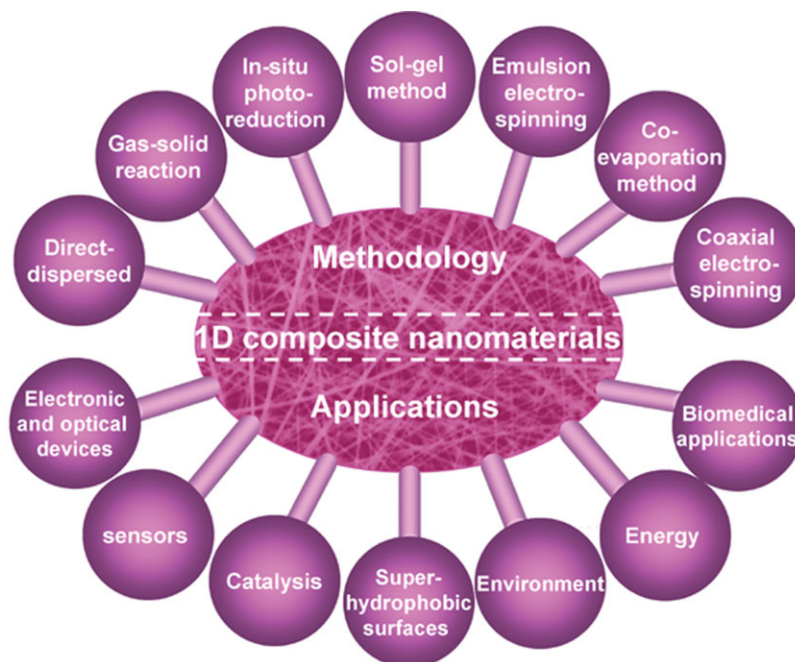


One-Dimensional Composite Nanomaterials: Synthesis by Electrospinning and Their Applications

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This Review provides an overview of the synthesis of one-dimensional (1D) composite nanomaterials by electrospinning and their applications. After a brief description of the development of the electrospinning technique, the transformation of an inorganic nanocomponent or polymer into another kind of polymer or inorganic matrix is discussed in terms of the electrospinning process, including the direct-dispersed method, gas–solid reaction, in situ photoreduction, sol–gel method, emulsion electrospinning method, solvent evaporation, and coaxial electrospinning. In addition, various applications of such 1D composite nanomaterials are highlighted in terms of electronic and optical nanodevices, chemical and biological sensors, catalysis and electrocatalysis, superhydrophobic surfaces, environment, energy, and biomedical fields. An increasing number of investigations show that electrospinning has been not only a focus of academic study in the laboratory but is also being applied in a great many technological fields.

1. Introduction

One-dimensional (1D) nanostructures in the form of fibers, wires, rods, belts, tubes, and rings have attracted plenty of attention due to their novel properties and intriguing applications in many areas in the past few years.^[1–18] A large number of advanced techniques have been developed to fabricate 1D nanostructures with well-controlled morphology and chemical composition. Among these methods, electrospinning seems to be the simplest and most versatile technique capable of generating 1D nanostructures (mainly nanofibers; other types of 1D nanostructure, such as nanorods, can be cut from nanofibers by special methods^[19,20]) from a variety of polymers.^[21–28] Compared to the commercial mechanical spinning process for generating microfibers, electrospinning mainly makes use of the electrostatic repulsions between surface charges to reduce the diameter of a viscoelastic jet or a glassy filament. One of the most important advantages of the electrospinning technique is that it is relatively easy and not expensive to produce large numbers of different kinds of nanofiber. Other advantages of the electrospinning technique are the ability to control the fiber diameters, the high surface-to-volume ratio, high aspect ratio, and pore size as non-woven fabrics. Moreover, nanofiber composites can easily be made via the electrospinning technique with the only restriction being that the second phase needs to be soluble or well dispersed in the initial solution. The advantage of the facile formation of 1D composite nanomaterials by electrospinning affords the materials multifunctional properties for various applications.

Electrospinning has been understood for almost a century, and may be considered as a variation of the electrospray process.^[29–32] During the process of electrospraying, the liquid drop elongates with increasing electric field. When the repulsive force induced by the charge distribution on the surface of the drop is balanced with the surface tension of the liquid, the liquid drop distorts into a conical shape. Once the repulsive force exceeds the surface tension, a jet of liquid ejects from the cone tip. Small droplets form as a result of the varicose break up of the jet in the case of low-viscosity liquids. If this phenomenon is applied to polymer solutions, a solid fiber is generated instead of breaking up into individual drops for the electrostatic repulsions between the surface charges and the evaporation of solvent. The first description of an apparatus for this electrospinning technique was demonstrated by Formhals in 1934 as a patent; however, it did not receive much attention until the early of 1990s.^[33] After that, Reneker and co-workers made a great contribution with this technique.^[34–41] In their work, they studied the electrospinning process for a series of different polymers. Moreover, they demonstrated the mechanism for the formation of polymer fibers during the electrospinning process. Electrospun fibers have found use in a broad range of applications owing to their low dimensions and large surface areas, such as templates for fabricating other nanostructures, filters, textiles, catalysis, chemical and biological sensors, nanofiber reinforcement, tissue engineering, wound healing, drug release and delivery, tumor therapy, and so on.^[21–28]

In the early days, electrospinning was mainly used to prepare polymeric nanofibers. Up to now, more than one hundred types of natural and synthetic polymer have been electrospun into



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nanofibers, including Nylon-6,6 (PA-6,6), polyacrylonitrile (PAN), polyurethane (PU), polycarbonate (PC), polybenzimidazole (PBI), polyvinyl alcohol (PVA), polylactic acid (PLA), polyethylene-co-vinyl acetate (PEVA), polymethacrylate (PMMA), polyethylene oxide (PEO), polyvinylcarbazole (PVK), polyethylene terephthalate (PET), polystyrene (PS),

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polyamide (PA), cellulose acetate (CA), poly(vinyl pyrrolidone) (PVP), polyvinylchloride (PVC), polyacrylamide (PAAm), polycaprolactone (PCL), poly(vinylidene fluoride) (PVDF), polyether imide (PEI), polyethylene glycol (PEG), nylon-4,6 (PA-4,6), and many more.^[21,28] Later, some scientists focused on the fabrication of ceramic nanofibers combined with electrospinning and calcination.^[42–63] Since polymeric and ceramic nanofibers fabricated by electrospinning have been reviewed by a number of authors, this article reviews current research activities that center on the use of electrospinning to prepare 1D composite nanomaterials. Generally, there are three kinds of 1D composite nanomaterial: polymer/polymer(organic), polymer/inorganic, and inorganic/inorganic composite systems. Here we specifically illustrate some innovative methods to show how to fabricate such 1D composite nanomaterials and their applications in a broad range of fields. The Review contains five sections: the next section describes the basic setup for the electrospinning, the electrospinning process, and the mechanism of the formation of spinning fibers under the influence of an electric field. The following section fully illustrates the strategies for the fabrication of 1D composite nanofibers combined with electrospinning. Section 4 highlights a range of applications associated with 1D composite nanomaterials in various areas. Finally, we draw conclusions regarding this new technique and the prospects of future research.

2. Electrospinning Process

2.1. Basic Setup for Electrospinning

The basic setup for electrospinning is very simple and easily controlled, as illustrated in Figure 1A. Generally, it consists of a high-voltage power supply, a spinneret, and an electrically conductive collector (a piece of aluminum foil or silicon). However, not all of these parts are necessary for electrospinning. For example, electrospinning devices without the use of a spinneret have been described by Yarin et al. and Kameoka et al.^[64,65] In a typical electrospinning experiment, the liquid (a polymer solution or melt) for electrospinning is pumped into a

syringe with a thin nozzle with an inner diameter on the order of 100 μm to about 1 mm. The nozzle serves as one electrode and the collector is connected with another electrode, which affords a high electric field of 100–3000 kV m^{-1} . The distance between the nozzle and the collector is usually 5–25 cm in most laboratory systems. In many cases, a syringe pump is also needed to feed the solution through the spinneret at a constant and controllable rate. The applied voltage makes the pendent drop of polymer solution highly electrified and the induced charges are evenly distributed over the surface. Once the strength of the electric field is high enough to allow the electrostatic forces to overcome the surface tension of the polymer solution, a liquid jet forms and moves towards the counter electrode. During the movement of the liquid jet, the solvent evaporates (or the melt solidifies), and solid fibers with certain diameters are precipitated as a randomly oriented, non-woven mat on the counter electrode. In addition to the distance between the nozzle and the collector and the applied voltage, the other parameters, such as viscosity, conductivity of the solution, and humidity of the environment, also affect the formation of the electrospun nanofibers. For example, the viscosity of a solution strongly influences the electrospun morphology and the diameter of the electrospun fibers.^[66,67] In some cases, a well-controlled humidity and temperature are also required to obtain a smooth, reproducible operation of electrospinning.^[42]

Sometimes, controlling the assembly of electrospun nanofibers is necessary for electronic devices or biomedical applications.^[68] Typical methods to achieve this object are the manipulation of the collector and the electric field. Several studies have demonstrated that aligned fibers could be obtained by using a rotating collector at a high speed;^[69,70] the mandrel rotation speed and fiber orientation strongly influence the properties of the electrospun nanofibers. The deposition of electrospun fibers can be not only on a solid collector but also on some common liquid.^[35] Smit et al. and Khilet al. demonstrated that continuous uniaxial fiber bundle yarns could be prepared by electrospinning onto a liquid reservoir collector;^[71,72] the electrospun fibers were determined by visual analysis to be aligned in the direction of the length of the yarn. It was proposed that surface tension made the fiber mesh collapse into a yarn when it moved from water to the rotating collector. During the electrospinning process, the jet can be controlled by an external electric field, resulting in the deposition state of the electrospun fibers on the collector.^[73] Tan and co-workers applied an electrostatic lens element and biased collection target to control the deposition of electrospun fibers, which allowed us to collect the electrospun fibers in other forms besides non-woven mats.^[74] Xia and co-workers demonstrated that using two parallel electrodes could collect aligned fibers in the gap. This was because the electric field exerted a pulling force on the electrospinning jet across the gap towards the parallel electrodes.^[75] In principle, by modifying the setup of the electrospinning, scientists can control the assembly of the electrospun nanofibers.

2.2. Mechanism Background

Although the setup is simple, the electrospinning process and mechanism are rather intricate. As mentioned above, an electrically charged jet of polymer solution at a pendent droplet

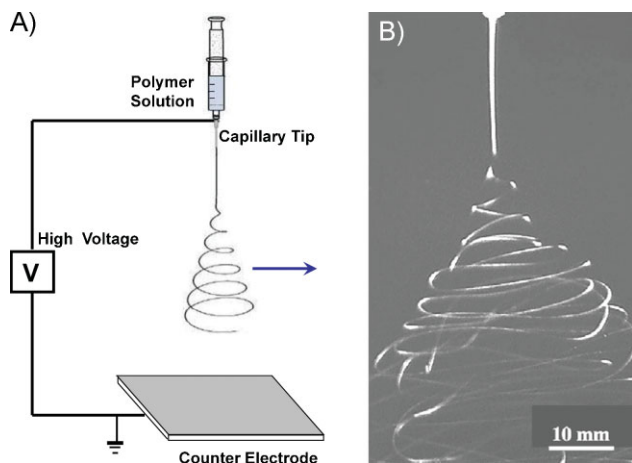


Figure 1. A) Schematic diagram showing a laboratory setup for electrospinning. B) Photographs of typical electrospinning jets captured by a high-speed video showing the bending instability of the jet. Reproduced with permission from Reference [76]. Copyright 2007, Elsevier.

forms in the presence of an electric field. The jet moves to the counter electrode in a nearly straight line at the beginning, then it bends into a complex path during the course of non-linear bending instability, resulting in the solid polymeric nanofibers after solvent evaporation. Reneker and co-workers used a high-speed videographic to observe the bending instability of the jet, they found that the jet will form loops in the horizontal plane during the motion towards the collector^[76] (Figure 1B). During the process, the stretching and acceleration of the unstable fluid filament lead to the extreme thinness of the fibers. The authors also analyzed and explained the instability using a mathematical model; they used a localized approximation to calculate the bending electric force on an electrified polymer jet. A discrete form of continuous quasi-1D partial differential equations was derived and used to calculate the jet paths during the course of bending instability.^[41] The results of the calculations agreed well with experimental observations. Brenner and co-workers developed a model to perform a stability analysis of a charged fluid jet in a tangential electric field as a function of all fluid parameters. During electrospinning there are three different instabilities: the classical Rayleigh instability, and electric-field-induced axisymmetric and bending instabilities.^[77] Under a high electric field for the formation of polymer fibers, the electrical instabilities are primary whereas the Rayleigh instability is suppressed. The dominant instability depends strongly on the radius and surface charge density of the jet. The stability theory is used to develop a quantitative method for predicting the parameter regimes where it occurs during the electrospinning process. All of these mathematical modeling studies urge us to better understand the essence of the electrospinning process, which can be used to guide the optimal design of new setups and to control the morphology and assembly of the electrospun fibers.

3. Methodology for Fabricating 1D Composite Nanomaterials

Electrospinning has exhibited a strong ability to generate polymeric nanofibers in the past decade. Combined with calcination or carbonation, ceramic or other inorganic nanofibers could also be synthesized using the electrospinning technique. In this section, we introduce various means combined with electrospinning to produce 1D functional composite nanomaterials. With these techniques, the obtained 1D composite nanomaterials show good structure, stability, and properties.

3.1. Direct-Dispersed Electrospinning

In order to insert an inorganic nanocomponent into a polymer fiber, the most straightforward strategy is to disperse the inorganic nanocomponent in a polymer solution, followed by electrospinning.^[78–88] However, the inorganic nanocomponents are easily aggregated or do not well disperse in polymer fibers. Our group has tried to make silver nanoparticles in PAN fibers using this method; the transmission electron microscopy (TEM) studies indicated that the silver nanoparticles had partially aggregated, the smallest diameter of the silver nanoparticles was about 20 nm, and the largest size we could reach was about 200 nm.^[78] In order to make the inorganic nanoparticles

effectively disperse in polymer nanofibers, sometimes a surfactant is needed. Yang and co-workers studied the dispersion of CdTe quantum dots (QDs) in PVP solid nanofibers by the direct-dispersed electrospinning method.^[79] The CdTe QDs congregated in the PVP fibers after electrospinning in the absence of cetyltrimethylammonium bromide (CTAB). In contrast, CdTe QDs could be well dispersed in the PVP fibers after adding a small amount of CTAB. Yang and co-workers presented the use of electrospinning to well-dispersed aqueous synthesized CdTe QDs in PVA nanofibers: a uniform and separate distribution of the CdTe QDs in the PVA fibers matrix was clearly revealed when the CdTe QD concentration was lower than 4 wt%.^[80] During the synthesis, a little dioctyl sulfosuccinate sodium salt (AOT) was added into the electrospun polymer solution in order to lower the surface tension and viscosity of the PVA solution. Although the author did not mention the effect of the surfactant (AOT) to the dispersion of CdTe QDs in PVA fibers, we think that AOT may make some contribution to the uniformity and well-dispersed nature of CdTe QDs in polymer fibers.

In addition to metal and semiconductor nanoparticles, carbon nanotubes (CNTs) are a good candidate for incorporation into the electrospun nanofibers for their potential improvement of the mechanical strength, thermal conductivity and electronic conductivity compared to polymer fibers. This work has been carried out by a number of groups and the corresponding examples of polymers include PAN, PEO, PVA, PLA, PC, PS, PU, and PMMA.^[89–108] Similarly, CNTs can be well incorporated in electrospun polymer fibers only after they are well dispersed in the electrospinning solution. For example, Ko and co-workers dispersed single-walled nanotubes (SWNTs) in different polymer solutions and electrospun them into nanofibers; the results showed that PAN/SWNTs composite nanofibers had a better alignment of SWNTs than PLA/SWNTs fibers.^[89] SWNTs could be well dispersed in dimethylformamide (DMF) solution of PAN before electrospinning, so in PAN/SWNTs composite nanofibers, SWNTs maintained their straight shape and were parallel to the axis direction of the PAN fiber (Figure 2). The diameter of polymer fibers and the differences in conductivity and wetting ability between the two polymers influenced the dispersed state of SWNTs in polymer fibers. The electrospun PAN/SWNTs composite nanofibers exhibited an enhanced thermal stability and a significant reinforcement effect at less than 3% volume SWNTs. In another paper, the authors also prepared a fibrous nanocomposite of *bombyx mori* silk and SWNTs and studied the mechanical properties of the SWNT reinforced fibers.^[90] The results showed an increase in Young's modulus up to 460% in comparison to the un-reinforced aligned fiber. A theoretical model was proposed by Cohen and co-workers to investigate the behavior of rodlike particles representing CNTs in electrospinning; they concluded that the rods were randomly oriented initially but gradually oriented along the jet line for the sinklike flow in a wedge.^[92] The authors obtained PEO nanofibers in which multiwalled carbon nanotubes (MWNTs) were embedded with the assistance of small molecules (sodium dodecyl sulfate) (SDS) or high-molecular-weight, highly branched polymer. TEM images indicated that the MWNTs were embedded in the nanofibers and mostly aligned along the fiber axis.

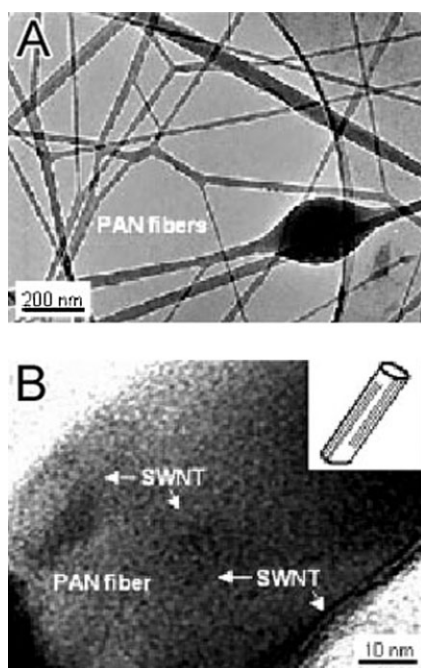


Figure 2. A) TEM image of PAN/SWNT composite nanofibers. B) High-resolution TEM image showing the uniform distribution and alignment of SWNTs in a PAN fiber with a diameter of about 50 nm. The inset shows a schematic illustration of the orientation of SWNTs in a PAN fiber. Reproduced with permission from Reference [89].

In order to improve the mechanical strength, CNTs sometimes need to be functionalized. Haddon and co-workers prepared PS/SWNTs and PU/SWNTs composite nanofibers by electrospinning a mixture of polymer and ester (EST)-functionalized SWNTs and studied their mechanical properties.^[95] The results showed that the tensile strength of EST-SWNT-PU mats was enhanced by 104% as compared to electrospun pure PU mats, while an increase of only 46% was achieved incorporating as-prepared SWNTs in the PU matrix. Reneker and co-workers demonstrated that PAN/MWNTs composite nanofibers could be prepared by electrospinning a mixture of the PAN and surface-oxidized MWNTs in DMF.^[96,97] TEM and 2D wide-angle X-ray diffraction (WAXD) data exhibited a high degree of orientation of MWNTs in the PAN/MWNTs nanofibers. The electrical conductivity, thermal stability, tensile strength, and tensile modulus were much improved. Electrospun polymer/CNT fibrous nanocomposites with high electrical conductivity have also been studied by Seoul and co-workers.^[98] The results showed that the conductivity of the CNTs/PVDF fiber mat electrospun from a PVDF/DMF solution with only 0.1 wt% CNTs reached $7 \times 10^{-6} \text{ S cm}^{-1}$. Jin and co-workers also prepared a PMMA nanocomposite containing well-dispersed MWNTs and pointed out that electrical conductivities of the synthesized PMMA/MWNTs nanocomposite films containing 1–5 wt% of MWNTs were between 10^{-4} and $10^{-2} \text{ S cm}^{-1}$.^[99]

3.2. Gas-Solid Reaction

As mentioned above, inorganic nanocomponents are easily aggregated and do not disperse well in polymer fiber matrix by

electrospinning. Our group first introduced a gas–solid reaction to the electrospinning technique to incorporate semiconductor nanostructures into polymer nanofibers; similar results were also reported by other groups.^[109–118] The synthetic strategy involved three steps: 1) Co-dissolve metal salt and polymer into one solvent to make a homogeneous solution; 2) electrospinning the above solution to obtain polymer/metal salt composite nanofibers. To prove the existence of the metal salt in the polymer nanofibers, we characterized the composite film with X-ray photoelectron spectroscopy (XPS). As an example, for the system of PVP/lead acetate, the $\text{Pb}4f_{7/2}$ and $\text{Pb}4f_{5/2}$ peaks were observed at 138.7 and 143.7 eV, respectively, indicating the existence of lead acetate.^[109] Moreover, TEM images showed that the fibers were homogeneous; 3) exposure of the electrospun polymer/metal salt composite nanofibers to H_2S gas at room temperature to synthesize PbS nanoparticles in situ in polymer nanofibers. The color of the composite fibers rapidly changed from white to yellow after exposure to H_2S . The UV/vis absorption spectrum also proved the formation of PbS nanoparticles. We were pleased to find that the obtained PbS nanoparticles were spherical in shape and were separated from each other. Compared to the direct-dispersion method, gas–solid reaction affords a simple way to disperse inorganic nanoparticles into polymer nanofibers. We also studied the effect of the kind of metal salt to the shape control of semiconductor nanostructures. When cadmium acetate was used to produce PVP/CdS composite nanofibers instead of lead acetate, the obtained CdS nanostructures were nanorods, not dense spherical nanoparticles; we thought that this might be due to the different interactions between the polymer molecules and different metal ions^[110] (Figure 3). It was emphasized that the semiconductor nanoparticles synthesized using this method were not only outside but also inside the polymer nanofibers. In order to make the semiconductor nanoparticles only form outside of the polymer nanofibers, one can adsorb the metal ions on the surface of the electrospun nanofibers, then expose the polymer nanofibers film containing metal ions to H_2S gas to synthesize semiconductor nanostructures in situ (Figure 4). To achieve this, the surface of the polymer nanofibers should be functionalized with some anion groups. Zhou and co-workers modified the carboxylic groups on the surface of PVA nanofibers, then synthesized PVA/ZnS composite nanofibers;^[111] our group functionalized the sulfonic groups on the surface of PS nanofibers and synthesized PS/CdS composite nanofibers.^[112]

In addition to the semiconductor nanoparticles, chloride nanoparticles can also be prepared by combining the gas–solid reaction and the electrospinning method. Yang and co-workers synthesized AgCl nanoparticles/PAN composite nanofibers using such a strategy, which is similar to our report on the fabrication of semiconductor/polymer composite nanofibers.^[118] Firstly, they prepared inorganic AgNO_3 /PAN nanofibers, then exposed the composite nanofibers to HCl gas to obtain AgCl nanoparticles in-situ in the polymer matrix. X-ray diffraction (XRD) proved that the formed AgCl crystals had a face-centered cubic (fcc) structure. TEM showed that the size of the AgCl nanoparticles was not only uniform but could also be controlled. When the molar ratio of AgNO_3 /PAN was 1:20, the average diameter of the particles was about 19.4 nm.

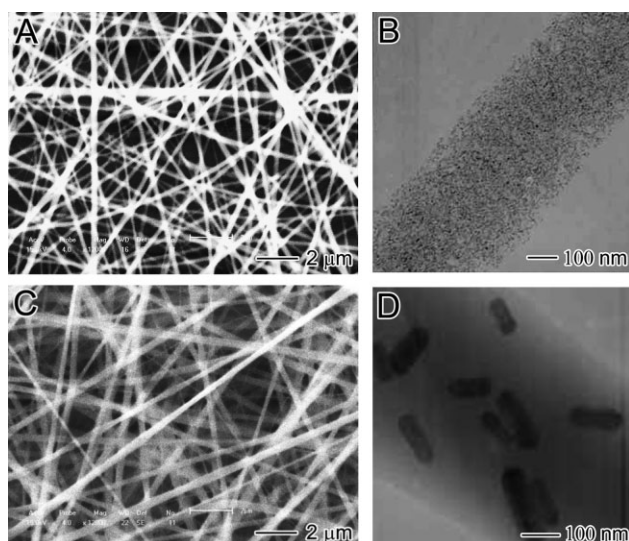


Figure 3. Electrospun PVP nanofibers incorporated with semiconductor nanoparticles synthesized by electrospinning combined with gas–solid reaction. A) SEM image of PVP/PbS composite fibers. B) TEM image of spherical PbS nanoparticles incorporated in PVP fibers, showing that the PbS nanoparticles with a diameter of about 5 nm are well dispersed in PVP fibers. C) SEM image of PVP/CdS composite fibers. D) TEM image of CdS nanorods formed in PVP fibers after reaction with H_2S gas. CdS nanorods are also well dispersed in PVP fibers. Reproduced with permission from References [109, 110].

When the molar ratio of AgNO_3/PAN increased from 1:10 to 1:5, the average diameter of the nanoparticles increased in size to 20.4 nm and 20.6 nm, respectively, and the density of AgCl nanoparticles also increased.

3.3. In situ Photoreduction

Photochemical reduction is a facile and versatile method to prepare metal colloids. UV irradiation of aqueous solutions of AgNO_3 induces photo-oxidation of water by excited Ag^+ , resulting in the formation of silver atoms Ag^0 , H^+ , and OH^\cdot radicals; subsequent Ag^0 will aggregate into silver clusters and colloidal silver.^[119,120] Diverting to the preparation of polymer/silver composites, one can disperse AgNO_3 into the

polymer matrix, then exposure the composite to UV irradiation for the photoreduction. Based on this idea, polymer/Ag composite nanofibers can be synthesized by introducing the electrospinning technique. Park and co-workers prepared Ag nanoparticles incorporated into antimicrobial ultrafine CA fibers. They used electrospun CA solution containing AgNO_3 to prepare CA/ AgNO_3 composite nanofibers,^[121] after photoreduction by UV irradiation, the color of the CA fibers was gradually changed to light yellow, indicating the formation of Ag nanoparticles. TEM showed that the synthesized Ag nanoparticles had an almost spherical shape. The diameter of Ag nanoparticles was related to the amount of added AgNO_3 . When the CA fibers contained 0.05 and 0.5 wt% AgNO_3 , the diameter of Ag nanoparticles was 3.3 and 6.9 nm, respectively. Our group also prepared PAN/Ag composite nanofibers using this method.^[122] Typical TEM images of as-prepared electrospun PAN/Ag composite nanofibers showed that monodisperse Ag nanoparticles were homogeneously covered on the surface of PAN nanofibers. Selected-area electron diffraction (SAED) proved that the Ag nanoparticles were fcc standard bulk single crystals. The diameter of Ag nanoparticles could be controlled by varying the molar ratio of $\text{Ag}^+:\text{PAN}$. The size of Ag nanoparticles was about 9 nm when the molar ratio of $\text{Ag}^+:\text{PAN}$ was 1:10, while it decreased to 5 and 3.5 nm by lowering the molar ratio of $\text{Ag}^+:\text{PAN}$ to 1:20 and 1:40, respectively.

Different from the formation of Ag nanoparticles, HAuCl_4 can only be reduced to form Au colloids under UV irradiation in the presence of some organic stabilizers such as PVP, PEG, and PVA. However, the photoreduction process is fairly slow, even with such organic stabilizers acting as scavengers. TiO_2 , a typical photocatalyst, can make this reaction much faster. Based on this fact, Xia and co-workers demonstrated that TiO_2/Au composite nanofibers could be synthesized by UV photoreduction of HAuCl_4 in the presence of TiO_2 nanofibers and organic stabilizers.^[123] Depending on the type and concentration of organic stabilizers, different shapes of Au nanoparticles, such as nanoparticles, fractal nanosheets, or nanowires could be synthesized on the surface of TiO_2 nanofibers. Such a technique could also be applied in the formation of other metal nanostructures on TiO_2 nanofibers, which might be used for chemical or biological sensing.

3.4. Sol–Gel Method

Combined with the sol–gel method, many kinds of composite nanofiber can be synthesized by electrospinning, including metal/polymer, metal oxide/polymer, sulfide/polymer and so on,^[124–128] if followed by calcination, metal oxide/polymer nanofibers can also be converted into ceramic or metal oxide/ceramic composite nanofibers.^[42–63]

Our group successfully prepared $\text{Ag}_2\text{S}/\text{PVP}$ composite nanofibers using such a method. Firstly, we prepared Ag_2S sol using an in situ reaction with AgNO_3 as precursor and CS_2 as the sulfide source in the presence of PVP

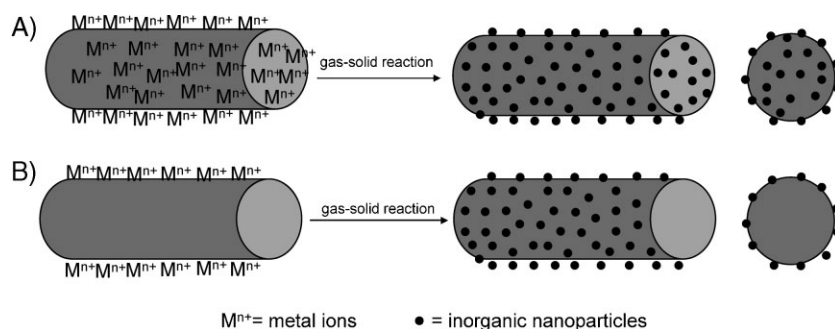


Figure 4. Schematic illustration of two kinds of polymer/inorganic composite nanofiber synthesized by electrospinning. A) Schematic image showing that inorganic ions are incorporated into electrospun nanofibers, followed by exposure to gas to synthesize inorganic nanoparticles in both outside and inside nanofibers. B) Schematic image showing that the surface of electrospun nanofibers is modified with metal ions, followed by exposure to gas to prepare inorganic nanoparticles only on the surface of electrospun nanofibers.

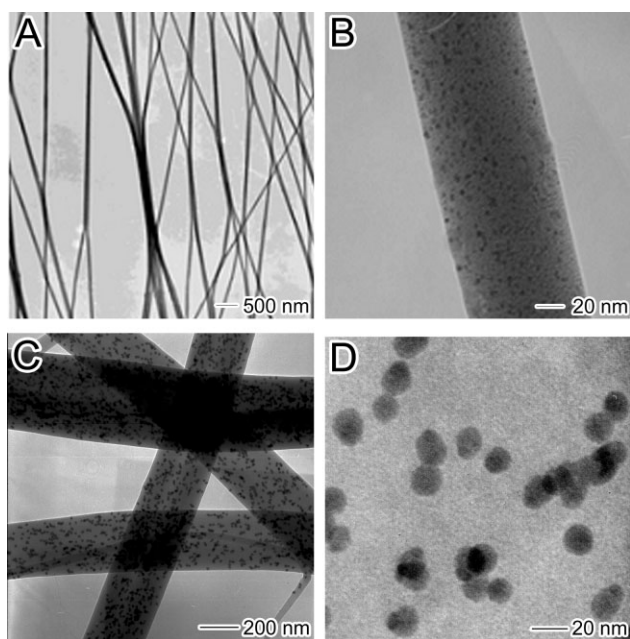


Figure 5. A) SEM and B) TEM images of PVP/Ag composite nanofibers by electrospinning an Ag sol in PVP ethanol solution. Part (B) shows the good dispersity and small size of the Ag nanoparticles in PVP fibers. C) SEM and D) TEM images of PVP/Ag₂S composite nanofibers by electrospinning an Ag₂S sol in PVP ethanol solution, showing that Ag₂S nanoparticles are spherical with a diameter of about 15 nm. Reproduced with permission from References [124, 126]. Copyright 2005 and 2006, respectively, IOP Publishing Ltd.

at room temperature, then the sample solution was electrospun into composite nanofibers.^[124] As the Ag₂S sol was compatible with the polymer of PVP, the obtained Ag₂S nanoparticles could be well dispersed into solid PVP fibers after electrospinning. XRD patterns showed that the formed Ag₂S could be ascribed to the monoclinic crystal system (β -Ag₂S). Through the calculation according to Scherrer's equation, the average size of Ag₂S nanoparticles was evaluated to be about 15 nm. Figure 5C and D shows TEM images of the obtained Ag₂S/PVP composite fibers; the synthesized dense Ag₂S nanoparticles were well dispersed in the polymer fibers. These Ag₂S nanoparticles were roughly spherical in shape and were separated from each other, each having a diameter of approximately 15 nm.

In the early days, scientists were interested in Ag/polymer composites for their applications in catalysis and biomedical engineering fields. Yang and co-workers synthesized Ag/PVP composite nanofibers using such a method; they prepared Ag sol using PVP as the polymer matrix and the reducing agent under refluxing condition for about 5 h, then electrospun the sol to synthesize composite nanofibers^[126] (Figure 5). In this way, small Ag nanoparticles were dispersed homogeneously in PVP fibers with an average diameter of about 8 nm. DMF is a reducing solvent, which could reduce AgNO₃ into zero-valent Ag atoms (Ag⁰) at room temperature in the absence of any external reducing agents. Youk and co-workers prepared silver sol using DMF as the reducing agent in the presence of different polymers;^[127] after electrospinning, silver nanoparticles dispersed well in the solid polymer nanofibers. For PAN, the Ag

nanoparticles were all spherical and their average diameters were less than 5.8 nm. For PVP and PVA/PVP composite fibers, the average diameter of the synthesized Ag nanoparticles was 3.4–4.5 and 6.0 nm, respectively.

Combining the sol–gel method with the electrospinning technique, Xia and co-workers synthesized polymer/metal oxide nanofibers.^[53] In a typical procedure, titanium tetraisopropoxide was mixed with acetic acid and ethanol in the presence of PVP for some time to prepare TiO₂ sol. After electrospinning, PVP/TiO₂ composite nanofibers were left in air for more than 5 h to allow the hydrolysis of titanium tetraisopropoxide to go to completion. The uniformity in contrast in the TEM image showed that TiO₂ was uniformly dispersed in the PVP matrix. Moreover, such PVP/TiO₂ composite nanofibers could be converted into TiO₂ nanofibers by calcination in air for 2 h. They have also put two different kinds of precursor into the polymer solution and obtained PVP/TiO₂/V₂O₅ composite nanofibers.^[128] Similarly, V₂O₅/TiO₂ composite nanofibers could be prepared after calcination. Interestingly, V₂O₅ were not compatible with TiO₂ but grew as single-crystal nanorods on the surface of TiO₂ nanofibers.

3.5. Emulsion Electrospinning Method

The emulsion electrospinning technique is expected to be promising in future biomedical applications, especially controlled drug delivery. As demonstrated in a previous report, hydrophobic drugs could be encapsulated into electrospun PLLA fibers but showed nearly zero-order kinetics of drug release.^[129] On the other hand, water-soluble drugs could be electrospun into a water-soluble polymer but such composite fibers for drug delivery could not be controlled because they could dissolve in blood or tissue fluid quickly.^[130] Therefore, the emulsion electrospinning method was proposed to electrospin the emulsion of a drug/polymer/solution system.^[131–137] In this way, the hydrophilic drug could be distributed inside the fiber, which avoided the burst release. Wnek and co-workers successfully encapsulated aqueous reservoirs of bovine serum albumin (BSA) in the fibers of poly(ethylene-co-vinyl acetate).^[131] Observation of electrospun fibers typically reveals the presence of small and larger domains within the perimeter of the fibers because they did not emulsify the prepared solution before electrospinning. The results indicated that BSA resided in such formed large domains. Jing and co-workers also made a contribution in this field^[132] (Figure 6). Firstly, they mixed SDS and amphiphilic poly(ethylene glycol)-poly(L-lactic acid) (PEG-PLLA) diblock copolymer in chloroform solution with a high-shear-mixing homogenizer at a speed of 6300–6500 r min⁻¹, then the aqueous drug solution was dropped into the polymer solution and emulsified for about 20 min. By electrospinning the water-in-oil emulsion, water-soluble drugs could be well encapsulated into solid nanofibers. SEM images and nitrogen elemental distribution in the fibers determined by EDS revealed that Dox was uniformly dispersed in PEG-PLLA fibers. The cross section of the electrospun fibers containing 2.06% Dox indicated no Dox crystals were found on the fibers. They have also studied the *in vitro* drug release of the electrospun fibers from Dox/PEG-PLLA; the diffusion mechanism was predominant at the early stage and the

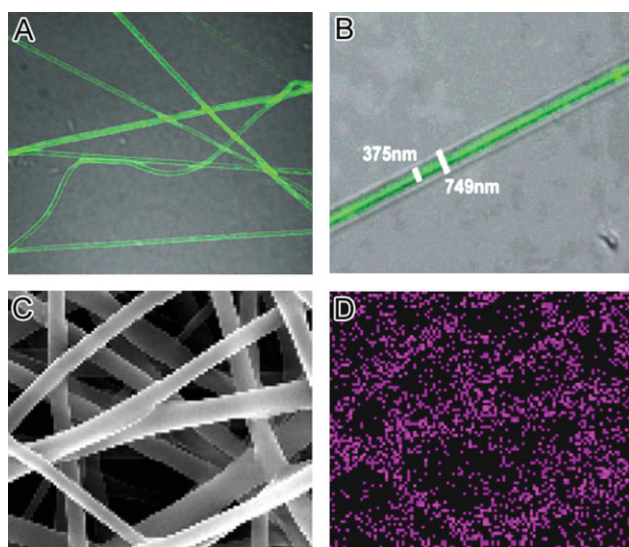


Figure 6. A,B) CLSM images of core/sheath nanofibers prepared by emulsion electrospinning. The concentration of PEO-FITC as core polymer is 45 mg mL^{-1} . C) ESEM photographs of PEG-PLLA fibers containing 2.06 wt% Dox. D) N elemental distribution in the fibers determined by EDS. Reproduced with permission from Reference [132], copyright 2005 Elsevier, and Reference [137].

enzymatic degradation mechanism became predominant a certain time later. Moreover, a loss of cytotoxicity was not observed during the release of Dox from the fibers.

In addition to the water-soluble drug, emulsion electrospinning can be applied to the fabrication of water-soluble polymer/hydrophobic polymer composite nanofibers. Similar to the drug encapsulation, water-soluble polymer becomes the core of a composite fiber after electrospinning. Jing and co-workers prepared PEO/PEG-PLA diblock copolymer core/sheath nanofibers by electrospinning a water-in-oil emulsion of them.^[137] Confocal laser scanning microscopy images showed that the electrospun composite nanofibers were uniform. The resultant nanofibers consisted of a green core and a colorless outer layer and the boundary between the two was quite sharp, which indicated a core/sheath structure. The stretching- and evaporation-induced de-emulsification could be explained by the formation of the core/sheath fibers.

3.6. Co-evaporation Method

We have discussed the mechanism of the electrospinning technique above. The discharged polymer solution jet undergoes an instability and elongation process, allowing the jet to become thin and long. The solid nanofibers then form during evaporation of the solvent. If we co-electrospin another component that could be dissolved in polymer solution, composite nanofibers would be obtained after the solvent evaporation. The idea is simply to synthesize composite nanofibers with functional polymers when they can not be electrospun alone. For example, MacDiarmid and co-workers showed that camphorsulfonic acid-doped polyaniline (PANI), a conducting polymer, could be electrospun into nanofibers blended with PEO; the conductivity of a single fiber was $\approx 0.1 \text{ S cm}^{-1}$.^[138] MEH-PPV with excellent photo- and electroluminescence could also be electrospun into nanofibers

by electrospinning the mixture of MEH-PPV and PVP in a mixed solvents.^[139] Similar to functional polymers, organic molecules or biomolecules are more easily incorporated into polymer nanofibers. For example, 1D composite nanomaterials consisting of enzyme and polymer have been fabricated by the co-evaporation electrospinning method. The composite nanofibers exhibited much improvement in the enzyme activity over bulk films. Moreover, the composite nanofibers are highly durable and can be easily recovered from solution.^[140] In addition to functional polymers and organic molecules or biomolecules, inorganic molecules could also be incorporated into polymer fibers by the electrospinning method. Huang and co-workers introduced tris(8-quinolinolato) aluminum into PVP nanofibers using co-evaporation electrospinning; the corresponding fluorescence images showed that the fibers had smooth surface and good luminescence.^[141] Gong et al. prepared $\text{H}_3\text{PW}_{12}\text{O}_{40}$ /PVA composite nanofibers based on such an idea.^[142] The Brunauer–Emmett–Teller (BET) surface area and swelling behavior of the fiber aggregate in water were investigated. They also prepared $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ /PVA, $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ /PVA, and $\text{H}_3\text{PW}_{11}\text{MoO}_{40}$ /PVA composite nanofibers and studied the photochromic property of the composite films.^[143–145] Our group synthesized a red luminescent $\text{Na}_9[\text{EuW}_{10}\text{O}_{36}]$, which could be dissolved in water solution in the presence of PVA. After electrospinning, $\text{Na}_9[\text{EuW}_{10}\text{O}_{36}]$ could be incorporated into PVA nanofibers.^[146] Figure 7A and B shows the TEM images of the obtained PVA/ $\text{Na}_9[\text{EuW}_{10}\text{O}_{36}]$, showing that $\text{Na}_9[\text{EuW}_{10}\text{O}_{36}]$ is well dispersed in polymer fibers with a diameter as small as several nanometers. The photoluminescence spectra of the hybrid fibers show characteristic red-light emission at room temperature. The luminescent composite nanofibers film was very stable. The digital photographs of the composite nanofibers in daylight and ultraviolet light after two months are shown in Figure 7C and D, indicating that this technique prevented the polyoxometalates turning to an inhomogeneous microphase and large aggregation.

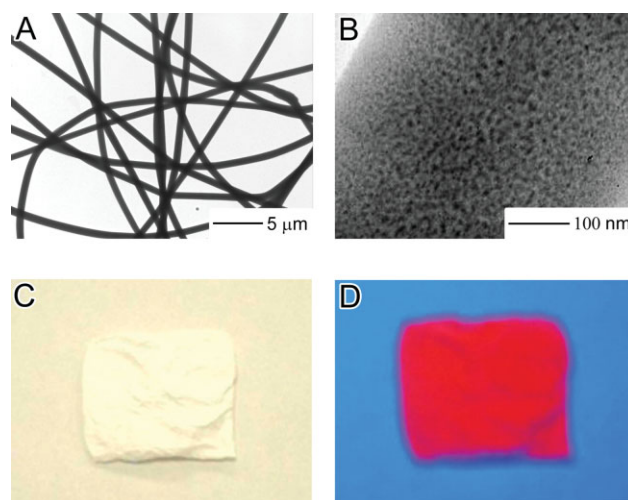


Figure 7. A,B) TEM images of PVA/ EuW_{10} composite fibers using co-evaporation electrospinning, showing that EuW_{10} nanoparticles are well dispersed in PVA fibers. C,D) Digital photographs of PVA/ EuW_{10} composite fiber film in natural light and ultraviolet light after two months, respectively. Reproduced with permission from Reference [146]. Copyright 2006, IOP Publishing Ltd.

In principle, the co-evaporation method affords a very simple means for the preparation of functional polymer/polymer and inorganic/polymer composite nanofibers.

3.7. Coaxial Electrospinning

As discussed above, the conventional setup for electrospinning usually contains a single capillary as the spinneret, which affords the fabrication of solid fibers. If we replaced the single capillary by two coaxial capillaries, the core/sheath nanofibers would form, which is called coaxial electrospinning. Therefore, the coaxial electrospinning technique affords us a chance to synthesize functional composite nanomaterials. In the past few years, there were many reports on the fabrication of composite nanofibers using coaxial electrospinning, including polymer/polymer, polymer/inorganic, and inorganic/inorganic composites. Greiner and co-workers have recently demonstrated that core/sheath nanofibers of polysulfone (PSU)/PEO, poly(dodecylthiophene) (PDT)/PEO could be prepared using coaxial electrospinning^[147] (Figure 8). During the coaxial electrospinning process, both liquids outflowing from the core and the surrounding concentric annular nozzles were not easily mixed because the spinning process took place very quickly and there would not be enough time for their mixing before solidification. For PSU/PEO, the outer and core diameters of the order of the core/sheath nanofibers were about 60 and 40 nm, respectively. For PDT/PEO coaxial fibers, the total fiber diameter was about 1000 nm, whereas the diameter of the core region was about 200 nm. Using a similar methodology, PMMA/PA-66, PC/PMMA, PC/PA-66, MEH-PPV/PVP, PHT/PVP, PC-PU, PVP-PLA, silk-PEO, PCL-zein, PVP-oil, poly(styrene-block-isoprene-block-styrene)/poly(methyl-

methacrylate-*co*-methacrylic acid) random copolymer, PCL/PEG core/sheath nanofibers, and even cell-encapsulated polymer have also been fabricated.^[148–161] In the field of cell engineering, PCL/gelatin core/sheath nanofibers have recently attracted much attention.^[162–164] Zhang and co-workers have synthesized PCL/gelatin core/sheath nanofibers using coaxial electrospinning.^[162] TEM images show the strong contrast between the PCL and gelatin, indicating the core/sheath structure. XPS data also proved this result for the absence of the N 1s signal at the binding energy of ≈ 400 eV on the XPS spectrum of PCL-gelatin nanofibers. Moreover, it could be concluded that the PCL shell was at least thicker than 10 nm, which was the uppermost for XPS detection. Enzyme can also be directly encapsulated into polymer fibers to form 1D composites via the coaxial electrospinning technique. Zussman and co-workers have fabricated two kinds of hollow polymer fiber containing enzyme; one is non-porous and the other is porous.^[165] The results show that the porous fibers exhibited higher rates of enzymatic reaction. When small enzymes such as alkaline phosphatase (AP) were encapsulated into porous polymer fibers, AP can diffuse out of the fibers through the pores, which can act as an enzyme-release device. On the other hand, when larger enzymes such as β -galactosidase (β -GAL) were encapsulated into polymer fibers, β -GAL remained in the fibers without any leaching, which can act as an enzymatic microreactor. Moreover, the porous polymer fibers exhibit a high level of enzymatic activity, indicating that substrate penetration is extremely good with this kind of fiber.

Coaxial electrospinning can also be applied to polymer/inorganic component systems.^[147,166–170] Song et al. demonstrated that core/sheath FePt/PCL composite nanofibers could be prepared by coaxial electrospinning.^[166] In contrast to the polymer/polymer composite nanofiber system, the polymer solution was replaced by a hexane solution of FePt nanoparticles as the inner fluid. Both TEM observation and XPS surface analysis confirmed that FePt nanoparticles with a diameter of about 4 nm were completely encapsulated within the PCL nanofibers. The encapsulated array of the discrete FePt nanoparticles could reach as long as 3000 nm along the fiber axis. Greiner and co-workers prepared PLA/Pd composite nanofibers by electrospinning PLA chloroform solution with Pd(OAc)₂ in tetrahydrofuran, followed by annealing for 2 h at 170 °C.^[147] TEM investigations showed the outer diameter of the coaxial fibers was about 500 nm and the core phase was about 60 nm (Figure 8B). It was proposed that PLA induced a 1D arrangement of Pd during the process of coaxial electrospinning.

In addition to polymer/polymer (organic) and polymer/inorganic composite nanofibers, inorganic/inorganic component composite nanofibers have also been fabricated using coaxial electrospinning.^[171–173] Chen and co-workers demonstrated that core/sheath LiCoO₂/MgO fibers could be synthesized by coaxial electrospinning combined with sol-gel process.^[171] The authors prepared the LiCoO₂ spinnable sol with the viscosity of 4.0 Pa s as the core fluid and MgO sol with the viscosity of 4.0 Pa s as the shell fluid. The N₂ pressures was applied for the LiCoO₂ and MgO precursor sols controlled at 0.3 MPa and 0.02 MPa, respectively, during the electrospinning process. Xia and co-workers claimed that they could control

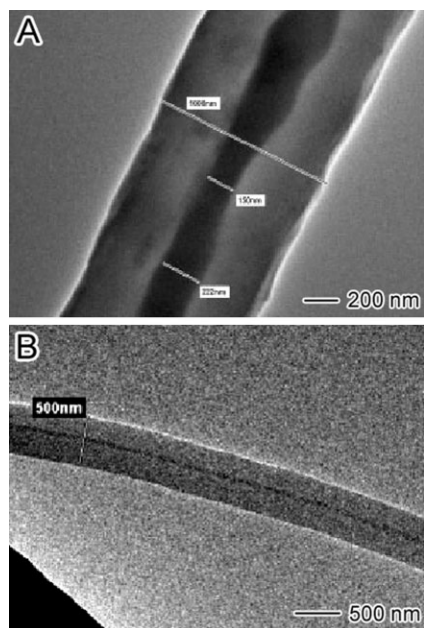


Figure 8. A) TEM image of unstained samples by coaxial electrospinning, showing the contrast between the core polymer (PDT) and shell polymer (PEO). B) TEM image of annealed (170 °C for 2 h) unstained samples of co-electrospun PLA and Pd(OAc)₂. Reproduced with permission from Reference [147].

the organic molecules or the inorganic nanoparticles onto the inner, the outer, or both the inner and outer surface of the ceramic nanotubes.^[172] In order to incorporate organic molecules or the inorganic nanoparticles onto the inner surface of TiO₂ nanotubes, they dissolved the corresponding materials in oil as the core fluid and TiO₂ sol in PVP ethanolic solution as the shell fluid, followed by the extraction of oil with octane or calcination to obtain TiO₂/dye and TiO₂/Fe₃O₄ composite nanofibers, respectively. Moreover, the hollow ceramic nanofibers can selectively adsorb inorganic nanoparticles by controlling the hydrophobic and hydrophilic properties of the inner and outer surface by functionalizing different self-assembled monolayers.

4. Applications of Electrospun 1D Composite Nanomaterials

As demonstrated in previous sections, electrospinning is a remarkably simple and powerful technique for generating 1D composite nanomaterials. Because of the multifunctional properties of the composite materials, they are expected to be applied in many fields, such as nanoelectronic and optical devices, chemical and biological sensors, catalysis and electrocatalysis, superhydrophobic surfaces, environment, energy, and biomedical fields.

4.1 Electronic and Optical Nanodevices

In the past few years much attention has been paid to the electrical and electro-optical properties of metallic and semiconducting nanowires for their potential applications in fabricating nanoscale electronic and optoelectronic devices.^[174–183] Recently, 1D composite nanomaterials synthesized by electrospinning have been studied as a model of electronic and electro-optical devices. Johnson and co-workers fabricated and electrically characterized electrospun nanofibers of a doped PANI/PEO blend with different diameters.^[184] It was found that the conductivities of these fibers were dependent on their diameters; the fibers with diameter below 15 nm were electrically insulating. The asymmetric fibers indicated that they were rectifying, consistent with the formation of Schottky barriers at the nanofibers–metal contacts. Pinto and co-workers demonstrated the fabrication of field-effect transistor (FET) behavior in the doped PANI/PEO composite nanofibers and observed saturation channel currents at surprisingly low source–drain voltages.^[185] The hole mobility in the depletion regime is $1.4 \times 10^{-4} \text{ cm}^2 \text{ Vs}^{-1}$.

Electrically bistable devices represent an ideal application to take advantage of 1D composite nanomaterials. Our group demonstrated the fabrication of 1D Ag-NP/TCNQ/PVP nanocomposites by the electrospinning process^[186] (Figure 9). The composite nanofiber device exhibited very interesting bistable electrical behavior. As the potential was lower than +29 V, the current was very low, indicating that the nanofibers had a high impedance. When the potential was higher than +29 V, an abrupt increase in current was observed, corresponding to the change in resistance of the composite nanofibers from 1.5×10^6 to 100 Ω . This changed the device from a low-conductivity OFF state to a high-conductivity ON

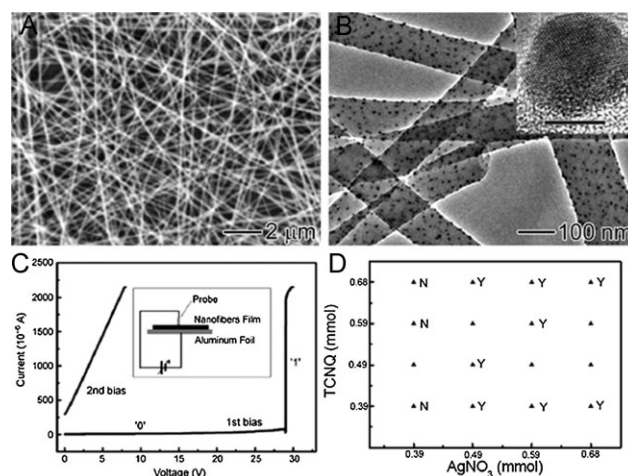


Figure 9. A) SEM image of Ag-NP/TCNQ/PAN composite nanofibers by electrospinning, followed by photoreduction. B) TEM image of Ag-NP/TCNQ/PAN composite nanofibers, showing that spherical Ag nanoparticles are well dispersed in PAN nanofibers. The inset shows a high-resolution TEM image of a single Ag nanoparticle; the crystal lattice is in accord with that of Ag. The scale bar represents 5 nm. C) *I*–*V* curve of Ag-NP/TCNQ/PAN composite nanofibers. The inset shows a schematic image of the measurement circuit. D) The electrical bistability of Ag-NP/TCNQ/PAN composite nanofibers with different AgNO₃/TCNQ ratios. N = no electrical bistability; Y = electrical bistability. Reproduced with permission from Reference [186].

state. Most importantly, the OFF state could be recovered from the ON state by simply applying a reverse-bias pulse, and the bistable properties were stable and reproducible. In principle, the electrospinning technique could directly fabricate metal nanoparticles/polymer composite nanofibers, which could be used for nonvolatile memory elements and nanoswitches. In a different study, our group found that the surface photovoltage response took a reversal when the electrospun TiO₂ nanofibers were coated with a layer of conducting polymers. These observations might be helpful for the construction of optoelectronic devices.^[187]

4.2. Chemical and Biological Sensors

Our group has demonstrated the fabrication of LiCl-doped TiO₂ nanofibers by using the electrospinning technique as the humidity sensors^[188] (Figure 10). We prepared a solution of tetrabutyl titanate, LiCl, and PVP in ethanol and acetic for electrospinning, followed by calcination to obtain TiO₂/LiCl composite nanofibers. The as-prepared humidity sensor based on the LiCl-doped TiO₂ nanofibers exhibits excellent sensing characteristics. The dependence of impedance on the relative humidity (RH) showed that LiCl-doped TiO₂ nanofibers exhibited greatly improved sensitivity compared to the pure TiO₂ nanofibers. And the composite nanofibers also exhibited an ultrafast response and recovery behavior. When the RH increased from 11% to 95%, the response time was less than 3 s; correspondingly, the recovery time was less than 7 s when the RH decreased from 95% to 11%. Moreover, the humidity sensor also had good reproducibility, linearity, and stability. The results showed that there was little difference between the highest and lowest impedance values from the curves for

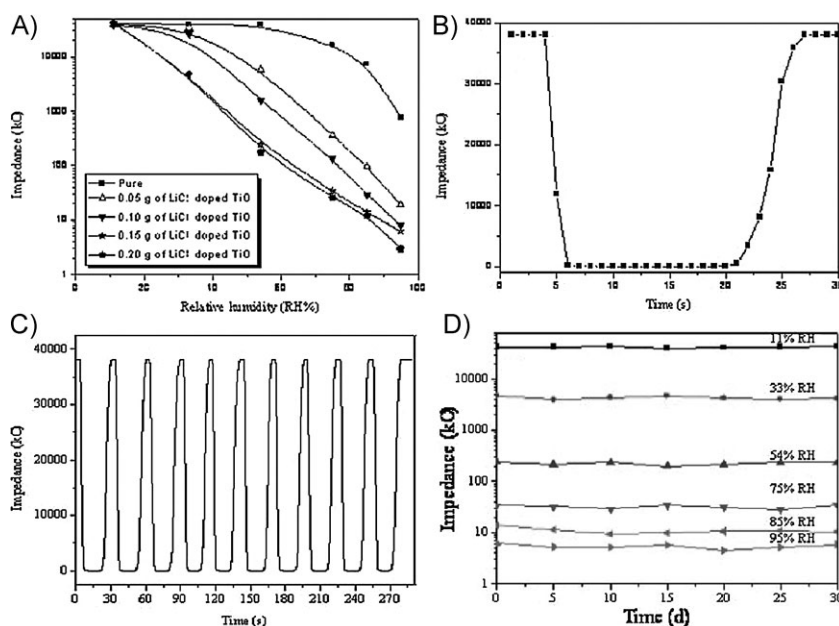


Figure 10. A) The dependence of impedance on the RH for TiO₂ nanofibers containing different contents of LiCl. B, C) Response and recovery characteristic curves based on the composite fibers containing 30.0% LiCl-doped TiO₂ nanofibers for 1 cycle and 10 cycles. D) Stability of the sensor after exposure in air for 30 days. Reproduced with permission from Reference [188]. Copyright 2008, American Chemical Society.

10 cycles. Moreover, there were almost no changes in the impedance when LiCl-doped TiO₂ nanofibers were exposed in air for 30 days. Similar results have been reported for KCl-doped TiO₂ nanofibers.^[189]

Samuelson and co-workers have demonstrated the fabrication of nanofibrous thin-film optical sensors composed of poly(acrylic acid)-poly(pyrene methanol) (PAA-PM) and thermally crosslinkable PU using the electrospinning technique.^[190] The decrease in fluorescence intensity of the composite fibers film with increasing concentration of analytes was caused by efficient quenching by electron-deficient analytes. The sensitivities of such composite nanofibers as optical sensors for metal ions (Fe³⁺, Hg²⁺) and 2,4-dinitrotoluene (DNT) detection were two to three orders of magnitude higher than those obtained previously from continuous thin-film sensors. The improvement was mainly due to the high surface-to-volume ratio of the nanofibrous film and the porous structure, which allowed the analytes to easily transport to the active sites on each nanofiber.

In addition to humidity and optical sensors, gas sensors based on the PANI/PEO composite nanofibers by electrospinning have also been fabricated by Craighead and co-workers.^[191] The sensor device exhibited a rapid and reversible resistance change on exposure to 0.5 ppm NH₃ gas. The authors also found that the response times were related to the diameter of the composite nanofibers. Both response time and sensitivity have been greatly improved compared to the previously reported PANI film sensors. This indicates that the electrospinning technique can afford a simple approach for the fabrication of 1D composite nanomaterials for sensing technology. Kim and co-workers demonstrated that a novel colorimetric sensor system could be prepared based on silica-enforced electrospun fibers embedded with conjugated poly-

mers of polydiacetylenes (PDAs).^[192] The color transition of PDA induced by the organic solvent was related to the structure of diacetylene monomer, indicating the possibility of use as chemosensors in response to organic solvents. The effect of silica in the composite nanofibers was to increase the stability of the sensors. However, the number of structurally diverse diacetylene monomers should be developed to detect more kinds of organic solvent.

Composite electrospun nanofibers can act as a biosensor, which has been defined as a device that converts a biological signal into an electrical output with the biological recognition mechanism. Sawicka and co-workers have demonstrated the fabrication of urease-immobilized PVP fibers by electrospinning a mixture of them in ethanol solution, which could be used as a urea biosensor.^[193] The PVP/urease composite nanofibers mats had a large surface area, which offered an improved adsorption rate and reduced the response time. The reaction began as soon as the composite mat was introduced to the urea solution and it

continued for 20 min. The storage stability was also studied. The composite mats remained activated after refrigeration for one week. The detection limit of the composite nanofibers mats was from 0.5 to 2.5 mM urea solutions. In principle, the electrospun nanofibers afford a cost-efficient urea-sensing material. However, the response time, the detection limit, and the storage stability all need to be improved, which may be realized by introducing the interactions between the detection molecules and the electrospun mats. Wei and co-workers have demonstrated that various enzymes could be encapsulated in nanoporous silica nanofibers by the electrospinning method, which could act as excellent biosensors.^[194] For example, horseradish peroxidase enzymes encapsulated in silica nanofibers could catalyze the conversion of H₂O₂ to water, along with the conversion of the colorless dye (phenol-4-aminoanti-pyrene) to a red color (quinoneimine), which can be easily detected by the naked eye.

4.3. Catalysis and Electrocatalysis

Electrospinning affords an effective way to fabricate a ceramic nanofiber mat, which is suitably used as a photocatalyst, with examples including TiO₂ and ZnO nanofibers.^[195,196] On the other hand, the electrospun mats from stable polymer or ceramic fibers are also good catalytic supports because they can provide a large surface area and a high porosity. In principle, composite catalysts based on the electrospun polymeric or ceramic nanofibers mats can be synthesized in two ways. The first method is to electrospin the mixed solution of polymer or ceramic precursors with the metal salt to yield mats of composite fibers. Subsequently, the metal salts in the composite nanofibers need to be reduced,

either by heating at high temperature or in the presence of a reducing agent, yielding polymer/metal or ceramic/metal composite nanofibers.^[197–201] The other method is post-treatment of the electrospun nanofibers mats to deposit metal nanoparticles on the surface of the fibers.^[202–207]

Erman and co-workers demonstrated the fabrication of catalytic palladium nanoparticles on electrospun copolymers of acrylonitrile and acrylic acid (PAN-AA) nanofiber materials.^[86] They used the homogeneous DMF solution of PAN-AA and PdCl₂ for electrospinning, followed by the reducing treatment in an aqueous hydrazine solution to obtain PAN-AA/Pd composite nanofibers. TEM images showed the Pd nanoparticles were spherical and dispersed homogeneously on the electrospun nanofibers. The size of Pd nanoparticles could be tuned by varying the amount of PdCl₂ and the copolymer composition (acrylic acid functional groups). They studied the catalytic activity of the PAN-AA/Pd composite nanofibers to selective hydrogenation of dehydrolinalool (3, 7-dimethyloct-6-ene-1-yne-3-ol, DHL) in toluene at 90 °C. The results showed that Pd nanoparticles incorporating PAN/AA copolymer nanofibers have 4.5 times higher catalytic activity than the conventional Pd/Al₂O₃ catalyst. Hou and co-workers also prepared PAN/Pd(OAc)₂ composite nanofibers using electrospinning. Furthermore, they converted the PAN/Pd(OAc)₂ composite nanofibers to carbon/Pd fibers by a carbonization process.^[197] They studied the catalytic activities of the composite nanofibers in the liquid-phase Sonogashira C–C coupling reaction of iodobenzene and phenylacetylene. The results showed that carbonized electrospun PAN/Pd composite nanofibers exhibited a higher catalytic activity and a high leaching resistance, retrieval, and reusability. Graeser and co-workers also prepared polymeric core/sheath fibers containing palladium, rhodium, platinum, or bimetal nanoparticles combining electrospinning with thermal decomposition (or hydrogen reduction) and chemical vapor deposition (CVD).^[167] TEM images showed that the metal or bimetal nanoparticles were distributed in a polymer or hollow core of the composite nanofibers. The resulting core/sheath composite nanofibers showed a high activity in hydrogenation reduction. Moreover, they were easily removed and reused, which make the composite nanofibers a very promising catalyst system.

Wei and co-workers prepared porous silica nanofibers containing silver nanoparticles by electrospinning the mixture solutions of tetraethyl orthosilicate, poly[3-(trimethoxysilyl)propyl methacrylate] (PMCM), and AgNO₃, followed by calcination at high temperature. During the heating, PMCM was thermally decomposed and AgNO₃ was converted into silver nanoparticles, resulting in porous silica/silver composite nanofibers^[198] (Figure 11). The size and density of the silver nanoparticles in the silica fibers could be controlled by varying the amount of AgNO₃ introduced, and the thermal treatment conditions. TEM images of the composite fibers exhibited a homogeneous distribution of silver nanoparticles inside the porous silica fibers. They studied the catalytic properties of the silica/Ag composite nanofibers for the reduction of methylene blue dye with sodium boron hydride as the reducing agent. It was concluded that the composite nanofibers showed very good catalytic properties, and no deactivation or poisoning of the catalyst was observed.

For homogeneous catalysis, systems of composite nanofibers combined with commercially available scandium triflate (Sc(OTf)₃) and PS were fabricated by electrospinning. In order to deduce the leaching, a layer of poly-*p*-xylylene (PPX) or poly-*p*-chloroxylylene (PPX-C) is deposited on the surface of PS/Sc(OTf)₃ composite fibers via CVD to form a core/sheath structure.^[199] The catalysis results indicated that the composite core/shell fibers (PPX-C as a shell layer) could achieve 100% conversion for the catalysis of the aza-Diels-Alder reaction, while the conventional catalysis in homogeneous solution or in microemulsion only achieved 80% conversion in longer reaction time. Moreover, such homogeneous catalysts with core/sheath structures could be used several times without loss of activity.

In addition to the above methods to fabricate polymer- or ceramic-supported metal nanoparticles, post-treatment is also an easy and reusable means or the preparation of polymer/metal and ceramic/metal composite nanofibers. Xia and co-workers demonstrated the decoration of Pt nanoparticles with different sizes on the surface of TiO₂ nanofibers using a polyol reduction method in the presence of PVP.^[202,203] Moreover, Pt nanowires with a length of 125 nm could also be coated on the surface of TiO₂ nanofibers using Pt nanoparticles as seeds. The resultant fiber mats exhibited excellent catalytic activities for the hydrogenation of methyl red. The results also showed that the catalytic ability for the Pt-nanowire-decorated mat was much better than those coated with Pt nanoparticles, which was attributed to the larger active surface area of the Pt-nanowire-based fibers. An electrocatalytic study for direct methanol oxidation of these supported Pt nanostructures has also been reported.^[203] As compared with a commercial Pt/C catalyst, the TiO₂ nanofibers decorated with both the small Pt nanoparticles (2 nm) and nanowires display improved catalytic durability, which might be due to a synergistic effect of TiO₂ nanofibers and small size for Pt nanoparticles or well-defined facets for Pt nanowires.

Han, Yang and co-workers also demonstrated the fabrication of carbon nanofibers containing Pt nanoparticles using post-treatment of electrospun fibers for the study of electrocatalysis.^[204] They prepared the electrospun PAN fibers by first using electrospinning, followed by thermal treatment to obtain carbon fibers with an average diameter of about 150 nm. Pt nanoparticles could be deposited on the surface of carbon fibers by using a multicycle cyclic voltammetry (CV) method. They concluded that the performance of the synthesized carbon/Pt composite nanofibers was superior to that of commercial Pt/C composites in terms of electrocatalytic activity and stability towards the oxidation of methanol. It was proposed that the high performance of the synthesized carbon/Pt composite nanofibers was related to the relatively high conductivity and the close contact between Pt particles and carbon nanofibers. In principle, such carbon nanofibers converted from the electrospun nanofibers could act as supporting materials for noble metal catalysts with higher performance.

4.4. Superhydrophobic Surfaces

Generally, superhydrophobic surfaces with self-cleaning applications with contact angles (CA) larger than 150° require a hierarchical micro/nanostructure and low surface energy. Such micro/nanostructures can be fabricated by electrospinning. In

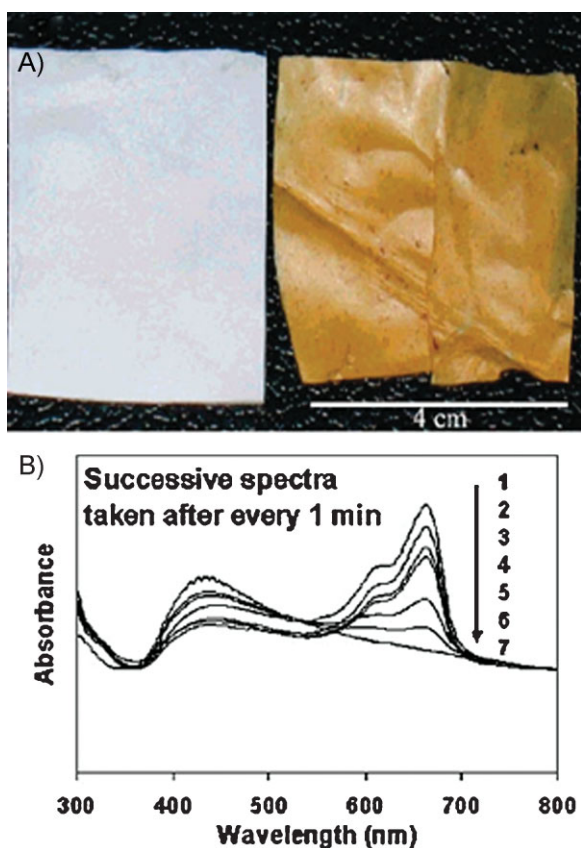


Figure 11. A) Electrospun PMCM-modified silica fiber mats containing AgNO_3 before and after heat treatment, showing that the color of the composite fibers changed from white to golden yellow after heat treatment. B) Successive UV/vis spectra of methylene blue dye reduction using silica/Ag composite nanofibers as the catalyst and NaBH_4 as the reducing agent. Reproduced with permission from Reference [198]. Copyright 2007, American Chemical Society.

the past five years, electrospun polymer and block-copolymer micro/nanostructure mats have been used for the fabrication of superhydrophobic surfaces.^[208–217] Here we discuss the applications of 1D composite nanofibers generated by electrospinning as superhydrophobic surfaces. In order to obtain a superhydrophobic surface, long alkyl chains are often further modified on the surface of a hydrophobic substrate. Ding and co-workers fabricated CA nanofibers by the electrospinning technique, which showed superhydrophilic properties.^[218] However, if modified with a simple sol–gel coating of decyltrimethoxysilane (DTMS) and tetraethyl orthosilicate (TEOS), the surface properties changed to superhydrophobic. It was concluded that the superhydrophobicity of the electrospun fibrous mates was due to the combined effects of high surface roughness and the hydrophobic DTMS sol–gel coating. The same group also prepared silica nanofibers by electrospinning the mixed solutions of PVA and colloidal silica nanoparticles, followed by calcination to remove the polymer.^[219] Similarly, after modification with fluoroalkylsilane, the electrospun silica nanofiber mats showed superhydrophobicity with a CA larger than 164° .

Without modification, the electrospun composites with micro/nanostructures also showed superhydrophobic properties. Jiang, Feng and co-workers prepared azobenzenesulfonic

acid (ABSA)-doped PANI/PS composite film by electrospinning their blending solutions.^[220] SEM images of the composite film exhibited a web of nanofibers with many submicrometer-sized spheres. Careful observation indicated that the surface of the microsphere was composed of many nanoscale protuberances and the nanofibers were linked with many nanoknots, which was similar to the structure of lotus leaf. The PANI/PS composite film was superhydrophobic, with both a high CA (higher than 150°) and low sliding angle (SA; lower than 5°). Moreover, the superhydrophobicity and conductivity were well maintained over a wide range of pH conditions, although the PANI could be doped in the lower pH and dedoped in the higher pH conditions. The superhydrophobic properties and conductivities were strongly related to the PS content. The conductivity of the electrospun composite film decreased upon increasing the content of PS before it reached 5 wt%. After this content, the conductivity did not change much any more. The CA for water decreased slightly from $166.5 \pm 2.4^\circ$ to $154 \pm 2.1^\circ$ after the PS content increased from 3.72 wt% to 7.10 wt%, which should be due to the increase in smoothness after the increase in PS content. The same group also demonstrated the fabrication of conductive, magnetic, and superhydrophobic Fe_3O_4 -filled carbon nanofibers by electrospinning PVA water solution with ferrous acetate (FeAc_2), followed by carbonization under argon atmosphere at 600°C .^[221] All of the conductive, magnetic, and superhydrophobic properties could be adjusted by the content of FeAc_2 in the electrospun composite nanofibers. For example, the composite Fe_3O_4 -filled carbon nanofibers were ferromagnetic with a saturation magnetization (M_s) and coercivity (H_c) of 62.8 emu g^{-1} and 150.7 Oe , respectively, with conductivity of about 3.4 S cm^{-1} when the FeAc_2 content is 50 wt%. With the same FeAc_2 content, the CA for water was $152.3 \pm 2.1^\circ$ on the electrospun Fe_3O_4 -filled carbon nanofibers.

In addition to the superhydrophobic surfaces, some special stimuli-responsive, smart materials that can switch between superhydrophobicity and superhydrophilicity can also be fabricated by the electrospinning technique. Jiang and co-workers prepared a series of temperature-responsive poly(N-isopropylacrylamide) (PNIPAAm)/PS composite films just by electrospinning their mixture solutions.^[222] With the correct proportion of each polymer, the wettability of the surface could be changed from superhydrophilicity (CA less than 20°) at 20°C to superhydrophobicity (CA greater than 150°) at 50°C . It was considered that the stimuli-responsive PNIPAAm made a great contribution to this unique surface property. In addition to the temperature, the change of pH value and redox properties also showed a chemical dual-responsive surface wettability. The same group prepared PAN/PANI coaxial nanofibers by electrospinning in association with in situ chemical polymerization.^[223,224] As we know, PANI has the conducting emeraldine salt and insulating emeraldine base forms, which can be reversibly converted by doping with acid or dedoping with base. For perfluorooctanesulfonic acid-doped PANI, hydrophobic function has been introduced to the surface. Combined with the roughness effect of the electrospun PAN nanofibers, the composite film was superhydrophobic with a water CA as high as 164.5° . The CA could be changed to be about 0° for a basic droplet with pH 13.07, and the reversible

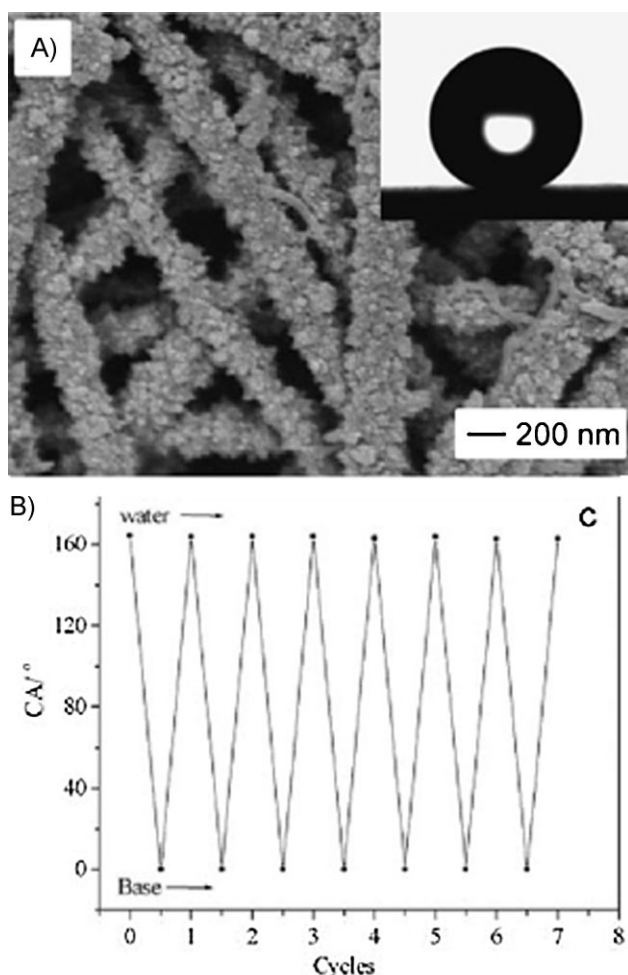


Figure 12. A) SEM image of PANI/PAN composite coaxial nanofibers, showing the roughness of the electrospun fibers film. Inset: water droplet on the surface of the PANI/PAN coaxial nanofibers film, showing a superhydrophobic characteristic. B) Reversible superhydrophobicity/superhydrophilicity for a water droplet and a basic droplet with pH 13.07 on the surface of PFOS-doped PANI-PAN coaxial nanofibers. Reproduced with permission from Reference [223].

cycles could also be repeated many times (Figure 12). The authors have also studied the effect of the redox state of PANI on the wettability of PANI/PAN coaxial nanofibers. The results indicated that PANI/PAN coaxial nanofibers also showed a reversible wettability with CA from $156.4 \pm 1.4^\circ$ to $116.9 \pm 3.0^\circ$. The authors claimed that such a dual-responsive composite surface could be applied in biologic separation and controllable growth of cells and sensors.

4.5. Environmental Applications

The contamination of water by toxic heavy metals and air by poisonous gas and volatile organic compounds (VOC) is a world-wide environmental problem. In general, adsorption-based methods are considered essential in performing the removal of heavy metals in water or poisonous gas and VOC in air. The electrospun nanofiber mat is a potential candidate as an environment-cleaning material due to its large surface area, porous structure, and cost-effective preparation. In particular,

inorganic nanoparticles incorporated into electrospun nanofibers are more attractive as the water cleaner because they can prevent the release of nanoparticles into the environment, and avoid or reduce the cost associated with separation of nanomaterials from treated water. Hota and co-workers demonstrated that boehmite nanoparticles could be incorporated into both the hydrophilic nylon and hydrophobic PCL polymer.^[225] A capacity for the sorption of Cd (II) of about 0.20 mg g^{-1} was achieved for the two kinds of composite nanofiber. Electrospun polymer/polymer composite fibers can also be used as a heavy metal ion adsorbent. Park and co-workers prepared wool keratose (WK)/silk fibroin (SF) composite fibers for removing heavy metal ions by adsorption on chemical or physical affinity.^[226] In fact, WK showed better performance than SF as a heavy metal ion adsorbent because WK has far more amino acids having polar side residues. However, the combination of SF with WK can improve the electrospinnability and structural stability. The results showed that the composite fiber mats had a good performance for the adsorption of metal ions. Furthermore, such an adsorption capacity has been maintained over several recycling process.

In addition to toxic heavy metals, poisonous gas and VOC can also be adsorbed by electrospun nanofibers. Our group demonstrated that ultrafine porous carbon fibers (UPCF) can be fabricated by electrospinning, followed by carbonization.^[227] In order to remove SO_2 more effectively, UPCF was modified with the nitrogenated compound. The results showed that the modified UPCF has a better adsorption capacity for SO_2 than UPCF and conventional porous carbon fibers. Moreover, the fatigue test showed that the modified UPCF also has good durability. The electrospun composite nanofibers have also proved to be an effective adsorbent for toluene. Lee and co-workers demonstrated that electrospun manganese (Mn)-dispersed PAN-based composite fibers with higher specific surface area and larger micropore volume can be prepared.^[228] The toluene adsorption capacity of a 0.23 wt.% Mn-loaded sample can be achieved for a 68 g toluene/100 g composite. In comparison, it is only about 40 g/100 g for a Mn-free sample.

Chemical warfare agents, such as nerve gas, blood agents, mustard gas, and other toxins are serious issues in the environment. Ramakrishna and co-workers have fabricated 1D composite nanomaterials containing poly(vinylchloride) polymer and a catalyst for the detoxification of nerve agents, which have been prepared from β -cyclodextrin and o-iodosobenzoic acid.^[229] The as-synthesized 1D composite nanomaterials have proved very effective for the decontamination of paraoxon, a nerve-agent stimulant. The results demonstrate that the 1D composite nanomaterials have higher capacity than the conventionally used activated charcoal. The electrospun composite nanomaterials may also be applicable in environmental fields by different kinds of filtration.^[230,231]

4.6. Energy Applications

Energy is one of the most important global problems facing society in the 21st century. At present, fossil fuels including coal, oil, and natural gas supply most of the energy we purchase and makes what we do possible. However, fossil fuels pose a dilemma for human society. Fossil fuels are not renewable; once

they are gone they are gone. Furthermore, pollutants emitted during the burning of fossil fuels degrade the environment and greenhouse gases lead to the global-warming problem. Therefore, developing technology and devices for highly efficient and clean energy is a meaningful challenge. Efficient use of energy is often connected with energy-conservation devices, such as solar cells, fuel cells, and energy-storage devices such as supercapacitors.^[230] For dye-sensitized solar cells (DSSCs), it is believed that metal oxide nanostructures with a 1D morphology have a better charge conduction for increasing energy-conversion efficiency. Electrospun TiO₂ nanofibers or nanorods are most widely studied as an electrode for DSSCs for their high surface area and large pores for the increased adsorption of dye sensitizers.^[232–237] In order to improve the adhesion between 1D TiO₂ nanomaterials and the conductive substrates, many methods have been investigated, such as hot press pretreatment, solvent vapor, mechanical grinding, use of an ultrathin surface treatment layer on conductive substrates, and so on.^[232–235] After the anchoring of ruthenium dyes onto the electrospun 1D TiO₂ nanomaterials to form composites for DSSCs, the best-performing DSSC gives a current density of 13.6 mA cm⁻², an open-circuit voltage of 0.8 V, a fill factor of 51%, and an energy-conversion efficiency of 5.8%.^[234] Organic-based photovoltaics can be realized through blending metal oxide semiconductor and conjugated polymer matrix, between which charge transfer will occur. The fabrication of poly(3-hexylthiophene)/ZnO composite nanofibers as photovoltaic devices has been widely studied.^[238,239] It is anticipated that the electrospinning technique will afford a facile and versatile method to prepare many kinds of such 1D composite nanomaterials for photovoltaic applications.

Fuel cells are now attracting enormous interest for applications in low-emission vehicles and home power generators. Among different kinds of fuel cell, the direct methanol fuel cells (DMFCs) have been widely studied recently for their room-temperature operation and potential high energy density. In DMFCs, supporting materials are necessary to load catalysts of platinum nanoparticles or its alloy. It has been proved that the supporting materials have a great effect on the catalytic activity of platinum nanoparticles. To improve the anode catalyst performance, the supporting materials should be stable, a good electron conductor, and have a large surface area. Therefore, various carbon materials such as mesocarbon, carbon fibers, and carbon nanotubes have been widely used as catalyst supports for DMFCs. Through the electrospinning technique, continuous nanoscale carbon fibers and nanoporous carbon fibers have been synthesized, which are good candidates for catalyst supports.^[240,241] Han and co-workers have synthesized Pt-cluster-supported carbon fibrous mats (CFMs/Pt) by the electrospinning and electrodeposition methods for DMFCs. In contrast to the commercial catalyst, the catalytic peak current on optimum CFMs/Pt electrode has increased.^[204]

Li ion batteries are one of the most promising power sources for electric vehicles and power tools. Recently, Kim and co-workers have fabricated carbon fibers by electrospinning followed by heating at high temperature for the anode material of lithium ion secondary batteries, which can attain a reversible capacity of up to 500 mA h g⁻¹.^[242] In order to retain the high capacity of carbon at relatively low temperature and improve

the electrical conductivity, Chen and co-workers have synthesized carbon/cobalt composite nanofibers via electrospinning and a subsequent heating treatment.^[243] The as-prepared carbon/cobalt composite nanofibers have a high conductivity, a large reversible capacity of more than 800 mA h g⁻¹, and good cycling performance. Fu and co-workers have also fabricated SWNTs/NiO composite nanofibers by electrospinning. The results show that SWNTs/NiO composite nanofibers can effectively improve the rate capability compared with pure NiO nanofibers.^[244]

Supercapacitors are widely regarded as the most promising electrochemical energy-storage systems with broad applications in the field of mobile devices and electric vehicles. Compared with lithium ion batteries and conventional capacitors, supercapacitors have the advantage of both high power density and stable cycle life. In combination with electrospinning and carbonization, composite carbon nanofibers containing CNTs have been produced for supercapacitors.^[245] The capacitance of electric double-layer capacitors of CNT-embedded carbon nanofibers is almost double that of virgin carbon nanofibers as electrodes. Lee and co-workers have prepared polypyrrole/carbon nanofibers/CNT three-component composite nanomaterials for supercapacitors.^[246] The capacitance of polypyrrole/carbon nanofibers/CNT composite nanomaterials is 333 F g⁻¹, which is much higher than virgin carbon nanofibers and carbon nanofibers/CNT composite, indicating that the electrochemical properties can be greatly improved by the introduction of the conducting polymers.

4.7. Biomedical Applications

From a biological viewpoint, electrospun nanofibers are the most promising material that can be applicable in medicine and pharmacy because almost all human tissues and organs, including bone, dentin, collagen, cartilage, and skin, have dimensions on this order. During the past few years, the field of application for electrospun polymeric nanofibers has developed very quickly; a series of natural polymers, such as proteins, polysaccharides, DNAs and lipids and synthetic polymers such as PU, PVA, PEO, PCL, PLA, polyglycolide (PGA), polydioxanone, polyphosphazene derivatives, and synthetic copolymers have been electrospun into nanofibers. Such electrospun materials can be applied for tissue engineering, immobilized enzymes, wound healing, artificial blood vessels, drug delivery, and so on.^[24–26,247,248] However, the limited properties of electrospun polymer nanofibers with only one component restrict their application in biomedical engineering. Therefore, electrospun composite nanofibrous scaffolds are an appealing option. In the following, we illustrate a few examples of applications of 1D electrospun composite nanomaterials for drug delivery, tissue engineering, and wound dressing.

4.7.1. Drug Delivery

Electrospun nanofibers for drug delivery have many advantages, such as easy implementation, little influence on the drug activity, well-controlled release rate, and so on.^[249–260] In most cases, the release of water-soluble drugs incorporated into a water-soluble polymer will exhibit an early stage burst. Therefore, the emulsion electrospinning method was proposed to electrospin the emulsion of a drug/polymer/solution system

to encapsulate drugs inside the polymer nanofibers,^[132] as discussed in Section 3. Hsiao and co-workers demonstrated that using electrospun composite nanofibers (PLGA/PLA/PEG-b-PLA) showed a sustained release profile after the initial burst compared to PLGA scaffold.^[257] This was because the drug could be trapped in electrospun nanofibers as a complex with the hydrophilic block of PEG-b-PLA, resulting in the sustained release behavior. However, such a method could not avoid the initial burst. Similar to emulsion electrospinning, coaxial electrospinning could also encapsulate drugs in the PCL fibers, forming a core/sheath structure.^[258] The degradation and drug release rates of the composite nanofibers were related to the hydrophilicity of the drugs. The drug release was smooth and no burst release occurred.

Another promising way to control the release profile of drugs is by coating a thin layer of polymer on the surface of drug-encapsulated electrospun nanofibers. Greiner and co-workers prepared bovine serum albumin (BSA)-loaded PVA nanofibers by electrospinning.^[259] By modifying a layer of PPX using a CVD method, they obtained BSA-loaded PPX/PVA composite fibers. In contrast with PVA fibers, no burst release for PPX/PVA composite fibers was observed. Moreover, the composite fibers exhibited a significantly controlled retarded release of BSA depending on the thickness of the coated PPX. Another type of polymer coating on the surface of electrospun nanofibers is conducting polymers, such as polypyrrole (PPy) and poly(3,4-ethylenedioxythiophene) (PEDOT). It is well known that conducting polymers can be actuated under applied voltages, which may apply for the control of drug release. Martin and co-workers demonstrated core/sheath structures of drug-loaded PLGA/PEDOT could be prepared by electrospinning the chloroform solution of PLGA with dexamethasone, followed by electrochemical deposition of PEDOT around the electrospun nanofibers.^[260] The results showed that the drug release could be controlled at desired points in time by using an electrical stimulation of the composite nanofibers. Figure 13 shows cumulative mass release of dexamethasone from PLGA nanofibers, core/sheath PLGA/PEDOT composite nanofibers without and with electrical stimulation of 1 V. For drug-loaded PLGA nanofibers, about 75% of the dexamethasone was released after seven days, while less than 25% of the dexamethasone was released after 54 days for drug-loaded PLGA/PEDOT composite nanofibers, indicating that the diffusion of drug through the walls of PEDOT coatings was difficult. On the other hand, a significant increase in the amount of dexamethasone released was found under externally applied voltage bias. This was because PEDOT could produce a mechanical force creating pressure within the composite nanofibers, which caused expulsion of dexamethasone and PLGA degradation products from the core/sheath PLGA/PEDOT composite nanofibers. Then the release of dexamethasone was much increased. This method to control the drug release affords us a useful means to integrate electronically active devices within living tissues.

4.7.2. Tissue Engineering

Electrospun nanofiber scaffolds have high surface area and high porosity, which is a good candidate for use in tissue engineering. Various biocompatible and biodegradable poly-

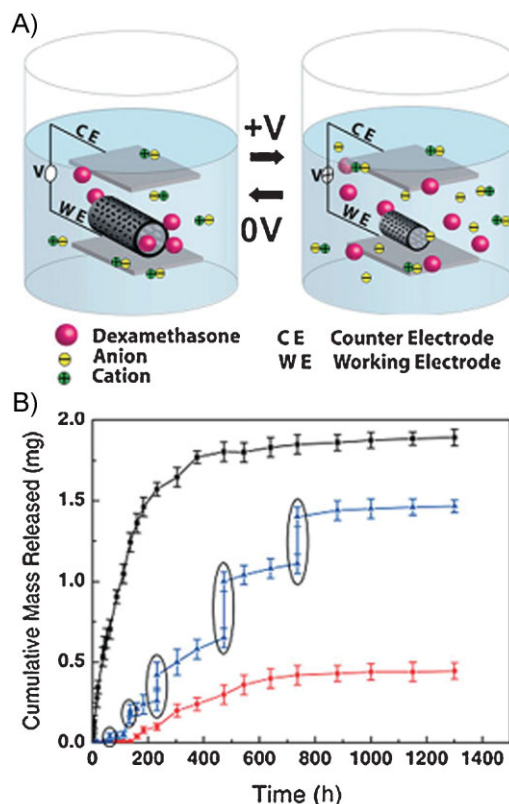


Figure 13. A) Schematic illustration of the release of dexamethasone from the PEDOT nanotubes under external electrical stimulation. B) Cumulative mass release of dexamethasone from PLGA fibers (black squares), PEDOT/PLGA composite fibers without (red circles) and with (blue triangles) electrical stimulation of 1 V applied voltage. Reproduced with permission from Reference [260].

mers have been electrospun to form fiber scaffolds.^[261–277] However, there are not many reports on the fabrication of electrospun scaffolds based on polymer/polymer and polymer/inorganic composites, which can enhance both the physical properties and biological functionality. Zhang and co-workers demonstrated that PCL/gelatin composite fibers could be prepared by electrospinning their mixed solutions in 2,2,2-trifluoroethanol solvent.^[268] Compared to that of either PCL or gelatin fibers alone, the mechanical properties and wettability were both improved. Moreover, as a promising scaffold for bone-marrow stromal cell (BMSC) culture, the PCL/gelatin composite fibers were more favorable for BMSC growth and migration than PCL scaffold alone. This was due to the good hydrophilicity, cellular affinity, and dissolution of PCL/gelatin composite nanofibers during cell culture, as well as the elongation and deformation properties of the composite scaffold. Another interesting example of electrospun composite scaffold is conducting-polymers-containing gelatin fibers, which have been investigated by Lelkes and co-workers.^[269] The results showed that the attachment and proliferation of H9c2 cell on PANI-gelatin composite fibers was comparable to TCP and smooth glass substrate (Figure 14). However, the effect of electrical stimulation on such electroactive scaffolds may be very interesting and should be further investigated. In addition to gelatin, other biological molecules are also

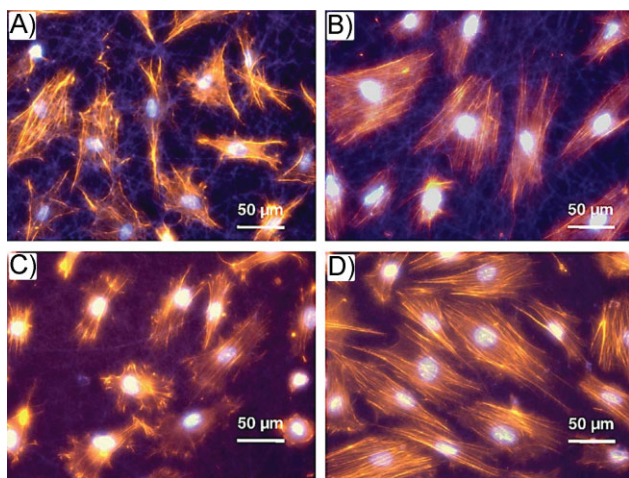


Figure 14. Morphology of H9c2 myoblast cells at 20 h post-seeding on A) gelatin fibers, B) 15:85 PANI-gelatin blend fibers, C) 30:70 PANI-gelatin blend fibers, and D) 45:55 PANI-gelatin blend fibers. Reproduced with permission from Reference [269]. Copyright 2006, Elsevier.

encapsulated into polymer nanofibers for tissue-engineering applications. Koh and co-workers successfully prepared PLLA/laminin composite nanofibers through three different methods: covalent binding, physical adsorption, and blended electrospinning. The results showed that blended electrospinning affords a useful and easy method to modify polymer nanofibers to produce composite biomimetic scaffolds for enhancing neurite outgrowth compared to the other two methods, which have potential applications in neural tissue repair.^[270]

Composite nanofibers with a core/sheath structure can also be used for tissue-engineering applications. Zhang and co-workers prepared collagen-coated PCL nanofibers by a coaxial electrospinning technique.^[271] The authors used the synthetic polymer (PCL) with better mechanical performance as the core and natural polymer (collagen) for functional purposes. The results showed that coatings of collagen on electrospun PCL nanofibers favored cell proliferation. The human dermal fibroblast (HDF) density on the PCL/collagen composite nanofibers with core/sheath structures increased linearly by 19.5% (two days), 22.9% (four days), and 31.8% (six days) compared to that on PCL nanofibers. Moreover, the collagen-coated PCL nanofibers encouraged cell migration inside the scaffolds, indicating the excellent integration between cells and the scaffolds.

Compared to random electrospun nanofibers, uniaxially aligned nanofibers are often used as a promising scaffold because they can guide the growth of neurons for their intrinsic anisotropic features. Aligned collagen/PCL composite nanofibers as the scaffold for glial cell migration were studied by Mey and co-workers.^[272] Combined with the advantages of the functionality (due to the collagen/PCL composites) and structures (due to the alignment of fibers), the aligned collagen/PCL composite nanofibers showed enhanced cell attachment, Schwann cell migration, axonal regeneration and neurite orientation, which could be a good material for artificial implants. Recently, Ramakrishna and co-workers have fabricated both random and aligned 1D PCL/gelatin composite nanomaterials by varying the ratios of PCL and gelatin

concentrations. The results showed that PCL/gelatin 70:30 composite nanofibers exhibited better mechanical and biodegradation properties for cell-culture studies. Compared to pure PCL nanofibers, the PCL/gelatin 70:30 composite nanofibers enhanced the nerve differentiation and proliferation. Furthermore, aligned composite nanofibers also improved the neurite outgrowth and cell differentiation process.^[273]

In addition to polymer/polymer or polymer/biological composite nanofibers, inorganic nanocomponents were also incorporated into polymer nanofibers for the application of tissue engineering. For example, the incorporation of calcium carbonate, calcium phosphate, and hydroxyl-apatite (HA), with similar crystallographic structure to inorganic materials found in natural bones, into the electrospun polymer scaffold made of a synthetic biodegradable or natural polymer was able to assist the bone cell regeneration. Fujihara and co-workers demonstrated the incorporation of calcium carbonate in the electrospun PCL scaffold by electrospinning the mixture of PCL and calcium carbonate at different compositions on the surface of electrospun PCL nanofibrous mats.^[274] Therefore, the mats consist of both functional layer (PCL/calcium carbonate) and mechanical support layer (PCL). The results showed that both composite mats with different PCL/calcium carbonate compositions exhibit good cell attachment and proliferation. Similar results have also been observed for beta-tertiary calcium phosphate incorporated into electrospun PLA scaffolds.^[275] In order to homogenous disperse the inorganic nanocomponents in electrospun polymer fibers, Kim and co-workers introduced hydroxyteric acid as a surfactant between the hydrophilic HA powders and the hydrophobic PLA into the electrospun solution.^[276] Initial cellular assays exhibited excellent cell attachment and proliferation and also enhanced expression of alkaline phosphatase, indicating its potential application as 3D scaffold for bone growth. Venugopal and co-workers also prepared a biomimetic collagen/HA composite nanofiber to study the osteogenesis and mineralization of osteoblasts.^[277] Compared to the pure gelatin equivalent, mineralization was significantly increased to 56% in such composite fibrous scaffolds.

4.7.3. Wound Dressing

Compared to conventional skin substitutes by freeze-drying methods, electrospinning exhibits the advantage of reduced morbidity of the wound dressing materials.^[278–283] Polymer/Ag composite nanofibers have been widely studied for the application of wound dressing because elemental Ag and Ag salts have been used as antimicrobial agents for decades. Hong and co-workers demonstrated that PVA/Ag composite nanofibers could be prepared by electrospinning PVA/AgNO₃ aqueous solution, followed by heat treatment or UV radiation.^[281] TEM images of the obtained PVA/Ag composite nanofibers showed that Ag nanoparticles were generated and well dispersed in the near surface of the electrospun nanofibers, indicating Ag ions have been reduced to Ag nanoparticles either by heat treatment or UV radiation. On the other hand, the heat treatment was superior in stability compared to UV radiation because crosslinks might be formed between two hydroxyl groups at high temperatures, which reduced the dissolution of Ag in the moisture environment. Electrospun

PVA/Ag composite nanofibers showed excellent antibacterial activity; however, the disadvantage was the gray–blue discoloration on the skin. In order to reduce the discoloration, silver-loaded zirconium phosphate nanoparticles have also been investigated as wound-dressing materials.^[282] The results showed that the composite fibers maintained the strong killing abilities against the tested bacteria strains, although Ag existed in the zirconium phosphate nanoparticles. Moreover, discoloration has not been observed in the nanofibers. Recently, Youngs and co-workers demonstrated that the encapsulation of silver-imidazole cyclophane gem-diol complex into hydrophilic Tecophilic nanofibers also showed excellent bactericidal activity.^[283] The composite fibers released silver nanoparticles in a sustained profile over a long time. Therefore, the rate of bactericidal activity of the silver complex was significantly improved, and the amount of silver used was much reduced. The composite fibers as scaffold were found to be effective against *E. coli*, *P. aeruginosa*, *S. aureus*, *C. albicans*, *A. niger*, and *S. cerevisiae*.

5. Conclusions and Outlook

Electrospinning affords us a remarkably easy and versatile technique for the formation of very thin fibers with large surface areas and superior mechanical properties. Many desirable properties can be achieved by electrospinning multicomponent mixtures and post-modification with functional reagents to form functional 1D composite nanomaterials. Several innovative electrospinning methods have been reviewed here, including direct-dispersed electrospinning, gas–solid reaction, in situ photoreduction, sol–gel processes, emulsions, co-evaporation, and coaxial electrospinning. Functional composite nanofibers achieved by these methods have been widely used in the applications of electronic and optical nanodevices, chemical and biological sensors, catalysis and electrocatalysis, superhydrophobic surfaces, environment, energy, and biomedical fields. Although many technical issues still need to be resolved or improved upon, there is no doubt that electrospinning has become one of the most powerful tools for fabricating functional 1D nanomaterials.

In addition to general investigation of the synthesized methods and applications, specific aspects of 1D composite nanomaterials by electrospinning technique should be focused on, for instance, the methodology for fabricating 1D composite nanomaterials, how to control the compatibility or avoid phase separation between inorganic or organic component and polymer fibers matrices, how to control the composition of 1D composite nanomaterials (do gradient components form in polymer fibers matrices?), and how to control the new structures of 1D composite nanomaterials (do patterns of inorganic component form in polymer matrices? Do hierarchical architectures form through the one-step electrospinning technique?). In terms of the applications of electrospun 1D composite nanomaterials, many important questions remain. For example, in the area of energy applications, the improvement of the energy-conversion efficiency is very important. Can we increase the energy-conversion efficiency by changing the composition (doping or blending?) or the structure of the 1D composite

nanomaterials? For energy applications, hydrogen is considered an important alternative energy vector. Can we increase the capacity of hydrogen storage via electrospinning (by introducing metal oxide catalysts into electrospun carbon fibers or trying to find new kinds of material)? In particular, in the area of biomedical applications, electrospun 1D composite nanomaterials have been applied very successfully in drug delivery, tissue engineering, and wound dressing. In this area, future work should be focused on the modification the composition and structure of the 1D composite nanomaterials for different applications in biomedical fields (for example, intelligent 1D composite nanomaterials for controlled drug delivery, aligned core/sheath nanofibers for neurite outgrowth, tubular nanofiber scaffolds for tissue-engineered vascular grafts, and so on).

It is expected that research on electrospinning will become more extensive in the near future. As the capability of the fabrication of 1D composite nanomaterials via electrospinning and their applications in broad range of applications improve, it is not only researchers in the areas of polymers and textile engineering but also the people with expertise in areas such as nanomaterials, ceramics, composite materials, and electronics that will pay attention to and work together in this field. With the involvement of a more developed scientific and engineering technique, electrospinning will allow for the fabrication of 1D composite nanomaterials with the broadest range of properties and applications.

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Keywords:

composite materials · electrospinning · nanomaterial synthesis · polymers

- [1] Y. N. Xia, P. D. Yang, Y. G. Sun, Y. Y. Wu, B. Mayers, B. Gates, Y. D. Yin, F. Kim, H. Q. Yan, *Adv. Mater.* **2003**, *15*, 353.
- [2] Z. L. Wang, *Adv. Mater.* **2000**, *12*, 1295.
- [3] J. T. Hu, T. W. Odom, C. M. Lieber, *Acc. Chem. Res.* **1999**, *32*, 435.
- [4] F. Cerrina, C. Marrian, *MRS Bull.* **1996**, *21*, 56.
- [5] J. M. Gibson, *Phys. Today* **1997**, *50*, 56.
- [6] S. Matsui, Y. Ochiai, *Nanotechnology* **1996**, *7*, 247.
- [7] S. H. Hong, J. Zhu, C. A. Mirkin, *Science* **1999**, *286*, 523.
- [8] J. A. Dagata, *Science* **1995**, *270*, 1625.
- [9] P. N. Dunn, *Solid State Technol.* **1994**, *37*, 49.
- [10] Special issue on carbon nanotubes. *Acc. Chem. Res.* **2002**, *35*, 997.
- [11] J. H. Golden, H. Deng, F. J. DiSalvo, J. M. J. Fréchet, P. M. Thompson, *Science* **1995**, *268*, 1463.
- [12] B. Gates, Y. D. Yin, Y. N. Xia, *J. Am. Chem. Soc.* **2000**, *122*, 12582.
- [13] M. P. Zach, K. H. Ng, R. M. Penner, *Science* **2000**, *290*, 2120.
- [14] R. R. He, M. Law, R. Fan, F. Kim, P. D. Yang, *Nano Lett.* **2002**, *2*, 1109.
- [15] L. J. Lauthon, M. S. Gudiksen, D. L. Wang, C. M. Lieber, *Nature* **2002**, *420*, 57.
- [16] Y. G. Sun, B. T. Mayers, Y. N. Xia, *Nano Lett.* **2002**, *2*, 481.

- [17] Y. J. Zhang, N. L. Wang, S. P. Gao, R. R. He, S. Miao, J. Liu, J. Zhu, X. Zhang, *Chem. Mater.* **2002**, *14*, 3564.
- [18] X. G. Peng, L. Manna, W. D. Yang, J. Wickham, E. Scher, A. Kadavanich, A. P. Alivisatos, *Nature* **2000**, *404*, 59.
- [19] O. Kriha, M. Becker, M. Lehmann, D. Kriha, J. Krieglstein, M. Yesef, S. Schlecht, R. B. Wehrspohn, J. H. Wendorff, A. Greiner, *Adv. Mater.* **2007**, *19*, 2483.
- [20] A. Stojiljkovic, S. Agarwal, *Macromol. Mater. Eng.* **2008**, *293*, 895.
- [21] Z. M. Huang, Y. Z. Zhang, M. Kotaki, S. Ramakrishna, *Composites Sci. Technol.* **2003**, *63*, 2223.
- [22] D. Li, Y. N. Xia, *Adv. Mater.* **2004**, *16*, 1151.
- [23] A. Greiner, J. H. Wendorff, *Angew. Chem. Int. Ed.* **2007**, *46*, 5670.
- [24] Q. P. Pham, U. Sharma, A. G. Mikos, *Tissue Eng.* **2006**, *12*, 1197.
- [25] C. Burger, B. S. Hsiao, B. Chu, *Annu. Rev. Mater. Res.* **2006**, *36*, 333.
- [26] C. P. Barnes, S. A. Sell, E. D. Boland, D. G. Simpson, G. L. Bowlin, *Adv. Drug Delivery Rev.* **2007**, *59*, 1413.
- [27] D. Liang, B. S. Hsiao, B. Chu, *Adv. Drug Delivery Rev.* **2007**, *59*, 1392.
- [28] J. W. Xie, X. R. Li, Y. N. Xia, *Macromol. Rapid Commun.* **2008**, *29*, 1775.
- [29] L. Rayleigh, *Philos. Mag.* **1882**, *14*, 184.
- [30] J. F. Cooley, US patent 692,631, 1902.
- [31] W. J. Morton, US patent 705,691, 1902.
- [32] C. T. R. Wilson, G. I. Taylor, *Proc. Camb. Phil. Soc.* **1925**, *22*, 728.
- [33] A. Formhals, US patent 1,975,504, 1934.
- [34] J. Doshi, G. Srinivasan, D. Reneker, *Polym. News* **1995**, *20*, 206.
- [35] D. H. Reneker, I. Chun, *Nanotechnology* **1996**, *7*, 216.
- [36] X. Fang, D. H. Reneker, *J. Macromol. Sci. Phys. B* **1997**, *B36*, 169.
- [37] G. Srinivasan, D. H. Reneker, *Polym. Int.* **1995**, *36*, 195.
- [38] H. Fong, D. H. Reneker, *J. Polym. Sci. Part B: Polym. Phys.* **1999**, *37*, 3488.
- [39] H. Fong, I. Chun, D. H. Reneker, *Polymer* **1999**, *40*, 4585.
- [40] A. L. Yarin, S. Koombhongse, D. H. Reneker, *J. Appl. Phys.* **2001**, *90*, 4836.
- [41] A. L. Yarin, S. Koombhongse, D. H. Reneker, *J. Appl. Phys.* **2001**, *89*, 3018.
- [42] D. Li, J. T. McCann, Y. N. Xia, *J. Am. Ceram. Soc.* **2006**, *89*, 1861.
- [43] R. Ramaseshan, S. Sundarrajan, R. Jose, S. Ramakrishna, *J. Appl. Phys.* **2007**, *102*, 111101.
- [44] W. Sigmund, J. Yuh, H. Park, V. Maneeratana, G. Pyrgiotakis, A. Daga, J. Taylor, J. C. Nino, *J. Am. Ceram. Soc.* **2006**, *89*, 395.
- [45] I. S. Chronakis, *J. Mater. Process. Technol.* **2005**, *167*, 283.
- [46] P. K. Panda, *Trans. Indian Ceram. Soc.* **2008**, *66*, 65.
- [47] K. M. Sawicka, P. Gouma, *J. Nanopart. Res.* **2006**, *8*, 769.
- [48] H. Q. Dai, J. Gong, H. Kim, D. Lee, *Nanotechnology* **2002**, *13*, 674.
- [49] H. Y. Guan, C. L. Shao, S. B. Wen, B. Chen, J. Gong, X. H. Yang, *Inorg. Chem. Commun.* **2003**, *6*, 1302.
- [50] X. F. Lu, D. L. Zhang, Q. D. Zhao, C. Wang, W. J. Zhang, Y. Wei, *Macromol. Rapid Commun.* **2006**, *27*, 76.
- [51] X. F. Lu, X. C. Liu, W. J. Zhang, C. Wang, Y. Wei, *J. Colloid Interf. Sci.* **2006**, *298*, 996.
- [52] H. Y. Wang, Y. Yang, Y. Wang, X. Li, S. Y. Feng, C. Wang, *Mater. Sci. Eng. B: Solid State Mater. Adv. Technol.* **2008**, *147*, 69.
- [53] D. Li, Y. N. Xia, *Nano Lett.* **2003**, *3*, 555.
- [54] P. Viswanathamurthi, N. Bhattacharai, H. Y. Kim, D. R. Lee, S. R. Kim, M. A. Morris, *Chem. Phys. Lett.* **2003**, *374*, 79.
- [55] N. Dharmaraj, H. C. Park, C. K. Kim, H. Y. Kim, D. R. Lee, *Mater. Chem. Phys.* **2004**, *87*, 5.
- [56] X. H. Yang, C. L. Shao, H. Y. Guan, X. L. Li, J. Gong, *Inorg. Chem. Commun.* **2004**, *7*, 176.
- [57] P. Viswanathamurthi, N. Bhattacharai, H. Y. Kim, M. S. Khil, D. R. Lee, E. K. Suh, *J. Chem. Phys.* **2004**, *121*, 441.
- [58] M. Wang, H. Singh, T. A. Hatton, G. C. Rutledge, *Polymer* **2004**, *45*, 5505.
- [59] X. G. Yang, C. L. Shao, Y. C. Liu, R. X. Mu, H. Y. Guan, *Thin Solid Films* **2005**, *478*, 228.
- [60] Z. W. Fu, J. Ma, Q. Z. Qin, *Solid State Ionics* **2005**, *176*, 1635.
- [61] H. Wu, D. Lin, W. Pan, *Appl. Phys. Lett.* **2006**, *89*, 133125.
- [62] E. T. Bender, P. Katta, A. Lotus, S. J. Park, G. G. Chase, R. D. Ramsier, *Chem. Phys. Lett.* **2006**, *423*, 302.
- [63] Y. Zhang, J. Li, Q. Li, L. Zhu, X. Liu, X. Zhong, J. Menga, X. Cao, *Scr. Mater.* **2007**, *56*, 409.
- [64] A. L. Yarin, E. Zussman, *Polymer* **2004**, *45*, 2977.
- [65] J. Kameoka, R. Orth, Y. Yang, D. Czaplewski, R. Mathers, G. W. Coates, H. G. Craighead, *Nanotechnology* **2003**, *14*, 1124.
- [66] Q. B. Yang, Z. Y. Li, Y. L. Hong, Y. Y. Zhao, S. L. Qiu, C. Wang, Y. Wei, *J. Polym. Sci. B: Polym. Phys.* **2004**, *42*, 3721.
- [67] Y. Y. Zhao, Q. B. Yang, X. F. Lu, C. Wang, Y. Wei, *J. Polym. Sci. B: Polym. Phys.* **2005**, *43*, 2190.
- [68] W. E. Teo, S. Ramakrishna, *Nanotechnology* **2006**, *17*, R89.
- [69] J. A. Matthews, G. E. Wnek, D. G. Simpson, G. L. Bowlin, *Biomacromolecules* **2002**, *3*, 232.
- [70] A. Subramanian, D. Vu, G. F. Larsen, H. Y. Lin, *J. Biomater. Sci. Polym. Ed.* **2005**, *16*, 861.
- [71] E. Smit, U. Buttner, R. D. Sanderson, *Polymer* **2005**, *46*, 2419.
- [72] M. S. Khil, S. R. Bhattacharai, H. Y. Kim, S. Z. Kim, K. H. Lee, *J. Biomed. Mater. Res. B* **2005**, *72*, 117.
- [73] G. I. Taylor, *Proc. Roy. Soc. London A* **1969**, *313*, 453.
- [74] J. M. Deitzel, J. D. Kleinmeyer, J. K. Hirvonen, N. C. B. Tan, *Polymer* **2001**, *42*, 8163.
- [75] D. Li, Y. L. Wang, Y. N. Xia, *Nano Lett.* **2003**, *3*, 1167.
- [76] T. Han, D. H. Reneker, A. L. Yarin, *Polymer* **2007**, *48*, 6064.
- [77] M. M. Hohman, M. Shin, G. Rutledge, M. P. Brenner, *Phys. Fluids* **2001**, *13*, 2201.
- [78] Q. B. Yang, D. M. Li, Y. L. Hong, Z. Y. Li, C. Wang, S. L. Qiu, Y. Wei, *Synth. Met.* **2003**, *137*, 973.
- [79] S. G. Wang, Y. X. Li, Y. Z. Wang, Q. B. Yang, Y. Wei, *Mater. Lett.* **2007**, *61*, 4674.
- [80] M. J. Li, J. H. Zhang, H. Zhang, Y. F. Liu, C. L. Wang, X. Xu, Y. Tang, B. Yang, *Adv. Funct. Mater.* **2007**, *17*, 3650.
- [81] H. Y. Wang, Y. Yang, X. F. Lu, C. Wang, *Chem. J. Chinese Univ.* **2006**, *27*, 1785.
- [82] X. Li, Y. Y. Zhao, X. F. Lu, H. Y. Wang, C. Wang, *Chem. J. Chinese Univ.* **2006**, *27*, 2002.
- [83] C. Wang, Z. Li, D. Li, Q. Yang, Y. Hong, *Int. J. Nanosci.* **2002**, *1*, 471.
- [84] Z. Y. Li, H. M. Huang, C. Wang, *Macromol. Rapid Commun.* **2006**, *27*, 152.
- [85] G. M. Kim, A. Wutzler, H. J. Radusch, G. H. Michler, P. Simon, R. A. Sperling, W. J. Parak, *Chem. Mater.* **2005**, *17*, 4949.
- [86] M. M. Demir, M. A. Gulgun, Y. Z. Menciloglu, B. Erman, S. S. Abramchuk, E. E. Makhaeva, A. R. Khokhlov, V. G. Matveeva, M. G. Sulman, *Macromolecules* **2004**, *37*, 1787.
- [87] M. Bashouti, W. Salalha, M. Brumer, E. Zussman, E. Lifshitz, *ChemPhysChem* **2006**, *7*, 102.
- [88] S. T. Tan, J. H. Wendorff, C. Pietzonka, Z. H. Jia, G. Q. Wang, *ChemPhysChem* **2005**, *6*, 1461.
- [89] F. Ko, Y. Gogotsi, A. Ali, N. Naguib, H. Ye, G. Yang, C. Li, P. Willis, *Adv. Mater.* **2003**, *15*, 1161.
- [90] J. Ayutsede, M. Gandhi, S. Sukigara, H. Ye, C. Hsu, Y. Gogotsi, F. Ko, *Biomacromolecules* **2006**, *7*, 208.
- [91] H. Ye, H. Lam, N. Titchenal, Y. Gogotsi, F. Ko, *Appl. Phys. Lett.* **2004**, *85*, 1775.
- [92] Y. Dror, W. Salalha, R. L. Khalfin, Y. Cohen, A. L. Yarin, E. Zussman, *Langmuir* **2003**, *19*, 7012.
- [93] S. Kedem, J. Schmidt, Y. Paz, Y. Cohen, *Langmuir* **2005**, *21*, 5600.
- [94] W. Salalha, Y. Dror, R. L. Khalfin, Y. Cohen, A. L. Yarin, E. Zussman, *Langmuir* **2004**, *20*, 9852.
- [95] R. Sen, B. Zhao, D. Perea, M. E. Itkis, H. Hu, J. Love, E. Bekyarova, R. C. Haddon, *Nano Lett.* **2004**, *4*, 459.
- [96] J. J. Ge, H. Q. Hou, Q. Li, M. J. Graham, A. Greiner, D. H. Reneker, F. W. Harris, S. Z. D. Cheng, *J. Am. Chem. Soc.* **2004**, *126*, 15754.
- [97] H. Q. Hou, J. J. Ge, J. Zeng, Q. Li, D. H. Reneker, A. Greiner, S. Z. D. Cheng, *Chem. Mater.* **2005**, *17*, 967.

- [98] C. Seoul, Y. T. Kim, C. K. Baek, *J. Polym. Sci. B: Polym. Phys.* **2003**, 41, 1572.
- [99] J. H. Sung, H. S. Kim, H. J. Jin, H. J. Choi, I. J. Chin, *Macromolecules* **2004**, 37, 9899.
- [100] X. L. Xie, Y. W. Mai, X. P. Zhou, *Mater. Sci. Eng. R* **2005**, 49, 89.
- [101] E. J. Ra, K. H. An, K. K. Kim, S. Y. Jeong, Y. H. Lee, *Chem. Phys. Lett.* **2005**, 413, 188.
- [102] B. Sundaray, V. Subramanian, T. S. Natarajan, K. Krishnamurthy, *Appl. Phys. Lett.* **2006**, 88, 143114.
- [103] H. S. Kim, H. J. Jin, S. J. Myung, M. Kang, I. J. Chin, *Macromol. Rapid Commun.* **2006**, 27, 146.
- [104] C. Kim, S. H. Park, J. I. Cho, D. Y. Lee, T. J. Park, W. G. Lee, K. S. Yang, *J. Raman Spectrosc.* **2004**, 35, 928.
- [105] J. Liu, T. Wang, T. Uchida, S. Kumar, *J. Appl. Polym. Sci.* **2005**, 96, 1992.
- [106] W. Zhou, Y. Wu, F. Wie, G. Luo, W. Qian, *Polymer* **2005**, 46, 12689.
- [107] J. Y. Lim, C. K. Lee, S. J. Kim, I. Y. Kim, S. I. Kim, *J. Macromol. Sci. Pure Appl. Chem.* **2006**, 43, 785.
- [108] G. M. Kim, G. H. Michler, P. Pötschke, *Polymer* **2005**, 46, 7346.
- [109] X. F. Lu, Y. Y. Zhao, C. Wang, *Adv. Mater.* **2005**, 17, 2485.
- [110] X. F. Lu, Y. Y. Zhao, C. Wang, Y. Wei, *Macromol. Rapid Commun.* **2005**, 26, 1325.
- [111] Z. F. Zhou, D. A. He, W. B. Xu, F. M. Ren, Y. T. Qian, *Mater. Lett.* **2007**, 61, 23.
- [112] X. F. Lu, H. Mao, W. J. Zhang, C. Wang, *Mater. Lett.* **2007**, 61, 2288.
- [113] H. Y. Wang, X. F. Lu, Y. Y. Zhao, C. Wang, *Mater. Lett.* **2006**, 60, 2480.
- [114] Y. Yang, H. Y. Wang, X. F. Lu, Y. Y. Zhao, X. Li, C. Wang, *Mater. Sci. Eng. B: Solid State Mater. Adv. Technol.* **2007**, 140, 48.
- [115] F. X. Dong, Z. Y. Li, H. M. Huang, F. Yang, W. Zheng, C. Wang, *Mater. Lett.* **2007**, 61, 2556.
- [116] J. Xu, X. J. Cui, J. H. Zhang, H. W. Liang, H. Y. Wang, J. F. Li, *Bull. Mater. Sci.* **2008**, 31, 189.
- [117] C. Wang, E. Y. Yan, Z. Y. Sun, Z. J. Jiang, Y. B. Tong, Y. Xin, Z. H. Huang, *Macromol. Mater. Eng.* **2007**, 292, 949.
- [118] J. Bai, Y. X. Li, S. T. Yang, J. S. Du, S. G. Wang, C. Q. Zhang, Q. B. Yang, X. S. Chen, *Nanotechnology* **2007**, 18, 305601.
- [119] W. Wang, S. A. Asher, *J. Am. Chem. Soc.* **2001**, 123, 12528.
- [120] Z. P. Zhang, L. D. Zhang, S. X. Wang, W. Chen, Y. Lei, *Polymer* **2001**, 42, 8315.
- [121] W. K. Son, J. H. Youk, T. S. Lee, W. H. Park, *Macromol. Rapid Commun.* **2004**, 25, 1632.
- [122] Z. Y. Li, H. M. Huang, T. C. Shang, F. Yang, W. Zheng, C. Wang, S. K. Manohar, *Nanotechnology* **2006**, 17, 917.
- [123] D. Li, J. T. McCann, M. Gratt, Y. N. Xia, *Chem. Phys. Lett.* **2004**, 394, 387.
- [124] X. F. Lu, L. L. Li, W. J. Zhang, C. Wang, *Nanotechnology* **2005**, 16, 2233.
- [125] X. F. Lu, W. J. Zhang, Q. D. Zhao, L. F. Wang, C. Wang, *E-polymers* **2006**, no. 033.
- [126] Y. Z. Wang, Y. X. Li, S. T. Yang, G. L. Zhang, D. M. An, C. Wang, Q. B. Yang, X. S. Chen, X. B. Jing, Y. Wei, *Nanotechnology* **2006**, 17, 3304.
- [127] W. J. Jin, H. K. Lee, E. H. Jeong, W. H. Park, J. H. Youk, *Macromol. Rapid Commun.* **2005**, 26, 1903.
- [128] R. Ostermann, D. Li, Y. D. Yin, J. T. McCann, Y. N. Xia, *Nano Lett.* **2006**, 6, 1297.
- [129] J. Zeng, X. Y. Xu, X. S. Chen, Q. Z. Liang, X. C. Bian, L. X. Yang, X. B. Jing, *J. Controlled Release* **2003**, 92, 227.
- [130] J. Zeng, L. X. Yang, Q. Z. Liang, X. F. Zhang, H. L. Guan, X. L. Xu, X. S. Chen, X. B. Jing, *J. Controlled Release* **2005**, 105, 43.
- [131] E. H. Sanders, R. Kloefkorn, G. L. Bowlin, D. G. Simpson, G. E. Wnek, *Macromolecules* **2003**, 36, 3803.
- [132] X. L. Xu, L. X. Yang, X. Y. Xu, X. Wang, X. S. Chen, Q. Z. Liang, J. Zeng, X. B. Jing, *J. Controlled Release* **2005**, 108, 33.
- [133] Y. Yang, X. H. Li, M. B. Qi, S. B. Zhou, J. Weng, *Eur. J. Pharm. Biopharm.* **2008**, 69, 106.
- [134] Y. Yang, X. H. Li, W. G. Cui, S. B. Zhou, R. Tan, C. Y. Wang, J. Biomed, *Mater. Res. Part A* **2008**, 86A, 374.
- [135] M. Angeles, H.-L. Cheng, S. S. Velankar, *Polym. Adv. Technol.* **2008**, 19, 728.
- [136] H. X. Qi, P. Hu, J. Xu, A. J. Wang, *Biomacromolecules* **2006**, 7, 2327.
- [137] X. L. Xu, X. L. Zhuang, X. S. Chen, X. R. Wang, L. X. Yang, X. B. Jing, *Macromol. Rapid Commun.* **2006**, 27, 1637.
- [138] A. G. MacDiarmid, W. E. Jones, Jr, I. D. Norris, J. Gao, A. T. Johnson, Jr, N. J. Pinto, J. Hone, B. Han, F. K. Ko, H. Okuzaki, M. Llaguno, *Synth. Met.* **2001**, 119, 27.
- [139] Q. Zhao, Z. H. Huang, C. Wang, Q. D. Zhao, H. Z. Sun, D. J. Wang, *Mater. Lett.* **2007**, 61, 2159.
- [140] T. E. Herricks, S. H. Kim, J. Kim, D. Li, J. H. Kwak, J. W. Grate, S. H. Kim, Y. N. Xia, *J. Mater. Chem.* **2005**, 15, 3241.
- [141] E. Y. Yan, Z. H. Huang, Y. Xin, Q. Zhao, W. Zhang, *Mater. Lett.* **2006**, 60, 2969.
- [142] J. Gong, C. L. Shao, Y. Pan, F. M. Gao, L. Y. Qu, *Mater. Chem. Phys.* **2004**, 86, 156.
- [143] J. Gong, X. D. Li, C. L. Shao, B. Ding, D. R. Lee, H. Y. Kim, *Mater. Chem. Phys.* **2003**, 79, 87.
- [144] J. Gong, C. L. Shao, G. C. Yang, Y. Pan, L. Y. Qu, *Inorg. Chem. Commun.* **2003**, 6, 916.
- [145] G. C. Yang, J. Gong, Y. Pan, X. J. Cui, C. L. Shao, Y. H. Guo, S. B. Wen, L. Y. Qu, *J. Phys. D: Appl. Phys.* **2004**, 37, 1987.
- [146] X. F. Lu, X. C. Liu, L. F. Wang, W. J. Zhang, C. Wang, *Nanotechnology* **2006**, 17, 3048.
- [147] Z. C. Sun, E. Zussman, A. L. Yarin, J. H. Wendorff, A. Greiner, *Adv. Mater.* **2003**, 15, 1929.
- [148] G. Kwak, G. H. Lee, S. H. Shim, K. B. Yoon, *Macromol. Rapid Commun.* **2008**, 29, 815.
- [149] D. Li, A. Babel, S. A. Jenekhe, Y. N. Xia, *Adv. Mater.* **2004**, 16, 2062.
- [150] X. J. Han, Z. M. Huang, C. L. He, L. Liu, X. J. Han, Q. S. Wu, *Polym. Composites* **2006**, 27, 381.
- [151] X. J. Han, Z. M. Huang, C. L. He, L. Liu, Q. S. Wu, *Polym. Composites* **2008**, 29, 579.
- [152] B. Sun, B. Duan, X. Y. Yuan, *J. Appl. Polym. Sci.* **2006**, 102, 39.
- [153] M. Wang, J. H. Yu, D. L. Kaplan, G. C. Rutledge, *Macromolecules* **2006**, 39, 1102.
- [154] H. L. Jiang, P. C. Zhao, K. J. Zhu, *Macromol. Biosci.* **2007**, 7, 517.
- [155] H. L. Jiang, Y. Q. Hu, Y. Li, P. C. Zhao, K. J. Zhu, W. L. Chen, *J. Controlled Release* **2005**, 108, 237.
- [156] Y. Z. Zhang, X. Wang, Y. Feng, J. Li, C. T. Lim, S. Ramakrishna, *Biomacromolecules* **2006**, 7, 1049.
- [157] M. L. Ma, V. Krikorian, J. H. Yu, E. L. Thomas, G. C. Rutledge, *Nano Lett.* **2006**, 6, 2969.
- [158] Q. Zhao, Y. Xin, Z. H. Huang, S. D. Liu, C. H. Yang, Y. F. Li, *Polymer* **2007**, 48, 4311.
- [159] J. E. Díaz, A. Barrero, M. Márquez, I. G. Loscertales, *Adv. Funct. Mater.* **2006**, 16, 2110.
- [160] A. Townsend-Nicholson, S. N. Jayasinghe, *Biomacromolecules* **2006**, 7, 3364.
- [161] S. Arumuganathan, S. Irvine, J. R. McEwan, S. N. Jayasinghe, *J. Appl. Polym. Sci.* **2008**, 107, 1215.
- [162] Y. Z. Zhang, Z. M. Huang, X. J. Xu, C. T. Lim, S. Ramakrishna, *Chem. Mater.* **2004**, 16, 3406.
- [163] Z. M. Huang, Y. Z. Zhang, S. Ramakrishna, *J. Polym. Sci. Part B: Polym. Phys.* **2005**, 43, 2852.
- [164] P. C. Zhao, H. L. Jiang, H. Pan, K. J. Zhu, W. L. Chen, *J. Biomed. Mater. Res. Part A* **2007**, 83A, 372.
- [165] Y. Dror, J. Kuhn, R. Avrahami, E. Zussman, *Macromolecules* **2008**, 41, 4187.
- [166] T. Song, Y. Z. Zhang, T. J. Zhou, C. T. Lim, S. Ramakrishna, B. Liu, *Chem. Phys. Lett.* **2005**, 415, 317.

- [167] M. Graeser, E. Pippel, A. Greiner, J. H. Wendorff, *Macromolecules*, **2007**, *40*, 6032.
- [168] J. T. McCann, M. Marquez, Y. N. Xia, *Nano Lett.* **2006**, *6*, 2868.
- [169] M. Wang, N. Jing, C. B. Su, J. Kameoka, C. K. Chou, M. C. Hung, K. A. Chang, *Appl. Phys. Lett.* **2006**, *88*, 033106.
- [170] G. Larsen, R. Spretz, R. Velarde-Ortiz, *Adv. Mater.* **2004**, *16*, 166.
- [171] Y. X. Gu, D. R. Chen, X. L. Jiao, F. F. Liu, *J. Mater. Chem.* **2007**, *17*, 1769.
- [172] D. Li, J. T. McCann, Y. N. Xia, *Small* **2005**, *1*, 83.
- [173] J. E. Panels, Y. L. Joo, *J. Nanomater.* **2006**, *2006*, 41327.
- [174] X. Duan, Y. Huang, Y. Cui, J. Wang, C. M. Lieber, *Nature* **2001**, *409*, 66.
- [175] G. Y. Tseng, J. C. Ellenbogen, *Science* **2001**, *294*, 1293.
- [176] Z. Zhang, X. Sun, M. S. Dresselhaus, J. Y. Ying, *Phys. Rev. B* **2000**, *61*, 4850.
- [177] S. H. Choi, K. L. Wang, M. S. Leung, G. W. Stupian, N. Presser, B. A. Morgan, R. E. Robertson, M. Abraham, E. E. King, M. B. Tueling, S. W. Chung, J. R. Heath, S. L. Cho, J. B. Ketterson, *J. Vac. Sci. Technol. A* **2000**, *18*, 1326.
- [178] N. I. Kovtyukhova, B. R. Martin, J. K. N. Mbindyo, P. A. Smith, B. Razavi, T. S. Mayer, T. E. Mallouk, *J. Phys. Chem. B* **2001**, *105*, 8762.
- [179] Y. Wu, R. Fang, P. Yang, *Nano Lett.* **2002**, *2*, 83.
- [180] T. T. Hanrath, B. A. Korgel, *J. Am. Chem. Soc.* **2001**, *124*, 1424.
- [181] X. Lu, T. Hanrath, K. P. Johnston, B. A. Korgel, *Nano Lett.* **2003**, *3*, 93.
- [182] J. F. Wang, M. S. Gudiksen, X. F. Duan, Y. Cui, C. M. Lieber, *Science* **2001**, *293*, 1455.
- [183] H. Kind, H. Yan, B. Messer, M. Law, P. Yang, *Adv. Mater.* **2002**, *14*, 158.
- [184] Y. Zhou, M. Freitag, J. Hone, C. Staii, A. T. Johnson, Jr, N. J. Pinto, A. G. MacDiarmid, *Appl. Phys. Lett.* **2003**, *83*, 3800.
- [185] N. J. Pinto, A. T. Johnson, Jr, A. G. MacDiarmid, C. H. Mueller, N. Theofylaktos, D. C. Robinson, F. A. Miranda, *Appl. Phys. Lett.* **2003**, *83*, 4244.
- [186] T. C. Shang, F. Yang, W. Zheng, C. Wang, *Small* **2006**, *2*, 1007.
- [187] X. F. Lu, Q. D. Zhao, X. C. Liu, D. J. Wang, W. J. Zhang, C. Wang, Y. Wei, *Macromol. Rapid Commun.* **2006**, *27*, 430.
- [188] Z. Y. Li, H. N. Zhang, W. Zheng, W. Wang, H. M. Huang, C. Wang, A. G. MacDiarmid, Y. Wei, *J. Am. Chem. Soc.* **2008**, *130*, 5036.
- [189] Q. Qi, T. Zhang, L. J. Wang, *Appl. Phys. Lett.* **2008**, *93*, 023105.
- [190] X. Wang, C. Drew, S.-H. Lee, K. J. Senecal, J. Kumar, L. A. Samuelson, *Nano Lett.* **2002**, *2*, 1273.
- [191] H. Q. Liu, J. Kameoka, D. A. Czaplewski, H. G. Craighead, *Nano Lett.* **2004**, *4*, 671.
- [192] J. Yoon, S. K. Chae, J. M. Kim, *J. Am. Chem. Soc.* **2007**, *129*, 3038.
- [193] K. Sawicka, P. Gouma, S. Simon, *Sens. Actuators B* **2005**, *108*, 585.
- [194] A. C. Patel, S. X. Li, J. M. Yuan, Y. Wei, *Nano Lett.* **2006**, *6*, 1042.
- [195] S. J. Doh, C. Kim, S. G. Lee, S. J. Lee, H. Kim, *J. Hazardous Mater.* **2008**, *154*, 118.
- [196] H. Q. Liu, J. X. Yang, J. H. Liang, Y. X. Huang, C. Y. Tangz, *J. Am. Ceram. Soc.* **2008**, *91*, 1287.
- [197] L. P. Chen, S. G. Hong, X. P. Zhou, Z. P. Zhou, H. Q. Hou, *Catal. Commun.* **2008**, *9*, 2221.
- [198] A. C. Patel, S. X. Li, C. Wang, W. J. Zhang, Y. Wei, *Chem. Mater.* **2007**, *19*, 1231.
- [199] M. Stasiak, A. Studer, A. Greiner, J. H. Wendorff, *Chem. Eur. J.* **2007**, *13*, 6150.
- [200] M. Stasiak, C. Roben, N. Rosenberger, F. Schleth, A. Studer, A. Greiner, J. H. Wendorff, *Polymer*, **2007**, *48*, 5208.
- [201] L. Chen, L. Bromberg, T. A. Hatton, G. C. Rutledge, *Polymer* **2007**, *48*, 4675.
- [202] E. Formo, E. Lee, D. Campbell, Y. Xia, *Nano Lett.* **2008**, *8*, 668.
- [203] E. Formo, Z. Peng, E. Lee, X. Lu, H. Yang, Y. Xia, *J. Phys. Chem. C* **2008**, *112*, 9970.
- [204] M. Y. Li, G. Y. Han, B. S. Yang, *Electrochem. Commun.* **2008**, *10*, 880.
- [205] S. J. Park, S. Bhargava, E. T. Bender, G. G. Chase, R. D. Ramsier, *J. Mater. Res.* **2008**, *23*, 1193.
- [206] C. H. He, J. Gong, *Polym. Degrad. Stab.* **2003**, *81*, 117.
- [207] K. Ebert, G. Bengtson, R. Just, M. Oehring, D. Fritsch, *Appl. Catal. A: General* **2008**, *346*, 72.
- [208] L. Jiang, Y. Zhao, J. Zhai, *Angew. Chem. Int. Ed.* **2004**, *43*, 4338.
- [209] K. Acatay, E. Simsek, C. Ow-Yang, Y. Z. Menceloglu, *Angew. Chem. Int. Ed.* **2004**, *43*, 5210.
- [210] S. Agarwal, S. Horst, M. Bognitzki, *Macromol. Mater. Eng.* **2006**, *291*, 592.
- [211] M. F. Zhu, W. W. Zuo, H. Yu, W. Yang, Y. M. Chen, *J. Mater. Sci.* **2006**, *41*, 3793.
- [212] R. Menini, M. Farzaneh, *Polym. Int.* **2008**, *57*, 77.
- [213] A. Singh, L. Steely, H. R. Allcock, *Langmuir* **2005**, *21*, 11604.
- [214] Y. L. Yoon, H. S. Moon, W. S. Lyoo, T. S. Lee, W. H. Park, *J. Colloid Interface Sci.* **2008**, *320*, 91.
- [215] M. Kang, R. Jung, H. S. Kim, H. J. Jin, *Colloid Sur. A: Physicochem. Eng. Aspects* **2008**, *313*, 411.
- [216] J. F. Zheng, A. H. He, J. X. Li, J. Xu, C. C. Han, *Polymer* **2006**, *47*, 7095.
- [217] Y. Miyauchi, B. Ding, S. Shiratori, *Nanotechnology* **2006**, *17*, 5151.
- [218] B. Ding, C. R. Li, Y. Hotta, J. Kim, O. Kuwaki, S. Shiratori, *Nanotechnology* **2006**, *17*, 4332.
- [219] M. Kanehata, B. Ding, S. Shiratori, *Nanotechnology* **2007**, *18*, 315602.
- [220] Y. Zhu, J. C. Zhang, Y. M. Zheng, Z. B. Huang, L. Feng, L. Jiang, *Adv. Funct. Mater.* **2006**, *16*, 568.
- [221] Y. Zhu, J. C. Zhang, J. Zhai, Y. M. Zheng, L. Feng, L. Jiang, *ChemPhysChem* **2006**, *7*, 336.
- [222] N. Wang, Y. Zhao, L. Jiang, *Macromol. Rapid Commun.* **2008**, *29*, 485.
- [223] Y. Zhu, L. Feng, F. Xia, J. Zhai, M. X. Wan, L. Jiang, *Macromol. Rapid Commun.* **2007**, *28*, 1135.
- [224] Y. Zhu, J. C. Zhang, Y. M. Zheng, J. Zhai, L. Jiang, *Chem. J. Chinese Univ.* **2006**, *27*, 196.
- [225] G. Hota, B. R. Kumar, W. J. Ng, S. Ramakrishna, *J. Mater. Sci.* **2008**, *43*, 212.
- [226] C. S. Ki, E. H. Gang, N. C. Um, Y. H. Park, *J. Membr. Sci.* **2007**, *302*, 20.
- [227] X. F. Song, Z. J. Wang, Z. Y. Li, C. Wang, *J. Colloid Interf. Sci.* **2008**, *327*, 388.
- [228] G. Y. Oh, Y. W. Ju, H. R. Jung, W. J. Lee, *J. Anal. Appl. Pyrolysis* **2008**, *81*, 211.
- [229] R. Ramaseshan, S. Sundarajan, Y. J. Liu, R. S. Barhate, N. L. Lala, S. Ramakrishna, *Nanotechnology* **2006**, *17*, 2947.
- [230] V. Thavasi, G. Singh, S. Ramakrishna, *Energy Environ. Sci.* **2008**, *1*, 205.
- [231] K. Yoon, B. S. Hsiao, B. Chu, *J. Mater. Chem.* **2008**, *18*, 5326.
- [232] M. Y. Song, D. K. Kim, K. J. Ihn, S. M. Jo, D. Y. Kim, *Synth. Met.* **2005**, *153*, 77.
- [233] K. Onozuka, B. Ding, Y. Tsuge, T. Naka, M. Yamazaki, S. Sugi, S. Ohno, M. Yoshikawa, S. Shiratori, *Nanotechnology* **2006**, *17*, 1026.
- [234] K. Fujihara, A. Kumar, R. Jose, S. Ramakrishna, S. Uchida, *Nanotechnology* **2007**, *18*, 365709.
- [235] R. Zhu, C. Y. Jiang, X. Z. Liu, B. Liu, A. Kumar, S. Ramakrishna, *Appl. Phys. Lett.* **2008**, *93*, 013102.
- [236] M. Y. Song, D. K. Kim, K. J. Ihn, S. M. Jo, D. Y. Kim, *Nanotechnology* **2004**, *15*, 1861.
- [237] R. Jose, A. Kumar, V. Thavasi, S. Ramakrishna, *Nanotechnology* **2008**, *19*, 424004.
- [238] D. C. Olson, S. E. Shaheen, M. S. White, W. J. Mitchell, M. F. A. M. van Hest, R. T. Collins, D. S. Ginley, *Adv. Funct. Mater.* **2007**, *17*, 264.

- [239] D. C. Olson, S. E. Shaheen, R. T. Collins, D. S. Ginley, *J. Phys. Chem. C* **2007**, *111*, 16670.
- [240] J. Liu, Z. R. Yue, H. Fong, *Small* **2009**, *5*, 536.
- [241] L. W. Ji, A. J. Medford, X. W. Zhang, *J. Polym. Sci. Part B: Polym. Phys.* **2009**, *47*, 493.
- [242] C. Kim, K. S. Yang, M. Kojima, K. Yoshida, Y. J. Kim, Y. A. Kim, M. Endo, *Adv. Funct. Mater.* **2006**, *16*, 2393.
- [243] L. Wang, Y. Yu, P. C. Chen, C. H. Chen, *Scripta Mater.* **2008**, *58*, 405.
- [244] H. W. Lu, D. Li, K. Sun, Y. S. Li, Z. W. Fu, *Solid State Sci.* **2009**, *11*, 982.
- [245] Q. H. Guo, X. P. Zhou, X. Y. Li, S. L. Chen, A. Seema, A. Greiner, H. Q. Hou, *J. Mater. Chem.* **2009**, *19*, 2810.
- [246] Y. W. Ju, G. R. Choi, H. R. Jung, W. J. Lee, *Electrochim. Acta* **2008**, *53*, 5796.
- [247] S. Agarwal, J. H. Wendorff, A. Greiner, *Polymer* **2008**, *49*, 5603.
- [248] J. Fang, H. T. Niu, T. Lin, *Chin. Sci. Bull.* **2008**, *53*, 2265.
- [249] H. Nie, B. W. Soh, Y. C. Fu, C. H. Wang, *Biotechnol. Bioeng.* **2008**, *99*, 223.
- [250] A. Chunder, S. Sarkar, Y. B. Yu, L. Zhai, *Colloids Surf. B* **2007**, *58*, 172.
- [251] P. Sikareepaisan, A. Suksamrarn, P. Supaphol, *Nanotechnology* **2008**, *19*, 015102.
- [252] P. Taepaiboon, U. Rungsardthoong, P. Supaphol, *Eur. J. Pharm. Biopharm.* **2007**, *68*, 387.
- [253] J. W. Xie, C. H. Wang, *Pharm. Res.* **2006**, *23*, 1817.
- [254] X. H. Zong, K. Kim, D. F. Fang, S. F. Ran, B. S. Haiao, B. Chu, *Polymer* **2002**, *43*, 4403.
- [255] E. R. Kenawy, G. L. Bowlin, K. Mansfield, J. Layman, D. G. Simpson, E. H. Sanders, G. E. Wnek, *J. Controlled Release* **2002**, *81*, 57.
- [256] H. L. Jiang, Y. Q. Hu, P. C. Zhao, Y. Li, K. J. Zhu, *J. Biomed. Mater. Res. Part B, Appl. Biomater.* **2006**, *79B*, 50.
- [257] K. Kim, Y. K. Luu, C. Chang, D. F. Fang, B. S. Hsiao, B. Chu, M. Hadjiargyrou, *J. Controlled Release* **2004**, *98*, 47.
- [258] Z. M. Huang, C. L. He, Z. Yang, Y. Z. Zhang, X. J. Han, J. L. Yin, Q. S. Wu, *J. Biomed. Mater. Res. Part A* **2006**, *77A*, 169.
- [259] J. Zeng, A. Aigner, F. Czubyko, T. Kissel, J. H. Wendorff, A. Greiner, *Biomacromolecules* **2005**, *6*, 1484.
- [260] M. R. Abidian, D. H. Kim, D. C. Martin, *Adv. Mater.* **2006**, *18*, 405.
- [261] W. J. Li, C. T. Laurencin, E. J. Caterson, R. S. Tuan, F. K. Ko, *J. Biomed. Mater. Res.* **2002**, *60*, 613.
- [262] H. Yoshimoto, Y. M. Shin, H. Terai, J. P. Vacanti, *Biomaterials* **2003**, *24*, 2077.
- [263] X. M. Mo, C. Y. Xu, M. Kotaki, S. Ramakrishna, *Biomaterials* **2004**, *25*, 1883.
- [264] H. J. Jin, J. S. Chen, V. Karageorgiou, G. H. Altman, D. L. Kaplan, *Biomaterials* **2004**, *25*, 1039.
- [265] S. Y. Chew, R. Mi, A. Hoke, K. W. Leong, *Biomaterials* **2008**, *29*, 653.
- [266] S. Ramakrishna, K. Fujihara, W.-E. TeO, T. Yong, Z. Ma, R. Ramaseshan, *Mater. Today* **2006**, *9*, 40.
- [267] X. L. Zhu, W. G. Cui, X. H. Li, Y. Jin, *Biomacromolecules* **2008**, *9*, 1795.
- [268] Y. Z. Zhang, H. W. Ouyang, C. T. Lim, S. Ramakrishna, Z. M. Huang, *J. Biomed. Mater. Res. Part B: Appl. Biomater.* **2005**, *72B*, 156.
- [269] M. Y. Li, Y. Guo, Y. Wei, A. G. MacDiarmid, P. I. Lekes, *Biomaterials* **2006**, *27*, 2705.
- [270] H. S. Koh, T. Yong, C. K. Chan, S. Ramakrishna, *Biomaterials* **2008**, *29*, 3574.
- [271] Y. Z. Zhang, J. Venugopal, Z.-M. Huang, C. T. Lim, S. Ramakrishna, *Biomacromolecules*, **2005**, *6*, 2583.
- [272] E. Schnell, K. Klinkhammer, S. Balzer, G. Brook, D. Klee, P. Dalton, J. Mey, *Biomaterials*, **2007**, *28*, 3012.
- [273] L. Ghasemi-Mobarakeh, M. P. Prabhakaran, M. Morshed, M. H. Nasr-Esfahani, S. Ramakrishna, *Biomaterials* **2008**, *29*, 4532.
- [274] K. Fujihara, M. Kotaki, S. Ramakrishna, *Biomaterials* **2005**, *26*, 4139.
- [275] H. S. Fan, X. T. Wen, Y. F. Tan, R. Wang, H. D. Cao, X. D. Zhang, *Mater. Sci. Forum* **2005**, *475–479*, 2379.
- [276] H. W. Kim, H. H. Lee, J. C. Knowles, *J. Biomed. Mater. Res. Part A* **2006**, *79A*, 643.
- [277] J. Venugopal, S. Low, A. T. Choon, T. S. Sampath Kumar, S. Ramakrishna, *J. Mater. Sci. Mater. Med.* **2008**, *19*, 2039.
- [278] E. D. Boland, G. E. Wnek, D. G. Simpson, K. J. Pawlowski, G. L. Bowlin, *J. Macromol. Sci. Pure Appl. Chem.* **2001**, *38*, 1231.
- [279] L. S. Nair, S. Bhattacharyya, C. T. Laurencin, *Expert Opin. Biol. Ther.* **2004**, *4*, 659.
- [280] M.-S. Khil, D.-I. Cha, H.-Y. Kim, I.-S. Kim, N. Bhattarai, *J. Biomed. Mater. Res. Part B* **2003**, *67B*, 675.
- [281] K. H. Hong, *Polym. Eng. Sci.* **2007**, *47*, 43.
- [282] Y. Y. Duan, J. Jia, S. H. Wang, W. Yan, L. Jin, Z. Y. Wang, *J. Appl. Polym. Sci.* **2007**, *106*, 1208.
- [283] A. Melaiye, Z. H. Sun, K. Hindi, A. Milsted, D. Ely, D. H. Reneker, C. A. Tessier, W. J. Youngs, *J. Am. Chem. Soc.* **2005**, *127*, 2285.

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