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Preparation of Functionalized Nanofibers and Their Applications

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1. Introduction

Recently, nano-scaled materials have been investigated with amazing increased interest due to their many advantages, such as large surface area and many active surface sites. Among different nano-scaled materials, nanofibers have been widely applied in industry due to the ease in production processes compared to other nano-materials. Nanofibers can be identified as fibers having diameters between tens and hundreds of nanometers. This nano-scaled diameter of fibers can give an enormous surface area per unit mass.

Nanofibers are usually fabricated by the electrospinning method as a non-woven mat. Non-woven fabrics are textile materials consisting of randomly oriented fibers connected together by physical entanglements or bonds between individual fibers, without any knitting or stitching. These non-woven nanofibers are the primary alternative for traditional textiles as filtration media, energy storage media, hygienic and health/personal care textiles, thermal and sound insulating materials, ecological materials, building materials, geo-textiles and automotive textiles.

2. Formation of nanofibers by electrospinning

2.1 Theory of electrospinning

New applications require fibers with increasingly smaller diameters. Since the surface area is proportional to the fiber diameter and the volume is proportional to the square of the diameter, the specific surface area is inversely proportional to the fiber diameter, leading to high specific surface areas for small fibers. In addition, pore size depends on the fiber diameter; therefore, small fibers produce non-wovens with a small pore size. There are several methods for producing small diameter fibers using high-volume production methods, such as fibrillation, island-in-sea, and the novel melt-blowing system, in addition there are highly accurate methods such as nano-lithography and self-assembly. However, the usefulness of above methods is restricted by combinations of narrow material ranges, high costs and low production rates. In comparison, electrospinning is a simple and low cost process and has an intermediate production rate. Electrospinning is a process for sub-micron scale polymer-based filament production (usually called nanofibers) by means of an electrostatic field. Due to these forces, the meniscus of a liquid flowing out of a capillary nozzle elongates, forming a fine jet, that is later atomized into fine droplets. The droplets obtained by this method are electrically charged. A basic electrospinning setup consists of


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three elements: an electrical generator (high voltage supply), a capillary (jet source) and a metal collector (target). Depending on the flow rate and potential of the capillary, the droplets can be of submicron size, with a narrow size distribution. The solution is usually electrically charged by the generator, and the collector is grounded, but it is also possible to invert the process by electrically charging the collector and grounding the solution. When the electrostatic forces exceed the surface tension force, the pendent droplet at the capillary tip is stretched into a cone (called Taylor cone), and a solution stream is ejected (Dzenis, Y.A., 2004). Whether the jet will form a continuous fiber or disperse into droplets depends on polymer molecular weight, polymer chain entanglement, and the solvent applied to the process (specifically, its evaporation rate). It is known from the literature that smooth fibers are produced when the product of intrinsic viscosity ($\eta$) and polymer concentration ($c$), known as the Berry’s number, $Be=\eta c$, is greater than a certain critical value $Becr$, which is characteristic of the polymer. Specific viscosity of a polymer solution is determined as the ratio:

$$\eta_p = (\eta_s - \eta_l)/\eta_s$$

where $\eta_p$ is the zero shear rate viscosity of the polymer solution at concentration ($c$), and $\eta_s$ is the solvent viscosity. From this equation, the intrinsic viscosity ($\eta$) of the polymer is determined as a linear extrapolation of specific viscosity $\eta_p$ measured for various concentrations to the concentration at $c=0$:

$$\eta = K M_W^a$$

where the constants ($K$) and ($a$) depend on the polymer, solvent and temperature.

### 2.2 Electrospinning setups

A basic electrospinning setup consists of three elements: an electrical generator (high voltage supply), a capillary (jet source) and a metal collector (target) (Fig. 1).

Fig. 1. Diagram of the electrospinning apparatus (J.S. Im et al., 2008).
In our group, polyacrylonitrile (PAN)-based nanofibers were obtained by the electrospinning method. The electrospinning was carried out under the following conditions: [10 wt% of PAN/DMF polymer solution, 15 kV] (J.S. Im et al., 2008).

Fig. 2. PAN-based electrospun carbon fibers.

3. Functionalization of nanofibers

3.1 Activation process for porous nanofibers
Nanofibers have many benefits because of their large surface area for active reaction sites. Activation processes for improving these active sites have been applied by chemical/physical activation. As a representative case of physical activation, the activation agent was embedded into the fibers and then removed by physically removing the agents. The process for PAN-based porous nanofibers physically activated by silica is presented in Fig. 3 (J.S. Im et al., 2009). The silica-activated carbon nanofibers are shown in Fig. 4 (J.S. Im et al., 2009). The pores generated by physical activation are clearly observed.

3.2 Heat treatment effect for physical properties
Heat treatment has been carried out widely because it can change physical properties. The electrical enhancement of PAN-based carbon fibers was presented by (J.H. Huang et al., 2006) in Fig. 5. A stabilization treatment was carried out at 280 °C for a duration of 4 h, and samples with the same stabilization process parameters were used as the starting material of the carbonization treatment. Cyclic voltammetry (CV) measurements were carried out in a potential window of 0 to 1 V with different scan rates ranging from 100 to 1000 mV/s. It is noted that the curve for electrospun PAN-based carbon fibers shows a zigzag-like behavior, which indicates the hydrogen ions in the electrolytes are not easily adsorbed on the surface pores of PAN-CFs. In contrast, after thermal treatments (especially after the carbonization process), the capacitive performance is still stable even at the scan rate of 1000 mV/s. This result reveals that the capacitive performance of PAN-based carbon fibers is improved by the carbonization process.
This enhancement of electrical properties has been attributed to the improved electrical conductivity caused by the orientation of carbon structures. It was presented that the electrical conductivity can be improved significantly by well-oriented carbon structures through heat treatment (J.S. Im et al., In Press). The test was carried out on a variety of heat treatment temperatures and amounts of carbon nanotube additives, as shown in Fig. 6. The electrical conductivity was improved over three fold by the effects of heat treatment.
Fig. 5. Capacitive behavior of (A) electrospun, (B) stabilized, (C) carbonized PAN-based carbon fibers.
Fig. 6. Electrical conductivity of carbon fiber/carbon nanotubes composite.

Fig. 7. The removal of multi-metal ions on (a) activated carbon fibers and (b) acid-treated activated carbon fibers as a function of pH at 25 °C.
3.3 Modification of nanofibers

The modification of nanofibers has been applied widely to give them improved properties. The result, which shows that the removal of multi-metal ions was improved by surface modification using acid treatment, is shown in Fig. 7 (S.J. Park et al., 2004). They explained that the surface functional groups containing oxygen content by acid treatment played an important role for the removal of metal ions.

A plasma treatment was carried out to enhance the surface energy of carbon nanofibers for good bonding to the matrix (V. Bruser et al., 2003). The gas-state plasma treatment was carried out by using the fluidized bed plasma reactor depicted in Fig. 8. The surface energy increased over two fold after 5 min of plasma treatment (V. Bruser et al., 2003).

![Fluidized bed plasma reactor](Fig. 8. Fluidized bed plasma reactor (V. Bruser et al., 2003).)

The effects of functionalized surface groups on nanofibers were investigated based on improved gas adsorption by our group (J.S. Im et al., 2009). The fluorination treatment of

![Surface energy graph](Fig. 9. Surface energy at 1.2 mbar and 80 W; gas composition: Ar:O₂=1:1 (V. Bruser et al., 2003).)
porous nanofibers was carried out in the gas state for 5 min. The capacity of methane storage was increased by attraction effects of fluorine on porous nanofibers.

Fig. 10. Mechanism of methane storage; (a) methane molecule, (b) electron-attracted molecule and (c) adsorbed methane molecule in the carbon silt pore (J.S. Im et al., 2009).

3.4 Nanofibers complex
The use of nanofibers as the reinforcing filler and conducting additive in polymers to improve their mechanical and electrical properties is generally encountered in polymer technology. Nanofibers, such as carbon and glass fibers, are routinely used in composites of a range of different polymers. Improvement in modulus and strength, achieved by using nanofibers in a composite, has been presented by many researchers. The improved storage modulus of epoxy resin by addition of carbon nanofibers is presented in Fig. 11 (Derrick R.

Fig. 11. Storage modulus of epoxy resin based on the effects of carbon nanofibers (Derrick R. Dean et al., 2009).
The transition temperature shifted significantly higher, indicating that the epoxy/carbon nanofiber composite can be stained up to higher temperatures. This mechanical improvement is attributed to the properties at the fiber/matrix interface and are therefore dependent on the surface area of the interface. S.G. Prolongo’s group synthesized Epoxy/carbon nanofiber composites by suing functionalized nanofibers with amino groups (S.G. Prolongo et al., 2009). They found that the dispersion of carbon nanofibers is improved by the functionalization process up to a nanofiber content of 1 wt%. They also found that improved dispersion of carbon nanofibers markedly affects the physical and thermo-dynamical mechanical properties of the epoxy nanocomposites. The addition of functionalized carbon nanofibers causes an important increase in the coefficient of thermal expansion and glassy storage modulus of nanocomposites.

The use of carbon nanofibers for enhanced electrical properties has also been reported widely. The group of Torsten presented results showing that a reduced specific resistance of epoxy resin was obtained by the addition of carbon nanofibers (Torsten Prasse et al., 2003). They also found that the orientation of carbon nanofibers were important for the electrical properties of the epoxy complex. When the carbon nanofibers were oriented along the direction of the applied electric field, the measured electrical properties were improved more efficiently.

![Graph showing specific resistance of epoxy resin as a function of carbon nanofiber weight fraction with different orientations of carbon nanofibers.](https://www.intechopen.com)

Fig. 12. Specific resistance of epoxy resin as a function of carbon nanofiber weight fraction with different orientations of carbon nanofibers (Torsten Prasse et al., 2003).

Metal/nanofiber complexes were also investigated to maximize the advantages of both metals and nanofibers. The self-assembly method of metal-complexed bolaamphiphiles was introduced by Masaki Kogiso’s group (Masaki Kogiso et al., 2004). The illustration is shown in Fig. 13.

For example, a TiO$_2$ photocatalyst was embedded in electrospun fibers to optimize the photocatalytic ability shown in Fig. 14 (J.S. Im et al., 2008). Due to the low density of electrospun nanofibers, it was possible to make the photocatalysts floating on water for enhanced absorbance of UV light.
4. Application of nanofibers

4.1 Energy storage materials

Nanofibers have been applied as a storage media for alternative energy sources such as hydrogen and natural gases. Porous carbon nanofibers have especially been investigated widely due to their large specific surface area and high pore volume. Hydrogen and natural gases can be stored by physical adsorption, indicating that the use of these gases is easy. The superior storage capacity of porous carbon nanofibers was presented through comparison with other porous carbon materials such as graphite, carbon nanotubes, and activated carbon, as shown in Fig. 15 (J.S. Im et al., 2009).
Fig. 15. The mechanism of hydrogen adsorption using various carbon materials; (a): activated carbon, (b): single walled carbon nanotube, (c): graphite, (d): electrospun activated carbon nanofibers (J.S. Im et al., 2009).
The main reason suggested for improved hydrogen adsorption was that electrospun activated carbon nanofibers might be expected to have an optimized pore structure with controlled pore size. This result may come from the fact that the diameters of electrospun fibers can be controlled easily, and optimized pore sizes can be obtained with a highly developed pore structure.

To find the optimized activation conditions, carbon nanofibers were activated based on varying the chemical activation agents, reaction time, reaction temperature, and the rate of inert gas flow. The role of the type of chemical activation and inert gas flow rate was explained by recent paper (A. Linares-Solano et al., 2009). When comparing potassium hydroxide and sodium hydroxide, a higher developed pore structure was observed with potassium hydroxide. A quicker flow rate of inert gas was also beneficial for an optimized pore structure for hydrogen adsorption of carbon nanofibers.

The MCF (metal-carbon-fluorine) system was introduced by using electrospun carbon nanofibers (J.S. Im et al., 2009). The transition metal and fluorine were introduced on the activated carbon nanofibers to use the gap of electronegativity between the metal and fluorine. As a result of this gap, the hydrogen molecules were attracted into the carbon pores effectively.

4.2 Ecological materials
Photocatalysts (usually TiO \textsubscript{2}) are used widely because of their high activity, chemical stability, robustness against photocorrosion, low toxicity and low cost. Nano-sized photocatalysts have been synthesized by many methods, such as the sol-gel process and thermal treatments, to enhance the photocatalytic ability with larger active sites. However, the recovery of nano-sized photocatalysts is not easy, making reuse difficult and secondary contamination likely. Therefore the immobilization method has been studied widely. Nanofibers have been investigated as one of the solutions using two methods: first,
photocatalysts were fabricated as a non-woven mat by the electrospinning method; second, photocatalysts were embedded into a matrix of electrospun nanofibers. These materials can render large active sites for the photodegradation of pollutants. The TiO\textsubscript{2} nanofibers were fabricated by C. Tekmen and A.K. Alves’s groups (C. Tekmen et al., 2008, A.K. Alves et al., 2009). S.G. Lee’s group synthesized SiO\textsubscript{2}/TiO\textsubscript{2} nanofibers by electrospinning and presented their synergy effects (S.W. Lee et al., 2007). The TiO\textsubscript{2} embedded PAN-based carbon nanofibers were prepared and investigated based on the floating effect with a low density of nano-web (J.S. Im et al., 2008). The photocatalytic efficiency was maximized because photocatalysts can be activated by UV-light without any interruption such as UV absorption of dust water.

Fig. 17. Mechanism of hydrogen adsorption enhancement by the MCF system.

Fig. 18. Photocatalytic effects of nanofibers involving TiO\textsubscript{2} based on the floating property.
Nanofibers have also been studied as a membrane for the filtration of heavy metals in groundwater (Y. Sang et al., 2008). The experimental setup was shown in Fig. 19. From static adsorption experiments, an efficient removal of Cu$^{2+}$, Cd$^{2+}$, and Pb$^{2+}$ was observed.

![Fig. 19. Nanofiber membrane test as a groundwater treatment (Y. Sang et al., 2008).](image)

### 4.3 Biomaterials

The biomedical applications of electrospun fibers remain the most interesting research area. Nanofibers can contribute in diverse emerging medical areas such as drug delivery, organogenesis, genomic medicine, rapid bedside clinical tests, and smart wound dressings. Among these applications, nanofiber-based three-dimensional scaffolds for tissue engineering and the design of nanofiber devices for sustained delivery systems have been attracted by the many advantages of electrospun fibers. The majority of nanofiber anti-

![Fig. 20. Controlled drug release of electrospun hydrogel nanofibers by fluorination treatment.](image)
neoplastic agent delivery systems have been envisioned for the treatment of malignant gliomas (a type of brain tumor). The current drug delivery system of choice is post tumor-resection implantation of a drug-eluting wafer. Thus, numerous studies have tried to elucidate the benefits of implanting a nanofiber delivery system over a wafer-based system. Recent results show that the released drug of electrospun nanofibers can be controlled by surface treatment (J.S. Im et al., 2009). Sustained drug release was observed by controlling the swelling rate of hydrogel nanofibers using a fluorination treatment. The scaffolding application of electrospun nanofiber mats has already been applied in the industrial field because their size range approximates the structural features present in tissues surrounding animals’ bodies. Based on the effects of various layered nanofiber matrices presented in Fig. 21, the ability of the scaffold was tested (S.H. Park et al., 2008).

![Fig. 21. Schematic diagrams and photographs of the three types of hybrid scaffolds used in the cell culture experiments. (a) Type I has no nanofiber matrix and only a PCL scaffold as a control specimen. PCL scaffolds combined with (b) a one-layer PCL/collagen nanofiber matrix (type II) and (c) a three-layer PCL/collagen nanofiber matrix (type III) (S.H. Park et al., 2008).](image)

The M.P. Lutolf group presented the concept of the stem cell niche and the role of the extracellular matrix in regulating stem cell survival and signaling. They used electrospun nanofibers as a basement membrane between two phases. By controlling the ratio of the polymer sources, the scaffold can easily have different properties. In Fig. 23, the lacunae in A1, B1 and C1 were enlarged and compared ((Hap/PLGA (%w/w); A1 (0/100), B1 (5/95) and C1 (10/90)) (H. Nie et al., 2009). Numerous osteoclast-like cells (identified by black circles) were observed to reabsorb the trabecular bone throughout the defects at this time-point. More isolated lacunae were observed in A1 and B1 than C1.
Fig. 22. The concept of the stem cell niche and role of the extracellular matrix in regulating stem cell survival and signaling. ECM: extracellular matrix; GF: growth factor; [GF]: growth factor concentration. Matrix (M.P. Lutolf and J.A. Hubbell, 2005).

Fig. 23. Histological specimens from nude mice tibias after 2 and 4 weeks of implantation of A1, B1 and C1. Original magnification is 400 × for all (H. Nie et al., 2009). The wound healing ability of nanofibers is shown in Fig. 24 (J.S. Choi et al., 2008). The wound of mouse was effectively healed by electrospun nanofibers within 14 days.

5. References


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Fig. 24. Extent of wound healing in diabetic C57BL/6 mice treated with various formulations (J.S. Choi et al., 2008).


“There’s Plenty of Room at the Bottom” this was the title of the lecture Prof. Richard Feynman delivered at California Institute of Technology on December 29, 1959 at the American Physical Society meeting. He considered the possibility to manipulate matter on an atomic scale. Indeed, the design and controllable synthesis of nanomaterials have attracted much attention because of their distinctive geometries and novel physical and chemical properties. For the last two decades nano-scaled materials in the form of nanofibers, nanoparticles, nanotubes, nanoclays, nanorods, nanodisks, nanoribbons, nanowhiskers etc. have been investigated with increased interest due to their enormous advantages, such as large surface area and active surface sites. Among all nanostructures, nanofibers have attracted tremendous interest in nanotechnology and biomedical engineering owing to the ease of controllable production processes, low pore size and superior mechanical properties for a range of applications in diverse areas such as catalysis, sensors, medicine, pharmacy, drug delivery, tissue engineering, filtration, textile, adhesive, aerospace, capacitors, transistors, battery separators, energy storage, fuel cells, information technology, photonic structures and flat panel displays, just to mention a few. Nanofibers are continuous filaments of generally less than about 1000 nm diameters. Nanofibers of a variety of cellulose and non-cellulose based materials can be produced by a variety of techniques such as phase separation, self assembly, drawing, melt fibrillation, template synthesis, electro-spinning, and solution spinning. They reduce the handling problems mostly associated with the nanoparticles. Nanoparticles can agglomerate and form clusters, whereas nanofibers form a mesh that stays intact even after regeneration. The present book is a result of contributions of experts from international scientific community working in different areas and types of nanofibers. The book thoroughly covers latest topics on different varieties of nanofibers. It provides an up-to-date insightful coverage to the synthesis, characterization, functional properties and potential device applications of nanofibers in specialized areas. We hope that this book will prove to be timely and thought provoking and will serve as a valuable reference for researchers working in different areas of nanofibers. Special thanks goes to the authors for their valuable contributions.

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