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An Electrospinning Technique to Fabricate Novel Polymer/Inorganic Composite Nanofibers

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Abstract: *Electrospinning is a simple and versatile method for generating polymer and inorganic nanofibers. When combined with functional inorganic nanoparticles, it provides a new technique to produce polymer/inorganic composite nanofibers. This article presents a brief overview of recent progress in fabrication of polymer/inorganic nanofibers by electrospinning. We fully demonstrate the fabrication of polymer/metal, polymer/carbon nanotubes, polymer/semiconductor, polymer/metal oxides, and other polymer/inorganic composite nanofibers based on the electrospinning technique.*

Keywords: *Electrospinning; Polymers; Inorganic; Composite; Nanofibers*

1. INTRODUCTION

In the past decades, the design and attainment of functional composite nanomaterials have been attracted much attention, since they can combine two or more components on a nanometer scale, which can process excellent physical and chemical properties.[1,2] Especially, the combination of electrical, magnetic and optical inorganic nanoparticles with good flexible polymers can result a new kind of nanocomposites with good process ability and improved physical, mechanical, and chemical properties.[3-5] These nanocomposites may have applications in catalytic membranes, ultrafiltration, nonlinear optical materials, and reinforcement of elastomers and plastics.[6] Many of reports have been published on the fabrication of polymer/inorganic composite nanomaterials. However, one-dimensional composite nanomaterials become major challenges for scientists worldwide now due to their potential applications in nanodevices.[7-8] Many methods are used to synthesize one-dimensional nanostructural materials, such as template-directed method,[9] vapor-phase approach,[10,11] solution-phase method[12-14] self-assembly,[15] and size reduction.[16] Recently, a simple electrospinning technique is favored to produce one-dimensional structures of polymers, inorganic materials and polymer/inorganic composite materials.

The electrospinning technique was first demonstrated in 1934 by Formhals through a patent.[17] He demonstrated an apparatus for producing polymer filaments using electrostatic repulsions between surface charges. In the early 1990s, Reneker's group developed this technique. They fabricated many thin fibers from a broad range of polymers

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using this method, which is called "electrospinning".[18-21] From then on, many scientists have focused on this technique and many papers on both experimental and theoretical studies were published.[22-25] In fact, the technique is similar to the commercial mechanical drawing to produce microscale fibers, which is both based on the outside force to reduce the diameter of a viscoelastic jet. However, the electrospinning method can produce thinner fibers. To the best of our knowledge, the thinnest fibers were generated by this method are 6±2 nm.[26] The apparatus of the electrospinning technique involves three parts: a high voltage electrostatic field, a spinneret and a collector. (Figure 1) In a typical process to produce polymer nanofibers, an electrical potential is applied between a droplet of a polymer solution in the capillary tube and the collector. Under the electrostatic interactions, the droplet of polymer solution will be distorted into a cone, which called "Taylor cone".[27] When the electrostatic forces produced by an electric field overcome the surface tension of the polymer solution, a charged jet from the solution will be ejected from the nozzle. The electrified jet undergoes a bending instable process and the jet extends through spiraling loops. Along with the evaporation of the solvent, the jet becomes thinner and longer until they reached the collector. The collector was often made of a metal foil or silicon piece, which were placed opposite the spinneret. The charged fibers are often deposited on the collector randomly. In order to obtain the alignment of electrospun fibers, the collector usually needs to be improved. A cylinder with high rotating speed and tapered, wheel-like disk were both used as the collector to produce oriented parallel fibers.[28,29] Xia et al. used a collector consisting of two conductive strips separated by a void gap of variable widths to obtain uniaxially aligned polymer fibers.[30,31] The aligned nanofibers have many applications such as in ordered electronic and photonic devices.

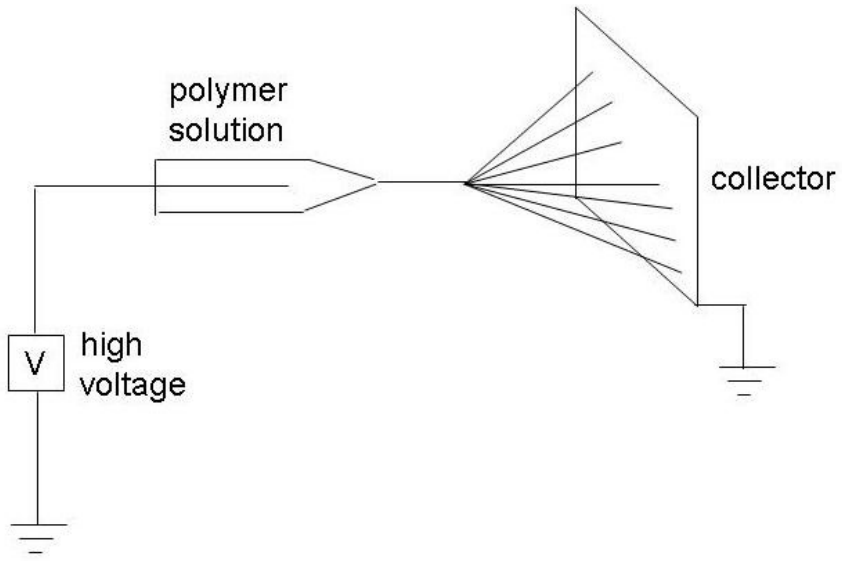

Figure 1: A Schematic for Electrospinning Technique

In the early work, people paid more attention to the fabrication of polymer nanofibers. Up to now, more than fifty different types of polymer micro-nanofibers, such as Nylon 66, polycarbonate (PC), polyacrylonitrile (PAN), poly(vinylalcohol) (PVA), poly(actic acid) (PAA), polystyrene (PS), poly(methyl methacrylate) (PMMA), polyamide (PA), poly(vinylpyrrolidone) (PVP), have been already fabricated.[32,33] Recently, inorganic nanofibers including aluminum oxide, nickel cobaltite, cobalt oxide, copper oxide, magnesium titanate, nickel oxide, nickel titanate, lead titanate, niobium oxide, titanium oxide, zirconium oxide, zinc oxide, vanadium pentoxide and tungsten oxide et al. were also prepared by the electrospinning method.[34-48] On the other hand, the electrospinning method is also playing an important role and has been regarded as one of the simplest and most effective techniques in the field of fabrication of one-dimensional polymer/inorganic nanomaterials. Various kinds of polymer nanofibers containing different functional inorganic nanoparticles have been prepared through this method.

In this paper, a brief overview is presented on the fabrication of polymer/inorganic nanofibers by electrospinning. We will fully demonstrate the fabrication of polymer/metal, polymer/carbon nanotubes, polymer/semiconductor composite nanofibers, and other polymer/inorganic composite nanofibers based on the electrospinning technique.

2. POLYMER/METAL COMPOSITE (PMC) NANOFIBERS

The PMC nanofibers can be applicable in catalysts, photonic and electric sensors, filters, and tissue engineering. Among the PMC nanofibers, polymer/Ag composite nanofibers were widely studied. Our group prepared PAN/Ag composite nanofibers by electrospinning N, N'-dimethylformamide (DMF) solution of PAN containing as-prepared Ag nanoparticles.[49] The average diameter of the Ag nanoparticles was about 100 nm (max. : 200 nm; min.: 20 nm). The interactions between Ag atoms and PAN molecular chains prevent the Ag nanoparticles from coagulating in the process of *in-situ* synthesis, but made the fiber thicker. Recently, Wang *et al.* put PAN/Ag^+ nanofibers film into hydrazine to transfer Ag^+ to Ag nanoparticles.[50] By this method, Ag nanoparticles can be well dispersed in PAN nanofibers and the diameter of Ag nanoparticles was about 10 nm. Lee *et al.* used DMF without hydrazine as a reducing agent to prepare PAN/Ag composite nanofibers.[51] This method was simple and only needed one-step process. The average diameter of the obtained Ag nanoparticles dispersed in polymer fibers was 6.8 nm and their size distribution was very narrow. Besides the solvent, the polymer can also be served as the reducing agent for reducing Ag^+ clusters to Ag nanoparticles. For example, PVP, as both the polymer matrice and the reducing agent, was used to prepare PVP/Ag composite nanofibers.[52] By this method, the diameter of the obtained Ag nanoparticles was only about 8 nm. Cho *et al.* also prepared polymer/Ag composite nanofibers by electrospinning.[53] They infiltrated silver nitrate on electrospun polyurethane (PU) fibers and reduced the Ag^+ ions with sodium borohydride. However, the obtained Ag particles are a little aggregated and not well dispersed on the surface of the PU fibers. Using both DMF and PVP, Ag nanoparticles can be well dispersed in polymer fibers. Jin et al. prepared PVP/Ag and poly(vinyl alcohol) PVA/PVP/Ag composite nanofibers using this method.[54] It is found that the average diameter of Ag nanoparticles

in PVP fibers is from 3.4 to 4.5 nm, while in PVA/PVP fibers is about 6.0 nm. It is known that silver nanoparticles could also be prepared by a UV photoreduction technique. Combined with the electrospinning method, Son et al. prepared antimicrobial ultrafine cellulose acetate (CA) fibers with Ag nanoparticles.[55] The diameter of Ag nanoparticles was related to the amounts of the added $AgNO_3$. When the CA fibers contains 0.05 and 0.5 wt. % $AgNO_3$, the diameter of Ag nanoparticles is 3.3 and 6.9 nm. Our group also prepared PAN/Ag composite nanofibers by the same method.[56] The diameter of Ag nanoparticles can be controlled by the molar ratio of the Ag^+: PAN (repeating unite).

Besides the polymer/Ag composite nanofibers, polymer/Au, polymer/Pd and polymer/Cu composite nanofibers were also studied. Kim *et al.* prepared semicrystalline polymer poly(ethylene oxide) (PEO) fibers containing Au nanoparticles.[57] They firstly synthesized dodecanethiol-capped gold nanoparticles, then dissolved it in chloroform solution of PEO. The composite solution was electrospun to prepare PEO/Au composite fibers. The average particle size was about 4 nm in diameter. Demir et al. prepared catalytic palladium (Pd) nanoparticles on electrospun copolymers of acrylonitrile and acrylic acid (PAN-AA) mats via a reduction of $PdCl_2$ with hydrazine.[58] It was found that spherical Pd nanoparticles were dispersed homogeneously on the surface of the nanofibers. The size of Pd nanoparticles depends on the amount of acrylic acid functional groups and $PdCl_2$ concentration in the spinning solution. The composite fibers were found to have higher catalytic activity. Our group also prepared PVA/Cu composite nanofibers.[59,60] As Cu nanoparticles were easily oxidized, $NaHSO_3$ was added into the electrospun solution before electrospinning. The results show that Cu nanoparticles can be well dispersed in PVA matrix. Moreover, as the molar ratio of Cu^{2+} to PVA repeating unite was proper, Cu/PVA coaxial nanocables could be obtained.

3. POLYMER/CARBON NANOTUBE COMPOSITE NANOFIBERS

It is well known that carbon nanotubes (CNTs) possess various good performances such as mechanical and electronic performances. It is expected that combination of CNTs with electrospun polymer nanofibers may greatly improve the mechanical strength, thermal conductivity and electronic conductivity of the fibers. Ko *et al.* dispersed single wall nanotubes (SWNTs) in different polymer solutions and electrospun them into nanofibers.[61] It is found that PAN/SWNTs nanofibers have a better alignment of SWNTs than PLA/SWNTs fibers do. In the former, SWNTs maintain a straight shape and are parallel to the axis direction of the PAN fibers. The reasons may be attributed to the differences in conductivity and wetting ability of the two polymers. They also prepared the nanocomposite fibers of bombyx mori silk and SWNTs.[62] It is found that the mechanical properties of the SWNTs reinforced fibers show an increase in Young's modulus up to 460% in comparison with the un-reinforced aligned fibers. Cohen and coworkers fabricated PEO nanofibers in which multiwalled carbon nanotubes (MWNTs) were embedded.[63] Sodium dodecyl sulphate (SDS) or highly branched polymer was used to disperse MWNTs in water. It is found that only a small portion of CNTs appeared to be well-oriented along the fiber axis. They also prepared PEO/SWNTs nanofibers[64] and proved that the high degree of orientation of PEO crystals was not significantly

affected by the wall-aligned SWNTs. Poly(vinylidene fluoride) (PVDF)/CNTs nanofibers were also fabricated by Seoul *et al.*[65] It is found that the conductivity of the CNT (0.1 wt %)/ PVDF fiber mat was 7×10^{-6} S/cm. However, the tensile strength, elongation at break, and other mechanical properties were not reported.

Reneker and co-workers reported PAN/MWNTs nanofibers obtained by electrospinning a DMF solution of the PAN and surface-oxidized MWNTs.[66,67] A high degree of orientation of MWNTs in the PAN/MWNT nanofibers was observed. The electrical conductivity and thermal stability were increased greatly. The tensile strength and tensile modulus for PAN/MWNT sheets were also studied in details. PS/SWNT and PU/SWNT nanofibers electrospun from a mixture of PU and ester-functionalized (EST) SWNT[68] showed that the tensile strength of EST-SWNT-PU membranes is enhanced by 104%, compared to electrospun pure PU membranes, while an increase of 46% was achieved by incorporating as-prepared SWNTs in the PU matrix. Kumar and co-workers also prepared PAN/SWNT composite nanofibers by electrospinning.[69] It is known that PAN/SWNT composites exhibited much higher electron beam radiation resistance than PAN membrane. PMMA/MWNTs nanocomposites obtained via an in-situ bulk polymerization of methyl methacrylate (MMA) in the presence of carbon nanotubes (CNTs) and electrospinning its DMF solution[70] exhibited the electrical conductivities of 10^{-4} and 10^{-2} S/cm, as the fiber mats contained 1 and 5 wt % of MWNTs. Sundaray et al reported the preparation of composite nanofibers of PMMA/MWNTs and even studied the electrical conductivity of a single fiber.[71] It is found that the room temperature DC electrical conductivity of a single fiber with 0.05% MWNT is about a ten orders of magnitude improvement, compared with the pure PMMA ones. PC/MWNT nanocomposite[72] has an ultra-highly nanoporous morphology. This structural characteristics and highly aligned parallel of MWNTs in the direction of fiber axis contributed to the mechanical deformation process of the single composite fibers. Zhou et al. studied PEO/MWNTs and PVA/MWNTs nanofibers and found the elastic deformation of MWNTs in these nanofibers.[73] Jin and co-workers presented a simple method to adhere the MWNTs to the surface of the highly porous nylon6 nanofibrous membranes and obtained nylon6/MWNTs composite nanofibers membrane.[74] For the presence of the MWNTs on the surface of the nanofibers, the conductivity of the membranes (1.5 wt.-%) is relatively high (2.2×10^{-2} S/cm).

4. POLYMER/SEMICONDUCTOR (PSC) AND POLYMER/METAL OXIDES COMPOSITE NANOFIBERS

Semiconductor and metal oxides nanoparticles have unique electrical, magnetic and optical properties, which can be applicable in solar cells, photodetectors, light-emitting diodes and switches areas *et al.* The composites of polymer/semiconductor and polymer/metal oxides nanoparticles have been extensively studied because of their flexible processable properties as well. Incorporation of functional nanoparticles into polymer fiber matrices are expected to be used as one-dimensional nanodevices. However, the nanoparticles tend to aggregate in the polymers. Our group developed the electrospinning technique. After the metal salts/nanofibers were obtained, they were exposed to H_2S gas to get metal sulfide semiconductors, which is called gas-solid reaction method. Firstly,

the well-dispersed PbS nanoparticles in PVP nanofibers were obtained.[75] TEM image shows that these PbS nanoparticles are roughly spherical in shape and have a diameter of approximately 5 nm. As Cd^{2+} was used to produce PVP/CdS composite nanofibers, CdS nanorods occurred, which homogeneously dispersed in the PVP fibers.[76] These nanorods have a diameter of about 50 nm and a length between 100 and 300 nm. Using these methods, ZnS:Cu/PVA and ZnS:Mn/PVA composite nanofibers were also achieved.[77,78] However, H_2S gas, as we know, was not environment-friendly. Our group developed a two-step method to synthesize PSC nanofibers. The synthetic strategy involved the preparation of composite sol and electrospinning the composite sol. The PVP/Ag_2S and PVA/ZnO composite nanofibers[79,80] prepared by this method show that the obtained Ag_2S nanoparticles are spherical in shape and are separated from each other, each having a diameter of approximately 15 nm. The average size of ZnO nanoparticles in PVA fiber matrices are 3-4 nm. PVA/ZnO composite nanofibers have been also prepared by Shao *et al.*,[81] which have an intense white-light emission. Zussman and co-workers have also prepared PEO/CdS nanorod composite nanofibers by directly electrospinning the mixture solution of PEO and CdS.[82] The result shows that CdS nanorods are embedded with unidirectional alignment of their long axis with respect to the stretching direction of the fibers. Hong et al. described the preparation of 1D assemblies of ZnO nanocrystal-supported PVA nanofibers.[83] These hybrid membranes was obtained by immersing the PVA nanofibers containing ZnAc in a basic ethanol solution to carry out a sol-gel reaction. By the method, they have also prepared PAN/TiO_2 composite nanofibers.[84]

Kim *et al.* fabricated PVA/SiO_2 composite thin fibers by electrospinnng.[85] The results indicated that PVA was changed from semicrytalline to amorphous state because of the increase of silica content. It is also possible to incorporate Fe_3O_4 nanoparticles into polymer fiber matrices by electrospinning. Tan et al. prepared poly(hydroxyethyl methacrylate) (PHEMA) and poly-l-lactide (PLLA) nanofibers containing Fe_3O_4 nanoparticles.[86] It is found that the nanofibers containing up to 35 wt.-% of Fe_3O_4 displayed superparamagnetism at room temperature. The saturation magnetization was 3.5 emu/g and 1.1 emu/g for Fe_3O_4/PHEMA and Fe_3O_4/PLLA nanofibers, respectively.

Drew *et al.* also reported the fabrication of metal oxide-coated nanofibers.[87] They put the nanofiber membranes in an aqueous solution of metal halide salts and halogen scavengers to apply SnO_2 and TiO_2 coatings. However, the surface of the coatings is not satisfied. Recently, our group prepared polypyrrole (PPy)/TiO_2 composite coaxial nanofibers.[88] We had the pyrrole monomers polymerize on the electrospun TiO_2 nanofibers. The results show that polypyrrole were uniformly coated on the TiO_2 nanofibers. And another surfactant-directed method was also investigated to prepare PPy/TiO_2 composite coaxial nanofibers.[89] By using this method, the thickness of the PPy shell on the TiO_2 nanofibers can be well controlled. The thickness is dependent on the mass ratio of the pyrrole monomer and TiO_2 nanofibers.

5. OTHER POLYMER/INORGANIC COMPOSITE NANOFIBERS

Besides the semiconductor nanoparticles, other inorganic nanoparticles or compounds were also incorporated into polymer fiber matrices. Gupta *et al.* prepared flexible,

elastomeric, and superparamagnetic nanofibers by electrically spinning a solution of elastomeric polyurethane containing ferrite nanoparticles of Mn-Zn-Ni.[90] The superparamagnetic behavior of the composites was not changed. Song *et al.* reported poly(e-caprolactone) (PCL)/FePt composite nanofibers by coaxial electrospinning.[91] It is found that FePt nanoparticles with a diameter of 4 nm were completely encapsulated within the PCL nanofibers. For polymer (MEHPPV)/molecular sieve (SBA-15) composite fibers[92], it is known that its emission spectrum show a blue shift, which might be applicable in the molecular electronics. Electrospun polyoxometalates/ polymer composite nanofibers were also well studied. Gong *et al.* prepared $H_3PW_{12}O_{40}$/ PVA composite nanofibers.[93] The brunauer-Emmett-Teller (BET) surface area and swelling behavior of the fiber aggregates in water were investigated. $H_6P_2W_{18}O_{62}$/PVA[94], $H_4SiW_{12}O_{40}$/PVA[95], $H_3PW_{11}MoO_{40}$/PVA[96] were also prepared. The results show that most of the composite nanofibers show reversible photochromism. Our group has also prepared $Na_9[EuW_{10}O_{36}]$/PVA composite nanofibers.[97] This electrospinning method prevents the polyoxometalates turning to an inhomogeneous microphase and large aggregation. The photoluminescence spectra of the hybrid fibers show characteristic of red-light emission at room temperature. Recently, our group incorporated metalloporphyrin molecules into PVP fiber matrices to obtain discontinuous composite nanofibers, which show various kinds of ordered patterns.[98] The patterns formation may be resulted from the self-assembling of the metalloporphyrin molecules in the PVP matrices at the electric field.

6. SUMMARY AND PROSPECT OF COMPOSITE NANOFIBERS

The electrospinning technique has made a great progress since the last decades. Tens of the polymer/inorganic composite nanofibers have been prepared successfully. The scientists are trying to manipulate the technique so as to control the structure, morphology, and assembly of the nanofibers. Meanwhile, their nanoeffects in biologcal, catalytic, electrical, magnetic and optical properties are being developed actively. It is expected that the successful fabrication of the polymer/inorganic composite nanofibers by electrospinning will create more materials with novel performances.

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