibers obtained by electrospinning into liquid nitrogen followed by drying in vacuum [180].

Porous carbonaceous materials have been widely used in gas storage, separation, purification, or as catalyst carriers, electrode materials for fuel cells, and electrochemical double-layer supercapacitors, because of their unique mechanical properties, heat resistance, chemical inertness, etc. Porous carbon nanofibers could be prepared by the combination of electrospinning and post-spun treatment. For example, PAN-based carbon fibers with porous structures have been fabricated by electrospinning the mixture solutions of PAN and other polymers, followed by removal of the polymer and carbonization of the remaining PAN [177, 182, 183]. Kim et al. prepared porous carbon nanofibers by the electrospinning of PAN solution containing zinc chloride [184]. Zinc chloride trapped in the electrospun PAN nanofibers acted as a dehydrating agent and thus enhanced the oxidation rate, affording a shortened stabilization time. During carbonization process, zinc oxide was formed and acted as the catalyst for creating micropores on the outer surface of carbon nanofibers by etching carbon atoms. Porous structures were also produced on carbon nanofibers during the stabilization and carbonization process by activation using chemical activation regents, such as zinc chloride [185], and KOH [186], or activation using SiO_2 nanoparticles [187-189].

3.5. Nanofibers with other secondary structures

In addition to the structures aforementioned, beaded, necklace-like, and ribbon nanofibers could be prepared by adjusting the processing and solution parameters for electrospinning. The beads formed in the electrospinning process were usually regarded as by-products, and the formation mechanism was studied by several groups [190, 191]. It was found that the viscoelasticity of the solution, charge density carried by the jet, and the surface tension of the solution were the key factors that influence the formation of the beaded fibers. Jin et al. fabricated necklace-like structure via electrospinning aqueous solution of PVA and SiO_2 particles [192]. The results indicated that the diameter of SiO_2 particles, the weight ratio of PVA to SiO_2, the voltage, and the relative content of $PVA/SiO_2/H_2O$ greatly influenced the morphology of electrospun fibers. Especially, the diameter of SiO_2 particles greatly influenced the morphology of produced fibers. For example, SiO_2 particles with diameter of 143 nm tended to aggregate into bunches in the fibers, while 265 and 910 nm SiO_2 particles tended to align along the fibers one by one, resembling necklaces. In addition to round nanofibers, electrospinning a polymer solution can produce thin fibers with a variety of cross-sectional shapes. Koombhongse and co-workers studied a series of polymer solutions, and various shaped fibers were observed, including branched fibers, flat ribbons, ribbons with other shapes, and fibers that were split longitudinally from larger fibers [193]. In the electrospinning process, a thin polymer skin was formed due to the rapid evaporation of the solvent. Following the escape of solvent inside the fibers, tube-like fibers were formed, which collapsed due to atmospheric pressure to create ribbon-like fibers. Branched fibers were formed by the ejection of smaller jets from the surface of the primary jets, while split fibers were obtained by the separation of a primary jet into two smaller jets. They proposed that fluid mechanical effects, electrical charge carried with the jet, and evaporation of the solvent all contributed to the formation of these special shaped fibers.

4. Application of electrospun nanofibers in electrochemical sensors

Electrospun nanofibers are featured with small diameter, extremely long length, high surface area and complex pore structure. As mentioned above, electrospinning has been applied to fabricate nanofibers with various compositions and secondary structures. These electrospun nanofibers readily assemble into three-dimensional membranes, which characterized as high porosity, interconnectivity, and a large surface-to-volume ratio, makes electrospun nanomaterials highly attractive to different applications, including sensors. Several reviews on the application of electrospun nanofibers in constructing sensors with different read-out mode and for different target were published in past several years [7-9, 194, 195]. Among various read-out modes, electrochemical read-out has attracted remarkable attentions in the ultrasensitive detection due to its high sensitivity and selectivity, inexpensive equipment and easy miniaturization. Various electrospun nanofibers, including polymer nanofibers, composite nanofibers, and metal or metal oxide nanofibers, have been used to prepare electrochemical sensors for a wide range of analytes. A summary of electrochemical sensors based on electrospun nanomaterials is illustrated in Table 1.

Materials	Fiber diameter (nm)	Analytes	Detection potential (V)	Linear Rang (µM)	Limit of Detection (µM)	Ref.
PVA	70-250	glucose	0.65	1000-10000	50	[40]
PVA/F108/AuNPs/Lac	~	4-CP	0.0	1-25	12.09	[196]
		2,4-DCP	-0.15	1-25	2.70	
		2,4,6-TCP	0.1	1-25	9.33	
nylon-6	95(RSD 27%)	glucose	~	1000-10000	6	[197]
nylon-6	~	glucose	0.70	1000-9000	2.5	[198]
nylon-6	~	glucose	0.50	1000-10000	6	[199]
nylon-6	~	pyrocatechol	-0.2	~100	0.05	[200]
PMMA/PANi-Au$_{nano}$	400-500	superoxide anion ($O_2^{\cdot -}$)	0.3	~	0.3	[201]
Pt/PANi	~	urea	-0.1	~20000	10	[202]
DNA/SWNT/PEO	50-300	glucose	0.5	~20000		[203]
PANCAA	~	glucose	0.8	0-7000	557	[204]
MWNT/PANCAA	~	glucose	0.8	0-7000	668	
PVDF/PAPBA	150	glucose	0.04	100-1600		[205]
nylon-6	140±15	cysteine	0.3	100-400	15	[206]
P$_2$W$_{18}$/PVA	~500	nitrite	-0.2	100-1500	0.96	[207]
CNF	200-500	NADH	0.45	0.02-11.47	0.02	[208]

Materials	Fiber diameter (nm)	Analytes	Detection potential (V)	Linear Rang (µM)	Limit of Detection (µM)	Ref.
CNF	200-500	DA	0.376	0.04-5.6	0.04	[209]
		UA	0.475	0.8-16.8	0.2	
		AA	0.200	2-64	2	
CNF	200-400	L-tryptophan	0.9	0.1-119	0.1	[210]
		L-tyrosine	0.8	0.2-107	0.1	
		L-cysteine	0.75	0.15-64	0.1	
CNF	200-400	xanthine	0.85	0.03-21.19	0.02	[211]
CNF	400-600	catechol	~	1-200	0.2	[212]
		hydroquinone	~	1-200	0.4	
CNF	100±25	glucose	0.2	~	~	[213]
Pd/CNF	200-500	H_2O_2	-0.2	0.2-20000	0.2	[214]
		NADH	0.5	0.2-716.6	0.2	
Pd/CNF	200-500	DA	0.402	0.5-160	0.2	[215]
		UA	0.550	2-200	0.7	
		AA	0.158	50-4000	15	
Pd/CNF	200-500	hydrazine	-0.32	10-4000	2.9	[216]
Pd/CNF	300-500	oxalic acid	1.07	200-13000 13000-45000	200	[217]
Ni/CNF	200-400	glucose	0.6	2 -2500	1	[218]
Ni/CNF	200-400	ethanol	0.55	250-87500	250	[219]
Rh/CNF	300-500	hydrazine	0.4	0.5-175	0.3	[220]
Pt/CNF	200-500	H_2O_2	0.0	1-800	0.6	[221]
ZnO	195-350	glucose	0.8	250-19000	1	[222]
Mn_2O_3-Ag	~	glucose	-0.45	~1100	1.73	[223]
Au	990±490	fructose	0.2	100-3000	11.7	[224]
Co_3O_4	105 ±10	glucose	0.59	~2040	0.97	[225]
CuO	90-240	glucose	0.4	6-2500	0.8	[226]
CuO	~2 µm	glucose	0.4	0.2 -600	0.0022	[227]
NiO	10 µm	glucose	0.5	1-270	0.033	[228]
Pd-CuO	90-140	glucose	0.35	0.2-2500	0.019	[229]
NiO-Ag	82.1± 13.8	glucose	0.1	~590	1.37	[230]
			0.6	~2630	0.72	
NiO-Au	width 580 ±44,	glucose	0.2	~2790	0.65	[231]
			0.6	~4550	1.32	

Materials	Fiber diameter (nm)	Analytes	Detection potential (V)	Linear Rang (µM)	Limit of Detection (µM)	Ref.
	thickness 60 ±21					
NiO-Pt	214±77	glucose	0.6	~3670	0.313	[232]
CuO-NiO	10 µm	glucose	0.5	3-510	0.001	[233]
NiO-CdO	~	glucose	0.6	~6370	0.35	[234]
Mn_2O_3	105	hydrazine	0.6	~644	0.3	[235]
CuO/Co_3O_4	150-350	fructose	0.3	10-6000	3	[236]
Hb	width ~2.5µm, thickness ~600 nm	nitrite H_2O_2	-0.65 -0.377	~4500 ~27	0.47 0.61	[237]
SWNTs-Hb	width ~2.5µm, thickness ~600 nm	TCA nitrite H_2O_2	-0.65 -0.65 -0.364	12-108 ~207 ~27.3	2.41 0.30 0.22	[238]
TiO_2-Pt	72.61±15.04	hydrazine	0.5	~1030	0.142	[239]
SiO_2@Au	~	H_2O_2	-0.4	5-1000	2	[240]

Table 1. Electrospun nanofibers based electrochemical sensors.

Abbreviations in the table: PVA: poly(vinyl alcohol); F108: PEO-PPO-PEO; Lac: laccase; 4-CP: 4-chlorophenol; 2, 4-DCP: 2, 4-dichlorophenol; 2, 4, 6-TCP: 2, 4, 6-trichlorophenol; PMMA: Poly(methyl methacrylate); PANi: polyaniline; PEO: poly(ethylene oxide); PANCAA: poly(acrylonitrile-co-acrylic acid); SWNT: Single-walled carbon nanotube; MWNT: Multi-walled carbon nanotube; PVDF: poly(vinylidene fluoride); PAPBA: poly(aminophenyl boronic acid); P_2W_{18}: α-$K_6[P_2W_{18}O_{62}]$ 14H_2O; CNF: carbon nanofiber; Hb: hemoglobin; TCA: trichloro-acetic acid.

4.1. Polymer nanofibers based electrochemical sensors

Since the first enzyme-based electrochemical biosensor was proposed by Clark and Lyons [241], numerous efforts have been afforded in this direction because of the simplicity and high selectivity of enzyme electrodes. The immobilization of enzymes on a suitable matrix and their stability are important factors in the fabrication of biosensors. Several methods have been developed for immobilization of enzymes, including physical adsorption, cross-linking, self-assembly, as well as entrapment in polymers or sol-gels. Due to the merits of high specific surface area and porous structure, electrospun polymer fibers would be a promising biocom-patible material for enzyme immobilization [1]. For example, Ren and co-workers prepared a

glucose biosensor by electrospinning a solution of glucose oxidase (GOx) and PVA, and directly collecting the fibers on a electrode [40]. Then GOx was immobilized by cross-linking the electrospun PVA/GOx composite membranes with glutaraldehyde. The immobilized GOx remained active inside the electrospun PVA fibrous membranes after the harsh process of electrospinning. The apparent Michaelis-Menten constant (K_M^{app}) for this biosensor was determined to be 23.66 mM. Liu et al. developed laccase (Lac) biosensor for the determination of phenolic compounds by in situ electrospinning of a mixture of PVA, Lac, PEO-PPO-PEO (F108) and Au nanoparticles, where F108 was used as an enzyme stabilizing additive and Au NPs were used to enhance the conductivity of the biosensor [196]. Under the optimal conditions, the biosensor showed a sensitivity following the order of 2, 4-dichlorophenol (2, 4-DCP) > 2, 4, 6-trichlorophenol (2, 4, 6-TCP) > 4-chlorophenol (4-CP). The obtained K_M^{app} values were 426.06, 9.41 and 73.36 μM for 4-CP, 2, 4-DCP and 2, 4, 6-TCP, respectively. The results indicated that Lac encapsulated into electrospun nanofibers retained its high catalytic activity. The sensing performance of this biosensor was attributed to the suitable electrochemical interface (e.g. biocompatibility, high surface area-to-volume ratio and superior mechanical properties) of PVA/F108/Au NPs/Lac.
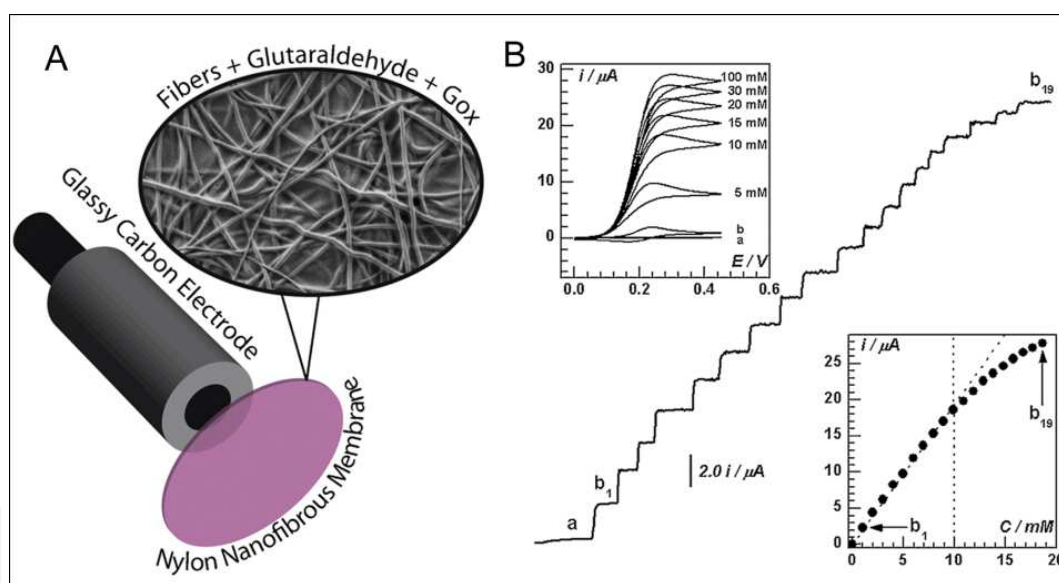

Figure 10. (A) Schematic picture of the nylon nanofibrous biosensing unit coupled with a glassy carbon electrode. Also shown a scanning electron microscopy detail of the nanofibrous structure. (B) Response current of nylon nanofiber-based glucose biosensors after the addition of glucose (1 mM each). Detection potential, + 0.5 V vs. Ag/AgCl. Supporting electrolyte, 0.1 M PBS (pH 6.5) containing 0.1 mM ferrocene methanol. Inset (bottom-right) shows the corresponding calibration plot. Inset (top-left) shows the catalyzed electrochemical oxidation of glucose mediated by ferrocene methanol, where curve a and b are the cyclic voltammograms (CVs) of the blank and of the ferrocene methanol (0.1 mM) in the absence of glucose. Other CVs are obtained upon addition of glucose from 5 to 100 mM. In all the CVs, scan rate=0.02 V s⁻¹; 0.1 M PBS (pH 6.5) [199].

In addition to the direct incorporation of enzyme into polymer nanofibers, post-spun modification is a widely used method for constructing enzyme-based biosensors. Mannino's group developed glucose biosensors by using electrospun nylon-6 nanofibrous membranes (NFM) as the enzyme immobilization matrix [197-199]. A piece of NFM was placed over the electrode

surface and secured with an o-ring (Fig. 10A). The highly porous morphology of the NFM allowed the analytes to diffuse toward the transducer, while the proteins might be retained by physical or chemical bonding with its large available surface. With the presence of mediator (ferrocene methanol) in the detection cell, a linear current response of this biosensor was obtained in the range of 1-10 mM, with detection limit of micromole-level (Fig. 10B). The K_M^{app} value for the immobilized GOx was 17 mM, which was greater than that obtained for homogeneous enzyme catalysis, but was comparable to that of GOx covalently bound to nylon [199]. These results indicated that this NFM provided favorable environment for the immobilization of GOx enzyme. Additionally, the nylon nanofibers membrane was also used to immobilize tyrosinase and construct an amperometric biosensor for the detection of phenolic compounds [200]. This biosensor showed excellent performance in respect to sensitivity, selectivity and reproducibility. Santhosh et al. developed an electrochemical sensor for the detection of superoxide anion ($O_2^{\cdot-}$) based on Au nanoparticles loaded PMMA-polyaniline (PANi) core-shell electrospun nanofiber membrane [201]. This membrane provided high surface area and porous structure for effective immobilization of superoxide dismutase (SOD), as well as offered excellent biocompatible microenvironment for SOD. Direct electron transfer was achieved between SOD and the electrode with an electron transfer rate constant of 8.93 s^{-1}. Jia et al. prepared a urea biosensor based on Pt nanoflower/PANi nanofibers [202]. PANi nanofibers were prepared by in situ polymerization of aniline on an electrospun PAN nanofiber template in an acidic solution with ammonium persulfate as the oxidant. Pt nanoflowers were further electrodeposited onto the PANi nanofibers backbone by cyclic voltammetry. Then, urease was physically adsorbed on the Pt/PANi modified electrode, followed with Nafion entrapment. This biosensor was applied for the sensitive urea detection in a flow injection analysis (FIA) system.

Carbon nanotubes (CNTs) have become the subject of intense investigation due to their remarkable electrical, chemical, mechanical and structural properties. Recent studies have demonstrated that CNT could greatly promote the electron-transfer reaction of proteins [242]. Therefore, CNT-filled electrospun nanofibers as matrix for the immobilization of enzyme are expected to further improve the analytical performance of enzyme electrode. Liu et al. prepared CNT-filled composite nanofibers by electrospinning DNA/SWNT/PEO blended suspension [203]. The noncovalent binding of DNA to the sidewalls of SWNTs was used to highly disperse SWNTs in the solution. The DNA/SWNT/PEO composite nanofibers were deposited on Pt-coated glass slides, and then directly used as substrate electrode for immobilization of GOx. This biosensor displayed the direct electrochemistry of GOx, suggesting that GOx immobilized on the nanofibers still maintained its electrochemical properties and the composite nanofibers promoted the electron transfer between the electrode and the redox center of enzyme. Nanofibrous membranes filled with multiwalled carbon nanotube (MWNT) were also electrospun from the mixture of poly(acrylonitrile-co-acrylic acid) (PANCAA) and MWNTs [204]. These nanofibrous membranes were directly deposited on Pt electrodes for the fabrication of glucose biosensors. Glucose oxidase (GOx) was covalently immobilized on the membranes through the activation of carboxyl groups on the PANCAA nanofiber surface. Compared with PANCAA nanofiber membrane, MWNT-filled PANCAA nanofiber membrane enhanced the maximum current response, while the electrode response time was

delayed. The MWNT filling also increased the K_M^{app} value, indicating that the secondary structure of immobilized GOx was disturbed.

Although good selectivity and high sensitivity were obtained with these enzyme-based biosensors, inevitable drawbacks such as the chemical and thermal instabilities originated from the intrinsic nature of enzymes as well as the tedious fabrication procedures might limit their analytical applications. Therefore, it is desirable to develop sensitive and selective non-enzymatic sensors. Manesh et al. prepared a non-enzymatic glucose sensor based on the composite electrospun nanofibrous membrane of PVDF and poly(aminophenyl boronic acid) (PAPBA), which was collected on indium tin oxide (ITO) glass plate [205]. The smaller size of PVDF/PAPBA nanofibers provided a large number of active sites for sensing action and the boronic acid groups in PAPBA were the sources for the preferential selectivity and sensing of glucose. The sensor retained 90% of the original activity after 50 days repeated usage and storage at 4 ℃, indicating an excellent long-term stability.

Scampicchio et al. studied the protective properties of nylon-6 nanofiber membrane against fouling and passivation of the carbon working electrode [243]. For example, the polyphenols oxidation usually results in the severe passivation of carbon electrode due to the adsorption of analytes or reaction intermediates. However, no voltammetric waves appeared at the nylon-6 nanofiber membrane coated electrode for the flavonoids (quercetin, myricetin and cathechin) oxidation. On the contrary, when phenol acids (caffeic, synapic, syringic, vanillic and gallic acid) were used, their typical oxidation waves emerged. Therefore, nylon-6 nano-fiber membrane could be used as a selective barrier to preserve the active surface of the electrode from passivation of flavonoids and to construct sensors with high selectivity. Furthermore, this protective nylon-6 nanofiber membrane was used to adsorb MWNTs and construct a sensor for the electrochemical detection of sulfhydryl compounds [206]. The membrane was easily peeled off, leaving the bare electrode surface back to its original electrochemical behaviour. Preliminary experiments indicated that the membrane coating protected the bare electrode from the passivation occurred during oxidation of cysteine. Cao and co-workers prepared a nitrite sensor based on polyoxometalate hybrid nanofibers, which was fabricated by electrospinning of a mixture of PVA and α-$K_6[P_2W_{18}O_{62}]$ $14H_2O$ (P_2W_{18}) onto the surface of an ITO electrode [207]. After thermal crosslinking at 135 ℃ for 24 hours, the P_2W_{18} hybrid nanofibers were insoluble in aqueous solutions even after a period of 24 hours, which ensured the electrochemical stability of the hybrid nanofiber-modified ITO electrode. This P_2W_{18} hybrid nanofiber modified electrode presented excellent electrocatalytic activity toward the reduction of nitrite, which could be attributed to the large electroactive surface area of the P_2W_{18} hybrid nanofibers.

4.2. Carbon nanofiber based electrochemical sensors

Carbon nanofibers (CNFs), a unique 1D carbon nanomaterial, have attracted great interests due to their high mechanical strength and excellent electric properties similar to carbon nanotubes (CNTs), but larger surface-active groups-to-volume ratio than that of the glassy-like surface of CNTs [244]. CNFs can be used as immobilization matrixes for biomolecules, while at the same time they can relay the electrochemical signal acting as transducers.

Therefore, a great number of CNF-based sensors or biosensors have been developed [245]. In combination with the carbonization process, electrospinning has been actively exploited as a valuable and versatile method for preparation of CNFs with the controllable structure and texture [62]. As a result, electrospun CNFs or their composite materials are expected to be a promising material for constructing ultrasensitive electrochemical sensors.

Our group has successfully prepared CNFs by electrospinning, followed by stabilization and carbonization processes. These electrospun CNFs were directly used to modify carbon paste electrode (CNF-CPE) and construct a sensor for mediatorless detection of NADH (Fig. 11) [208]. This electrochemical sensor showed low detection limit down to nM-level, wide linear range and good selectivity for determination of NADH in the presence of ascorbic acid (AA). CNF-CPE was also employed for the simultaneous determination of AA, dopamine (DA), and uric acid (UA) by using differential pulse voltammetry (DPV) method [209]. Three well-defined peaks with remarkably increased peak current could be achieved at the CNF-CPE. Low detection limits of 0.04 μM, 2 μM and 0.2 μM for DA, AA and UA were obtained. Some oxidizable amino acids such as L-tryptophane, L-tyrosine and L-cysteine play important roles in many biochemical processes. However, the determination of these amine acids usually suffers from high overpotential and poor reproducibility. We found that the electrospun CNF modified electrode displayed high electrocatalytic activity toward the oxidation of these amino acids with enhanced peak currents and low overpotentials [210]. This sensor showed excellent analytical performance for the detection of the three amino acids. In addition, electrospun CNF modified electrode was also used for non-enzymatic electrochemical detection of xanthine [211], and simultaneous determination of dihydroxybenzene isomers (catechol and hydroquinone) [212]. These sensors exhibited high sensitivity, stability and selectivity, as well as good anti-fouling properties. The practical application of these sensors for determining the target analytes was evaluated, and satisfactory results were obtained. Recently, we fabricated a novel composite electrode by mixing the electrospun CNF with the ionic liquid 1-butyl-4-methyl-pyridinium hexaflurophosphate (PFP) [246]. This CNF/PFP electrode exhibited strong current response and low background noise at the studied composite ratio. When used as electrochemical sensor, it showed high sensitivity and good selectivity for simultaneous detection of DA, AA and UA, guanine and adenine, as well as high signal-to-noise ratio (S/N) and good stability for amperometric detection of NADH under physiological conditions.

Recently, Lee's group prepared porous carbon nanomaterials by electrospinning, thermal treatment and activation process, and then constructed GOx-based glucose biosensors [213, 247, 248]. Silica nanoparticles with average size of 16±2 nm were used as physical activation agent. It was found that micro- and mesopores were induced through the physical activation process, which increased the specific surface area by over 42-fold compared to the untreated materials [247]. These carbon nanomaterials were also treated by oxyfluorination at 1 bar for 5 min using a mixed gas of oxygen and fluorine to introduce hydrophilic functional groups. After the activation and oxyfluorination treatment, the GOx immobilization was maximized by enlarged sites of carbon electrode and improved interfacial affinity between the carbon surface and the GOx. Subsequently, high sensitivity was obtained for this glucose sensor. They also investigated the influence of carbonization temperature on the carbon structure, and
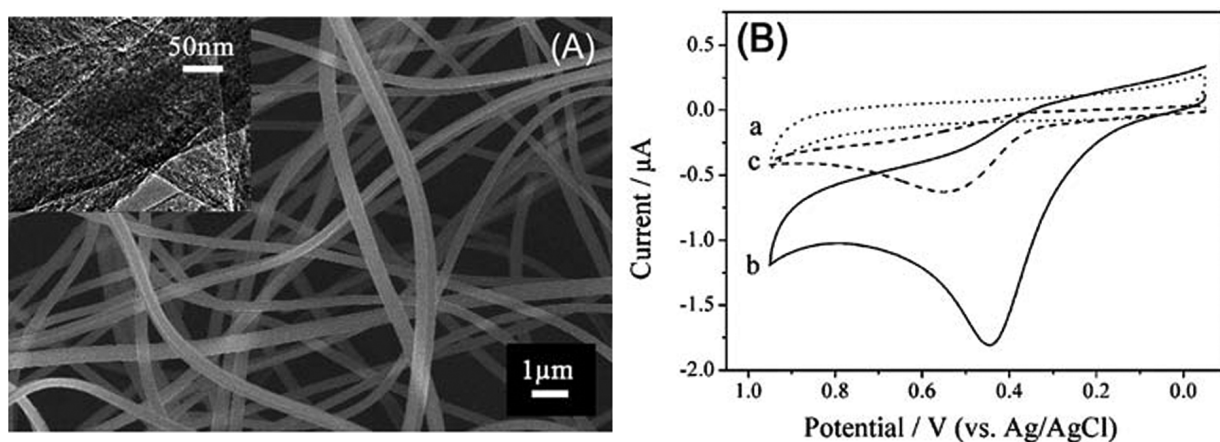
Figure 11. (A) SEM image of electrospun CNFs. Inset shows TEM image of CNFs. (B) CVs of 0.1 M PBS (pH 7.0) a) plain and b) containing 1 mM NADH at the CNF-CPE; c) Corresponding CV of (b) with the CPE. Scan rate: 50 mV s^{-1} [208].

subsequent analytical performance [213]. Raman spectra indicated the crystallization and orientation of the carbon fibers was improved with the increase of carbonization temperature. The electrical conductivity was also improved after heat treatment at higher temperature. The sample treated at 2473 K showed the highest sensitivity for glucose detection among the tested samples, which was ascribed to the high porosity, crystallization and orientation of the carbon structure. Additionally, CNTs were used as an electrically conductive additive to prepare CNT-embedded carbon fibers [248]. Combined with physical activation and oxyfluorination treatment, the prepared glucose sensor showed improved sensitivity and rapid response time as a result of more efficient GOx immobilization and electron transfer.
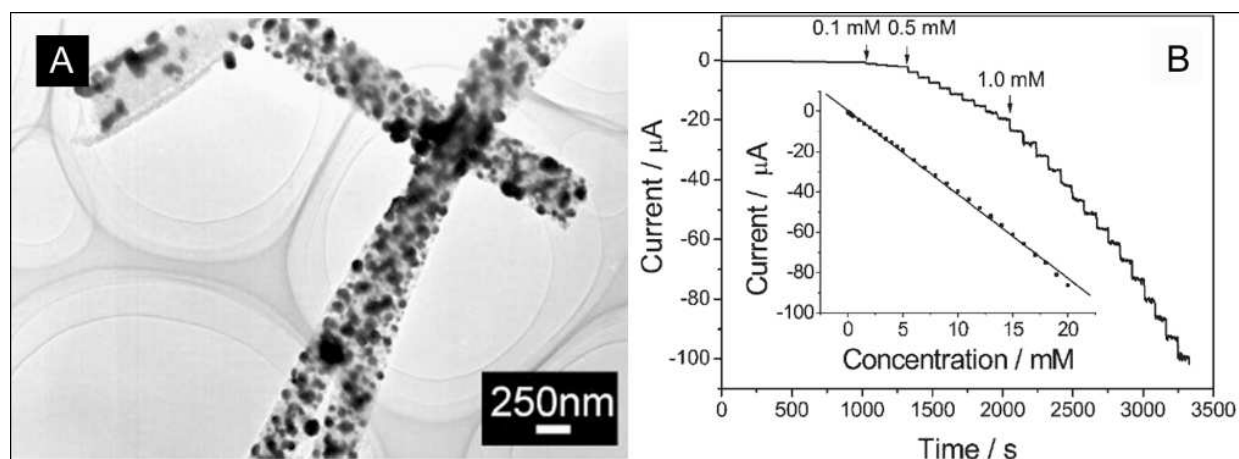

Figure 12. (A) Typical TEM image of Pd/CNF nanocomposites; (B) Current-time responses of the Pd/CNF-CPE on successive injection of specific concentration of H_2O_2 into N_2-saturated PBS (0.1 M, pH 7.0), inset shows the calibration curve for H_2O_2 concentration between 0.2 μM and 20 mM [214].

Metal nanoparticle/CNF nanocomposites have received great attention in catalysis, fuel cell, and chemical/biological sensing applications. In conventional synthesis method, CNFs usually suffer from harsh oxidation or modification with polymers in order to realize

selective deposition of metal nanoparticles on the surface of CNFs. These surface function-alization approaches provide efficient avenues for the deposition of metal nanoparticles, but tend to degrade the mechanical and electronic properties of CNFs because of the introduction of a large number of defects or polymer shell. Electrospinning provided a simple and efficient method to prepare metal nanoparticle/CNF nanocomposites with high quality and purity. Recently, palladium nanoparticle-loaded carbon nanofibers (Pd/CNFs) were synthesized by the combination of electrospinning, reduction and carbonization processes [214]. The metallic Pd nanoparticles were well-dispersed on the surface or completely embedded into CNFs (Fig. 12A), which rendered the Pd nanopatticles high stability and resistance to the aggregation and desquamation. Pd/CNF-modified electrode exhibited high electrocatalytic activities towards the reduction of H_2O_2 and the oxidation of NADH. For H_2O_2, the Pd/CNF-modified electrode displayed a wider linear range from 0.2 μM to 20 mM with a detection limit of 0.2 μM at -0.2 V (Fig. 12B), and the detection was free of interference from the coexisted AA and UA. In the case of NADH, the linear range at the Pd/CNF-modified electrode was from 0.2 μM to 716.6 μM with a detection limit of 0.2 μM at 0.5 V. The high sensitivity, wide linear range, good reproducibility, and the minimal surface fouling make this Pd/CNF-modified electrode a promising candidate for amperometric H_2O_2 or NADH sensor. Pd/CNFs modified electrode also displayed excellent electrocatalytic activities towards DA, UA and AA [215]. The oxidation overpoten-tials of DA, UA and AA were decreased significantly compared with those obtained at the bare electrode. Due to the different extent of the peak potential shift, these three com-pounds could be determined simultaneously by CV or DPV at the Pd/CNF modified electrode. The Pd/CNF composite materials were also applied for the detection of hydra-zine and oxalic acid with attractive analytical performances [216, 217]. Nickel nanoparticle-loaded carbon nanofibers (NiCF) were also fabricated by using the similar method to that of Pd/CNF [218]. NiCF paste (NiCFP) electrode exhibited excellent electrocatalytic perform-ance for the oxidation of glucose. The amperometric responses of the NiCFP electrode to glucose showed a linear range from 2 μM to 2.5 mM with the detection limit of 1 μM at the applied potential of 0.6 V. The proposed electrode, featured with good resistance to surface fouling and high operational stability, could be used as a promising nonenzymat-ic glucose sensor. The NiCFP electrode also showed high electrocatalytic activity toward the ethanol oxidation, and was used as enzyme-free ethanol sensor [219]. The detection exhibited high response, good stability and acceptable reproducibility. Similarly, Hu et al. prepared rhodium nanoparticle-loaded carbon nanofibers by electrospinning [220]. Rh nanoparticles with the diameter of 30-70 nm were uniformly distributed on the CNF surface. This nanocomposite was used for determination of hydrazine with high sensitivity and selectivity. Very recently, a Pt nanoparticle-loaded electrospun carbon nanofiber electrode was prepared by a simple wet-chemical method [221]. CNF paste electrode was firstly prepared using electrospun CNFs, then it was immersed into H_2PtCl_6 solution to adsorb $[PtCl_6]^{2-}$. After that, HCOOH was added to reduce the metal precursors. Large amounts of Pt nanoparticles could be well deposited on the surface of the electrospun CNF electrode without using any stabilizer or pretreatment procedure. In application to electrochemical

sensing platform, the Pt/CNF electrode exhibited high sensitivity and good selectivity for amperometric detection of H_2O_2.

4.3. Metal/metal oxide nanofiber based electrochemical sensors

Electrospinning has been proved to be a simple method for large-scale producing metal or metal oxide nanofibers. One of the most important applications of these nanomaterials is to develop their potential in chemical sensing or biosensing, profiting from their small size, large surface-to-volume ratios and high aspect ratios. Reliable and fast determination of glucose is of considerable importance in biotechnology, clinical diagnostics and food industry. Up to now, numerous electrospun metal/metal oxide nanofiber based glucose sensors or biosensors have been reported. For example, Ahmad and co-workers prepared an amperometric glucose biosensor based on a single ZnO nanofiber which was produced by electrospinning of PVP/zinc acetate mixture solution and subsequent high-temperature calcination [222]. A single ZnO nanofiber was transferred on Au electrode and functionalized with GOx via physical adsorption. The K_M^{app} value was estimated to be 2.19 mM, indicated that the immobilized GOx possessed a high enzymatic activity. Huang et al. fabricated highly porous Mn_2O_3-Ag nanofibers by a two-step procedure (electrospinning and calcinations) [223]. The as-prepared Mn_2O_3-Ag nanofibers were employed as the immobilization matrix for GOx to construct oxygen-reduction based glucose biosensor. The Mn_2O_3-Ag nanofibers could effectively mediated the direct electron transfer between the electroactive center of GOx and the electrode. This biosensor displayed good analytical performance for glucose detection due to the merits of this porous nanofiber, such as high surface area for enzyme loading, and high electrocatalytic activity toward the reduction of oxygen. Recently, electrospun Au nanofiber based biosensor for the detection of fructose and glucose was also developed by Russell's group [224]. The gold fibers were prepared by electroless deposition of gold nanoparticles on an electrospun PAN-HAuCl$_4$ fiber. Fructose dehydrogenase was covalently coupled to the Au fiber surface through glutaraldehyde crosslink to a cystamine monolayer. The enzyme exhibited mediated electron transfer directly to the gold electrode, and catalytic currents characteristic of fructose oxidation in the presence of a ferrocene methanol mediator were observed. This fructose sensor could also be used to determine glucose by using glucose isomerase to convert glucose to fructose.

Compared with the enzyme-based glucose biosensors, nonenzymatic glucose sensors are preferential because they avoid the problem of enzyme denature and intricate enzyme immobilization process. The nonenzymatic electrochemical glucose sensors significantly depend on the properties of electrode materials, on which glucose is oxidized directly. Various electrospun metal oxide nanofibers have been used to construct nonenzymatic glucose sensors. For example, Ding et al. fabricated Co_3O_4 nanofibers by electrospinning and subsequent calcination [225]. The as-prepared Co_3O_4 nanofibers were applied to construct a non-enzymatic sensor for glucose detection in alkaline solution. The catalytic property of the as-prepared Co_3O_4 nanofibers towards glucose oxidation was related to CoOOH and CoO_2. The negatively charged Co_3O_4 nanofibers surface could strongly repel

the negatively charged UA and AA molecules, thus resulting in good selectivity. Other metal oxide nanofibers, such as CuO [226, 227], and NiO [228] were also prepared by using the similar method and used for nonenzymatic detection of glucose. The direct glucose detection on these metal oxide nanofiber modified electrodes usually carried out in alkaline electrolyte and mediated by $Ni(OH)_2/NiO(OH)$ or $Cu(OH)_2/CuO(OH)$ redox couples. The study also demonstrated that the content of metal precursor in the electrospinning solution and the calcination temperature greatly influenced the morphology and catalytic activity of the produced nanomaterials [227, 228]. In contrast to the monometallic nanomaterials, bimetallic ones usually show enhanced electrocatalytic activity due to the synergistic effect. Wang et al. initially prepared electrospun palladium (IV)-doped CuO composite nanofiber based non-enzymatic glucose sensors [229]. The as-prepared nanofibers had a rough surface and consisted of the agglomeration of oxide nanoparticles with average size of about 40 nm. This sensor exhibited high sensitivity for the determination of glucose with the detection limit of 19 nM. Following a facile two-step synthesis route of electrospinning and calcination, Ding and co-workers prepared NiO-Ag hybrid nanofibers, NiO nanofibers, and porous Ag [230]. The NiO-Ag hybrid nanofibers consisted of homogeneous distribution of NiO and irregular distribution of Ag nanoclusters. The as-prepared samples were then applied to construct non-enzymatic sensors for glucose detection. The NiO-Ag hybrid nanofiber modified electrode showed 55-fold higher sensitivity than that obtained on the porous Ag modified electrode at 0.1 V, and 5.2-fold higher sensitivity, lower detection limit and wider linear range than that of the NiO nanofiber modified electrode at 0.6 V (Fig. 13). The significant improvement obtained with NiO-Ag nanofiber were attributed to the use of abundant nanofibers which could provide numerous electron transfer tunnels, the highly porous structure which minimized the diffusion resistance of analytes, and the synergetic effect between NiO and Ag. This method have also been extended to prepare NiO-Au [231], and NiO-Pt [232] bimetallic nanofibers. The as-prepared hybrid nanofibers were employed for the nonenzymatic glucose detection in alkaline electrolyte and showed improved analytical performance compared to the monometallic counterparts. Binary metal oxide nanofibers, including CuO-NiO [233], and NiO-CdO [234] have also exploited as the candidates for developing nonenzymatic glucose sensors. These binary metal oxide nanofibers showed good analytical properties for glucose detection due to the large amounts of reactive sites on the electrode surface and improved conductivity of NiO nanofibers by the incorporation of secondary metal oxide.

In addition to the predominant glucose sensors, the applications of electrospun metal/metal oxide nanofibers in the preparation of sensors for other important analytes were also investigated. For example, Ding et al. constructed an amperometric sensor for hydrazine detection by using electrospun Mn_2O_3 nanofibers [235]. Wang and co-workers exploited electrospun $CuO-Co_3O_4$ nanofibers as active electrode materials for direct enzyme-free fructose detection [236]. These works demonstrated that electrospun metal/metal oxide nanometerial is one of the promising catalytic electrode materials for constructing ultrasensitive electrochemical sensors.
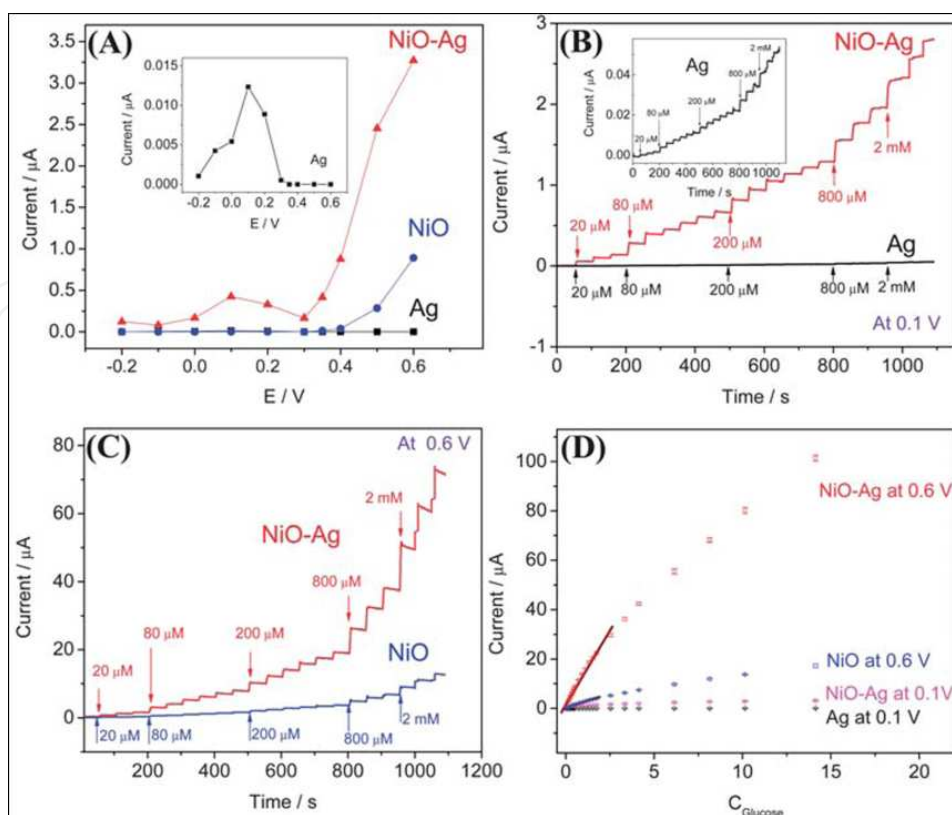
Figure 13. (A) Hydrodynamic voltammograms of 200 µM glucose at the porous Ag/GCE, NiO NFs/GCE and NiO-Ag NFs/GCE; (B) Amperometric response of porous Ag/GCE and NiO-Ag NFs/GCE to successive additions of glucose at an applied potential of 0.1 V; (C) Amperometric response of porous NiO NFs/GCE and NiO-Ag NFs/GCE to successive additions of glucose at an applied potential of 0.6 V; (D) the corresponding calibration curves [230].

4.4. Other electrospun nanofibers based electrochemical sensors

Ding et al. developed an amperometric biosensor by directly electrospinning deposition of hemoglobin (Hb) microbelts on the surface of glassy carbon electrode (Fig. 14A) [237]. This porous Hb microbelt coating closely contacted to the electrode surface and showed enhanced direct electrochemistry of Hb (Fig. 14B). The Hb microbelts based amperometric biosensor showed a fast response to the analytes and low detection limits of 0.61 µM for H_2O_2 and 0.47 µM for nitrite. The K_M^{app} value of 0.093 mM was obtained for the electrocatalytic reduction of H_2O_2, reflecting the high affinity of Hb to the substrate H_2O_2. SWNT-Hb composite microbelts were also fabricated by the same group and employed as active material to prepare mediator-free biosensors [238]. The direct electrochemistry of Hb at SWNT-Hb/GCE was more prominent than that obtained at the Hb microbelt/GCE because of the enhanced electron transfer by incorporated/embedded SWNTs and the porous 3D structure of Hb microbelt coating. Sensitive amperometric detection of trichloroacetic acid (TCA), nitrite, and H_2O_2 was obtained with the detection limits of 2.41 µM, 0.30 µM and 0.22 µM, respectively. TiO_2-Pt nanofibers were fabricated by electrospinning PVP/ethanol solution containing platinum acetate and Ti(OiPr)$_4$, followed by calcination in air at 500 °C for 3 h [239]. The as-prepared TiO_2-Pt hybrid nanofibers were used as the electrochemical catalyst for hydrazine detection. Au-coated SiO_2

core-shell nanofibers were prepared by the seed-mediated growth Au shell on electrospun SiO_2 nanofibers [240]. Then horseradish peroxidase (HRP) was immobilized on the SiO_2@Au nanofibers modified electrode via physical adsorption to construct an amperometric H_2O_2 biosensor. This biosensor exhibited high biological affinity to H_2O_2 and the HRP enzyme on the gold shell kept its activity with a low-diffusion barrier.
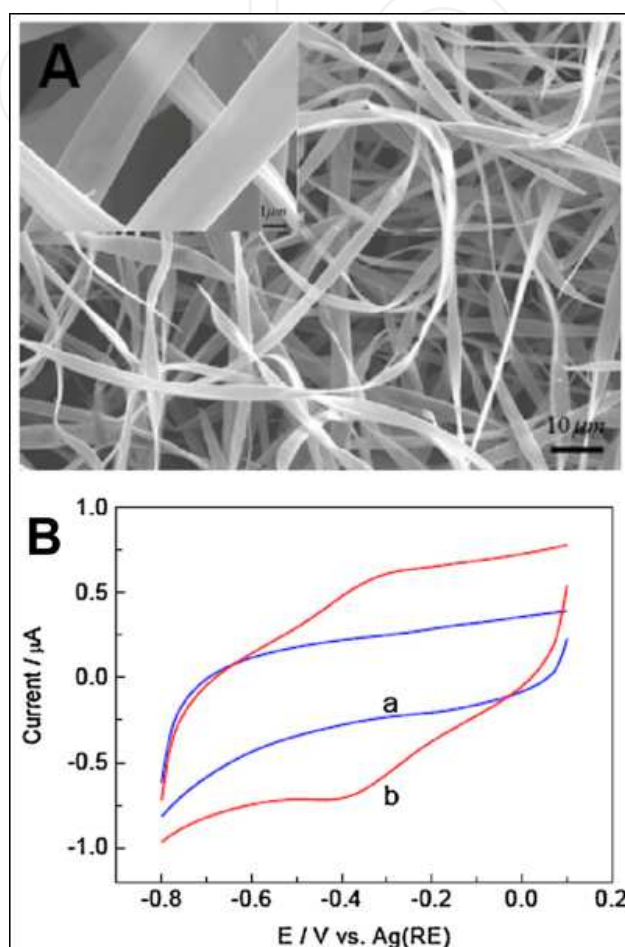

Figure 14. (A) Typical SEM images of Hb microbelts at low (scale bar=10 μm) and high (inset, scale bar=1 μm) magnification; (B) CVs of the bare GC electrode (a) and Hb microbelts modified GC electrode (b) in 0.1 M pH 7.0 phosphate buffer solution. Scan rate, 100 mV s^{-1} [237].

5. Conclusions and remarks

In past few years, numerous studies have demonstrated that elctrospinning is a simple and versatile method for fabricating nanofibers of organic or inorganic materials. Various functional components, such as nanoparticles, CNTs, proteins, DNA and so on, have been incorporated into the electrospun nanofibers. These composite nanofibers exhibited excellent properties and extended the applications of electrospun nanomaterials. With the profound understanding the electrospinning process and the development of setup for electrospinning,

nanofibers with core/sheath, hollow and porous structures have been directly generated by electrospinning or prepared through the combination of electrospinning with some post-spun treatments. Due to the small size, high surface area, and high porosity, electrospun nanomaterials have been witnessed as a promising candidate for a wide range of applications. One of the important applications is the construction of electrochemical sensors or biosensors, where electrospun nanomaterials acted as matrix for the immobilization of enzyme or as the active electrocatalysts. Electrospun nanofiber-based electrochemical sensors or biosensors have exhibited excellent analytical performances for a number of analytes.

In spite of the significant progress in the area of electrospinning, several challenges have to be resolved before large-scale fabrication and extensive applications of electrospun nanomaterials. Most important is that more experimental studies and theoretical modeling are required in order to achieve a better control over the size and morphology of electrospun fibers. To date, it is still not easy to generate uniform nanofibers with diameters below 100 nm, in particular, on the scale of 10-30 nm. Additionally, it is still necessary to systematically investigate the correlation between the processing/solution parameters and the secondary structures of produced nanofibers. Frankly speaking, the application of electrospun nanomaterials in electrochemical sensors is still in its infancy stage, where the applied materials and analytical targets are limited. The majority of polymers have poor conductivity, which limited their direct applications in electrochemical sensors. In this case, it is desirable to develop conductive polymer nanofibers based electrochemical sensors. However, it is still rarely reported in the literatures. Electrospun carbon nanofiber is another good alternative, but the limited catalytic activity and larger diameters confined their analytical performances. Metal nanoparticle loaded carbon nanofibers showed great promise in the preparation of ultrasensitive electrochemical sensors, while the diameter of nanoparticles is difficult to control by using the current one-step method. For the analytical targets, it is still focused on the small molecules at the present research, predominated by glucose. Therefore, there is a large scope to extend the analytes to other significant molecules, particularly the biomolecules such as DNA, proteins, and cells.

There is no doubt that electrospinning has become one of the most powerful techniques for fabricating 1D nanomaterials with broad range of functionalities. Electrospun nanofibers have emerged as a kind of great promising material for constructing ultrasensitive electrochemical sensors or biosensors. We can believe that with the extensive interdisciplinary research more and more electrspun nanofiber-based electrochemical sensors or biosensors with excellent properties will emerge in the near future and will be practically applied in environmental monitoring, food analysis and clinical diagnostics.

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