Electrospinning-derived nanofibrous mats for dual-layer sports textile

Dong, Yuliang

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NANYANG
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**ELECTROSPINNING-DERIVED NANOFIBROUS MATS FOR
DUAL-LAYER SPORTS TEXTILE**

DONG YULIANG

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2017

ELECTROSPINNING-DERIVED NANOFIBROUS MATS FOR DUAL-LAYER SPORTS TEXTILE

DONG YULIANG

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2017

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

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Date

A rectangular box containing a handwritten signature in dark ink. The signature is written in a cursive style and reads "Dong Yuliang".

.....
Dong Yuliang

Abstract

Properties of textiles have great influences on the thermo-physiological and skin sensorial wear comfort of the human body. Sportswear is expected to have good moisture management property, which is key factor to achieve wear comfort. For some sports, they are also expected to have low friction with skin and antibacterial capability. To meet these demands, single-layer fabrics are utterly incompetent. Thus, model dual-layer textiles that consist of a thin hydrophobic electrospun inner layer and a thick hydrophilic electrospun outer layer are designed and fabricated to verify the possibility to simultaneously achieve dual functionalities, including good moisture transport property, with low friction with skin or good antibacterial property. The hydrophobic inner layer ensures low water absorption and transmission of sweat via capillary motion, while the hydrophilic outer layer draws the sweat out from the inner layer and facilitates evaporation to the surrounding environment.

In the PhD work presented in this thesis, electrospun nanofibrous mats are used as the model textiles because they have large specific surface area due to a lot of interpenetrating pores between the nanofibers, which could facilitate both the capillary motion and effect of surface modification and incorporation of functional materials. Also, to let the moisture transport away fast, fairly thin hydrophobic inner layers could be achieved by electrospinning because it could control the thickness accurately.

To improve the moisture transport property, the capillary motion in the textile is facilitated by decreasing the pore size or increasing the surface hydrophilicity. Dual-layer mats composed of a thick layer of hydrophilic polyacrylonitrile (PAN) nanofibers and a thin layer of hydrophobic polystyrene (PS) nanofibers with and without interpenetrating nanopores are fabricated respectively. Then the mats are coated with polydopamine (PDOPA) to different extents to tailor the water wettability of the PS layer. It is found that with a large quantity of nanochannels, the porous PS nanofibers exhibit a stronger capillary effect than the solid PS nanofibers. The capillary motion in the porous PS

nanofibers can be further enhanced by slight surface modification with PDOPA while retaining the large hydrophilicity difference between the two layers, inducing a strong push-pull effect to transport water from the PS to the PAN layer.

To lower the friction between the textile and skin, both of the hydration of the skin and the chemical component of textiles are modified. Core-shell nanofibers with a PAN-rich core and a poly (vinylidene fluoride) (PVDF)-rich shell are fabricated by single-spinneret electrospinning and used as the inner layer of the dual-layer mats. The dual-layer textile has good moisture transport property and the inner layer of the textile has lower friction with the skin, because the PAN in the inner layer could increase the wettability of the layer, thus improve the capillary effect, and the PVDF-rich shell could lower the friction between the textile and the skin. The synergistic combination of a considerably hydrophobic PAN/PVDF inner layer and a highly hydrophilic CA outer layer induces a strong push-pull effect, resulting in efficient moisture-wicking.

To introduce antibacterial property to the dual-layer textile, zinc oxide (ZnO) NPs were covalently attached on the surface of the ethoxysilane-functionalized cross-linked PVDF inner layer. The results of related testes show that the incorporation of the ZnO NPs could render the textile antibacterial property as well as enhance the water wettability of the inner, thus the moisture transport property of the textile is also strongly improved. Also, the ZnO NPs show very good anti-wash property due to the covalent bonding with the inner layer. Thus the potential health risk caused by the detachment of the NPs could be avoided.

In summary, the research results presented in this thesis provide effective strategies to enhance the capillary motion and moisture transport property of the textile, as well as achieve dual functionalities. The design concepts demonstrated in this PhD research can be used as model systems for development of novel multifunctional textiles in industries.

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Abbreviations

CA	cellulose acetate
EDX	Energy Dispersive X-ray Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
MMT	Moisture management tester
PAN	polyacrylonitrile
PDMS	polydimethylsiloxane
PDOPA	polydopamine
PET	polyester
PP	polypropylene
PS	polystyrene
PTFE	polytetrafluoroethylene
PVDF	poly (vinylidene fluoride)
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
UV	Ultraviolet
XPS	X-ray photoelectron spectroscopy
XRD	X-ray Diffraction
ZnO	Zinc Oxide

Chapter 1

Introduction

In this chapter, a brief introduction to the background of sports textile is presented, and then the hypothesis of this work is proposed. It is hypothesized that the electrospinning-derived dual-layer nanofibrous mats composed of a hydrophilic outer layer and a hydrophobic inner layer could effectively transport the moisture from inner layer to outer layer. This is due to the following factors: the strong push-pull power induced by the distinct surface hydrophobicity difference between the inner and outer layers, and that the moisture could pass the thin hydrophobic inner layer by capillary action within the nanoporous structure of nanofibrous fibers. Based on the double layer structure, multi-functions like low friction, antibacterial and UV-protection properties could be introduced by tailoring the electropun layers and attachment of nanoparticles. To verify the hypotheses, the objectives and scope is divided into three aspects: (1) single- and dual- layer nanofibrous mats were fabricated by electrospinning and lamination. We investigated the morphology and structure of the textiles, and correlated them to the moisture management properties; (2) in the dual-layer structure, core-shell PAN/PVDF was used as the inner layer to lower the friction as well as keep good moisture management; (3) in the dual-layer structure, ZnO/PVDF is used as the inner layer to render the dual-layer fabric antibacterial property as well as keep good moisture management. Finally, the novel achievements of this research work are summarized.

1.1 Background and problem statement

Sports textile is one of the branches of technical textile, and is designed and fabricated to meet the specific requirements for the sports activities. A wide range of woven, knitted and nonwoven fabrics are commercially available for sportswear.¹ Nowadays more and more people would like to wear sportswear as casual fashion clothing because it is more comfortable, and the crossover between sport and leisure is hence blurred.² Driven by this trend, the sports textile market is expanding very fast, and an increasing number of producers and researchers are focus on improving the wear comfort of the sports textiles.³ Moisture management, which is defined as the capability of a textile to transport the moisture away from skin to outer surface of the textile, is one of the most important factors to achieve wear comfort,⁴⁻⁶ because it could primarily influence both thermo-physiological comfort and skin sensorial wear comfort of the wearers,^{7, 8} especially for the people live in tropical countries. Since both the temperature and humidity in tropical countries are quite high, the residents will suffer excessive perspiration. If the sweat cannot be transported away from skin and evaporated to the environment in time, the thermal regulation of the body will be broken up, and the excessive heat accumulated may cause heat stress and affect sports performance. Also, the touch with saturated textile will annoy the wearers.

The mechanism of the moisture transport in the textile is very similar to the wicking of the liquid in capillaries. The capillary motion of the sweat in textile is induced by the intermolecular interactions between the fiber surface and sweat, and it depends on the diameter of capillary and the surface energy of the - textile.⁴⁻⁶ Thus for the natural hydrophilic fibers, such as cotton and wool, which have a high surface energy, capillary effect is stronger. However, since the moisture release property of these fibers is very poor, the capillary motion will stop when all the parts of the textile are equally wet, and the moisture is apt to stay inside the textiles. Therefore, in industry, single-layer textiles consisting of synthetic hydrophobic fibers, such as polyester and polypropylene (PP) are widely used in commercial sportswear owing to their good moisture release capability.⁹ To further enhance the moisture management capability, the hydrophilization

of hydrophobic fibers via surface modification to improve the capillary motion is an effective strategy. For instance, Masuduzet al.¹⁰ modified the surface of polyester textile by applying a hydrophilic surface finishing agent that contains nanocrystalline cellulose, leading to improved water wettability. The enhancement of the water wettability of PP fibers by surface adsorption of different soybean proteins has also been reported.¹¹

The single layer textile could not have rapid capillary motion as well as good water release ability at the same time, and the capillary motion will stop when all the parts of the textile are equally wet. To provide a drier micro-climate gap between skin and textile, the dual-side textiles are fabricated from a hydrophobic inner layer and a hydrophilic outer layer by weaving, wrap or circle knitting technologies.¹² In the dual-side textiles, the sweat could transport through the hydrophobic inner layer to the hydrophilic outer layer by the force induced from the large hydrophobicity difference between the two layers, which is defined as push-pull effect.¹² The comparison of single layer and dual-layer textiles is shown in Figure.1.1. However, in related studies, the hydrophobic inner side of the dual-side textiles has not been modified, because the two sides of the textiles are fabricated together, which will affect the speed of capillary motion. It is expected that by further reducing capillary diameter and modifying the surface of the capillary, the sweat could be transported away from the inner layer to the outer layer much faster instead of accumulating between the skin and the inner layer.

Figure 3.1 The schematic demonstration of the comparison of single layer and dual-layer textiles.

Another issue related to the skin sensorial wear comfort is the friction between the textile and the skin of wearers. When a person is playing sports, the inner surface of the sportswear may slide over his/her skin, inducing friction, and usually, the easy gliding textiles with low friction and minimum skin deformation is preferred due to the enhanced skin sensorial wear comfort and reduced skin irritation.¹³ For example, for sock fabrics that come in direct contact with the foot, friction between skin and sock due to cyclic relative movements can cause friction blisters.¹⁴ Since fluoropolymers have very low coefficients of friction due to their low surface energy, researchers have already fabricated the fluoropolymers contained socks to reduce the friction.^{15, 16} However, the friction between the textiles and skin will increase very fast when the surface gets wet, and not only the friction between sock fabric and feet should be took into consider, the friction between the cloth textile and skin should also be reduced. However, usually the fluoropolymers are quite hydrophobic, which will reduce the speed of capillary motion.¹⁷ Thus, how to keep good moisture management property as well as reduce the friction between the skin and the textile should be studied.

The antibacterial property of the sports textile is also an important issue. The sports textile in contact with skin is a very good substrate for the growth of micro-organisms, due to the moisture, heat and secretion induced from the increasing of metabolism during sports.¹⁸⁻¹⁹ Although a broad range of micro-organisms coexists in a natural equilibrium with human body and living environments, a rapid and uncontrolled fast thriving of microbes can lead to some serious problems, including the degradation phenomena of the fibers, unpleasant odor and the increase of potential health risks.¹⁸⁻²¹ To render the textile antibacterial property, nanoparticles like Zinc oxide (ZnO) and silver have been loaded into the fabric during weaving, or attached directly onto the surface of the fabric.²²⁻²⁶ However, since the NPs have larger specific surface and higher reactivity, they may bring some potential health risk with human exposure. Skin exposure to NPs may cause the going through of the NPs into the stratum cornea. It is reported that the NPs could move in the human body, go through the cell membranes and damage the genetic material.^{27, 28} Thus, on one hand, compared with loading the NPs inside the fabric, the

direct touch between the NPs and the bacteria may provide more efficient antibacterial property; on the other hand, the fastness of the attachment of the NPs must be strong enough if the NPs are located on the surface of the fabrics and exposed out.

1.2 Hypotheses

To address the aforementioned issues, three new designs have been put forward in this thesis work, as elaborated in the subsections below. To test these design concepts, model textiles are fabricated by electrospinning, which is a popular technique used to convert polymer bulk materials into polymer nanofibers.²⁷⁻²⁹ Electrospun nanofibers are chosen because they have large specific surface area due to a lot of interpenetrating pores between the nanofibers, which could facilitate both the capillary motion and effect of surface modification and incorporation of functional materials. Also, to let the moisture transport away fast, fairly thin hydrophobic inner layers could be achieved by electrospinning because it could control the thickness accurately.³⁰⁻³² The concept of the design could be extended on textiles made of microfibers.

1.2.1 Design 1: Moisture wicking by enhancing capillary action

Compared with single-layer textiles, dual-layer textiles have great potential to achieve better moisture transport properties because the components and structures of the two layers can be tailored independently. In this work, we hypothesized that the moisture wicking capability of dual-layer textiles can be greatly enhanced by reducing the diameter of the capillary and modification of the surface of the capillary. As shown in Figure 1.1, in the new design tested in this study, dual-layer moisture-wicking textiles are composed of a hydrophilic electrospun outer layer and a hydrophobic electrospun inner layer. In this design, the hydrophobic inner layer ensures low water absorption and transmission of sweat via capillary motion, while the hydrophilic outer layer draws the sweat out from the inner layer and facilitates evaporation to the surrounding environment. So far, the capillary motion in the inner layer of the dual-layer system has not been

studied. Theoretically, capillary motion of the inner layer can be controlled by tailoring the size of interpenetrating pores and water wettability of the textiles.⁴⁻⁶ The smaller the pore size and the better the wettability, the stronger the capillary effect. Thus, the electrospun porous nanofibers are used as inner layer in our design to reduce the pore size, and the nanofibers are modified to increase the pore surface hydrophilicity, which can also facilitate the capillary motion. The scheme of the design is shown in Figure 1.2. In chapter 4, the related verification results will be presented and discussed.

Figure 4.2 The schematic demonstration of the dual-layer electrospun mats with hydrophobic porous PS as inner layer and hydrophilic PAN as outer layer.

1.2.2 Design 2: Dual functionalities - Moisture wicking and low friction with the skin

The friction between the textile and the skin is influenced by both the hydration of the skin and the surface properties of textiles. Some works on changing the chemical structures of the textiles are already published.^{15, 16} In the new design proposed in this study, the issues of the hydration of the skin and the surface properties of textiles are addressed simultaneously. Specifically, core-shell nanofibers with a polyacrylonitrile (PAN)-rich core and a poly (vinylidene fluoride) (PVDF)-rich shell are fabricated by single-spinneret electrospinning and used as the inner layer of the dual-layer mats. The

PAN in the inner layer could increase the wettability of the layer, thus improve the capillary effect, and the PVDF-rich shell could lower the friction between the textile and the skin. To further decrease the hydration of skin, the core-shell nanofibers are combined with a piece of thick base-treated Cellulose Acetate nanofibrous mats, which could facilitate the moisture transport by push-pull effect. Therefore, in the dual-layer structure, the inner layer could provide a drier environment between skin and textile to lower the friction, and from the chemical point of view, compared with other polymers, the PVDF-rich shell has a lower coefficient of friction with skin. The scheme of the design is shown in Figure 1.3. In chapter 5, the related verification results for this design will be discussed.

Figure 1.3 The schematic demonstration of the dual-layer electrospun mats with PAN-PVDF core-shell nanofibers as inner layer and hydrophilic cellulose as outer layer.

1.2.3 Design 3: Dual functionalities - Moisture wicking and antibacterial property

To render the textile antibacterial property, a new type of antibacterial dual-layer textile is also proposed in this study, in which ZnO nanoparticles are covalently incorporated onto the inner layer by sol-gel reaction. Compared with other studies,²⁴⁻²⁶ the sol-gel reaction is simple and effective, and the cost of raw materials and equipment is low. The size and shape of the ZnO nanoparticles which could directly influence the antibacterial

property also could be accurately controlled in the sol-gel reaction. Since the ZnO nanoparticles are covalently attached, the anti-wash property of them is good and the potential risk induced by the nanoparticles inside the skin could be reduced. Also, the drier environment between skin and textile provided by the dual-layer structure could lower the speed of accumulation of microbes. The scheme of the design is shown in Figure 1.3. In chapter 6, the related verification results for the design will be presented and discussed.

Figure 1.4 The scheme of the dual-layer electrospun mats with ZnO-bonded PVDF as inner layer and hydrophilic PAN as outer layer.

1.3 Objectives

The PhD work presented in this thesis is focused on design and fabrication of electrospun dual-layer mats with improved moisture wicking, and antimicrobial properties and low friction. The objectives include the following:

1. The first objective is to correlate moisture transport properties of nanofibers with their chemical components and surface morphologies, investigate the underlying mechanism

of moisture management, as well as verify if the porous nanofibers can truly enhance the capillary effect.

2. The second objective is to demonstrate the proof-of-concept that the textiles with proper core-shell morphology are capable of achieving low friction with skin as well as good moisture transport property.

3. The third objective is to verify that zinc oxide (ZnO) nanoparticles could be covalently introduced into dual-layer system as an effective and durable anti-bacterial agent without sacrificing the good moisture transport property.

1.4 Dissertation overview

Chapter 1 briefly introduces background and problem statement of the sports textile, and then proposes the hypothesis of the study, followed with the objectives of the study.

Chapter 2 reviews the literature concerning the requirements of textile, such as the moisture management, friction, and antibacterial property and UV protection. The potential and limitation of electrospun nonwoven mats compared with conventional fabric are discussed.

Chapter 3 discusses the mechanism of the basic experimental methods including electrospinning, lamination, materials synthesis, and characterization techniques including SEM, TEM, XRD, FTIR, and XPS. Also, the moisture management related experiments including moisture management test, contact angle test and water absorption test, and the measurement of friction and antibacterial property are introduced.

Chapter 4 firstly investigates the moisture transport related property, including the moisture management, contact angle, water absorption and dry rate of single and dual-layer electrospun nonwoven mats, and then discusses hydrophilicity of the mats surface after modification, and its influence on capillary motion in the hydrophobic layer and

moisture transport properties of the dual-layer mats.

Chapter 5 discussed the fabrication of PAN/PVDF blend electrospun nanofibers with core-shell structure, and compares the friction of pure PAN, pure PVDF and core-shell PAN/PVDF electrospun nanofibers. Then combines the core-shell nanofibers with hydrophilic base treated cellulose acetate electropun mats, and investigates its influence on moisture transport properties.

Chapter 6 investigates the fabrication of ZnO nanoparticles incorporated PVDF electrospun mats, and then discusses the morphology, antibacterial property and anti-wash property of the mats. Then combines the ZnO NPs incorporated PVDF electrospun mats with hydrophilic PAN electropun mats, and investigates its influence on moisture transport properties and antibacterial property.

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Chapter 7 summarizes the results mentioned in Chapter 4, 5 and 6, and draws the study together. Then verifies the original hypothesis of the thesis by the results, and proposes the direction of future research.

1.5 Major findings and outcomes

1. For the first time, PAN/porous PS dual-layer electrospun nanofibrous mats were designed and fabricated. It is found that the capillary motion in the nanofibers could be strongly enhanced by the large quantity of inter-penetrating nanochannels with size of less than 100 nm created on the nanofibers. Through tailoring the structures and morphologies of the inner layer of the mats, the significant enhancement of the push-pull effect, which leads to good moisture property, is demonstrated.

2. Using core-shell nanofibers with a PAN-rich core and a PVDF-rich shell, the proof-of-concept of multifunctional textile with low friction and good moisture transport properties is demonstrated.

3. The concept of dual-functional textile with antibacterial property and good moisture transport properties is verified. As the antibacterial agent, the covalently bonded ZnO nanoparticles are proved to be effective and durable.

These research findings provide effective strategies to enhance the capillary motion and moisture transport property of the textile, as well as achieve dual functionalities. The design concepts demonstrated in this PhD research can be used as model systems for development of novel multifunctional textiles in industries.

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Chapter 2

Literature Review

In this chapter, the market trend for sports textile is reviewed firstly, and then some specific requirements for the sports textile, including good moisture management, low friction and good antibacterial capability are introduced. In the following section, detailed research approaches, including tailoring the chemical components of the textiles, surface modification of the textiles, design of dual-side textiles and the introduction of fluoropolymers and antibacterial agents to the textiles are reviewed to address the above requirements. The multi-functional textiles which can meet more than one requirement are also introduced. Following that, conventional fabric and fabric made from microfibers and nanofibers are compared, and the potential and limitation of fabrics made from micro- and nano-fibers are discussed. Meanwhile, the challenges in the area of sports textile that remain are summarized. Finally, why the nanofibrous mats are used in the PhD study as the model system is explained.

2.1 Key requirements for sports textiles

In 21st century, the global market of sports clothing is expanding very fast and is projected to reach 196.2 billion US Dollars by 2020. On one hand, as shown in Figure 2.1,¹ the market is driven by the increase of participation, especially the female participation in sports and fitness activities due to the growing focus on healthy lifestyles in both developing and developed countries. On the other hand, in the modern society, the crossover between sport and leisure is blurred. For example, according to Cotton Incorporated's 2014 Sports Apparel Survey, more than 9 in 10 consumers say they wear athletic wear for activities other than exercise, and increased consumer demand has prompted U.S athletic apparel sales to grow at double the rate of non-active apparel sales for several years.² Thus, there are growing numbers of researchers and industries engaged in the developing market focus on studying and improving the sports textile to meet the increasingly demanding expectations of the customers and attract the buyers who are willing to pay more money on the sports clothing to enjoy the sports and leisure activities.

Figure 2.1 The global market of sports clothing¹.

Among all the requirements on sports textiles, the wear comfort of sportswear is surely the most important criterion and a major sales aspect.³ In fact, in a survey by Cotton Incorporated, 73% of consumers who usually wear active apparel for purposes other than exercise say comfort is the reason. Comfort could be defined as a pleasant state of physiological, psychological, neurophysiologic and physical harmony between a human being and the environment.⁴ For the sports textiles, they should meet both the thermo physiological wear comfort, which directly influences the thermoregulation of the wearer, and the skin sensorial wear comfort, which are related to the feeling of the textiles in

touch with the wearer's skin.⁵⁻⁷ Therefore, the moisture management property of the sports textile, which can directly both effect the thermoregulation of the body and the feeling of the touch between the textile and the skin, is of the most importance, and the low friction, which could also influence the skin sensorial wear comfort, is also an critical requirement of the sport textiles. Due to the continuously increasing awareness of health, the antibacterial property also have called more attention of the producers and customers.^{8,9}

2.2 Moisture management of sports textiles

As mentioned above, nowadays, with the rising living standards, the most important property of the sports textile is wear comfort, specifically moisture management property, which is defined as the capability of a textile to transport the moisture away from skin to outer surface of the textile, is the key factor to achieve wear comfort.¹⁰

Firstly, the moisture management property can directly influence the thermo-physiological comfort of the wearers. Usually, to reach thermo-physiological comfort, the temperature of the body should be kept at around 37 °C, and during exercise and other activities, the temperature of human body will rise and more heat energy is created due to the increasing of metabolism. Then, to reduce the body temperature, the heat is transported away from body to the environment by conduction, convection, radiation and perspiration. Therefore, the moisture management property of the textile, and the coupled heat and moisture transport have gained more and more attention in the textile market.¹¹

Secondly, the moisture transport could also affect the skin sensorial wear comfort. If the sweat cannot be transported away and accumulates on the skin and the inner side of the textile, the feeling of wetness of skin and the touch between skin and wet inner side of textile will make the wearers very uncomfortable.^{12, 13}

Thirdly, cutaneous health is also affected by the wetness of skin. If the textile next to the skin acts as an obstacle of moisture management, as the wetness of the skin increases, the

skin becomes more susceptible to abrasive damage, permeability by chemicals and microbial growth.¹⁴ Therefore, the moisture management is always the most critical issue for the sports textile, especially for the people living in topical countries. Since both the temperature and humidity in the countries are quite high, people suffer excessive perspiration and more heat energy and sweat need to be transported away from the skin quickly.

The mechanism of the moisture transport in the textile is very similar to the wicking of the liquid in capillaries.¹⁵ The capillary motion of the textile is induced by the intermolecular interactions between the fiber surface and sweat, and the capillary pressure is determined by the interfacial tension, the effective radius of the interface and the wetting angle of the liquid on the surface of the capillary. The smaller the radius or the larger interfacial tension, the greater tendency of the liquid to move up the capillary, and the motion will stop when all the parts of the textile are equally wet. Thus, the moisture management property is primarily determined by the chemical structure of the fibers. Usually, the hydrophilic fibers, including the natural fibers such as cotton, have a high surface energy (around 45mN/m),¹⁶ therefore the capillary effect for the textiles is stronger. While the synthetic polymers such as polypropylene is hydrophobic, have a low surface energy (around 30mN/m), therefore the capillary effect for the textiles is very weak.¹⁷ Since the surface tension of water (around 71×10^{-3} N/m at room temperature) and sweat (around 70×10^{-3} N/m at room temperature¹⁸) is quite close, the difference between the water and sweat is ignored in the discussion. However, there are many bonding sites for water molecules on the surface of hydrophilic fibers, which make the sweat stay on the fibers and the water release property of such textile is very bad. But for the hydrophobic fibers, there is few bonding sites for water molecules on the surface of the fibers, thus the sweat will not stay on the fibers, which render the fibers good water release property.¹⁸⁻²⁰ As discussed above, neither the natural hydrophilic fibers nor the synthetic hydrophobic fibers could have strong water absorption as well as good water release property at the same time. For very slight sports activities, the natural hydrophilic fibers are preferred due to their good skin sensorial wear comfort;^{21, 22} while for heavy sports activities, the synthetic hydrophobic fibers are preferred due to their good water release property.^{23, 24}

2.2.1 Tailoring the chemical components of the textiles

To further enhance the wicking ability of the textiles, some hydrophobic fibers are blended with hydrophilic fibers to improve the water absorption property of the textiles. For example, some researchers⁹ spun profiled polyester fibers and nature cotton fibers together at different blend ratios to yield composite yarn and then tested the water absorption property and drying rate of the composite yarns, and pointed out that for certain ratio of cotton and polyester and proper yarn type, the composite yarns have good water absorption (with a absorbed water height of 230 mm) and release (with a remaining water ration of 0.57%) properties. Also, Cotton and Angora rabbit fiber were blended by Oglakcioglu²⁵ to improve the thermal balance property of the textile, It is known that cotton fiber has good comfort properties and Angora rabbit fiber is a special fur fiber which possesses good softness, whiteness and warmth. The aim of this study was to combine the excellent characteristics of these fibers to produce knitted fabrics with better comfort properties. The results indicated that the increase of Angora fiber ratio in the fabric and the spinning system affected the thermal comfort properties. The statistical analyses showed that only the fabrics including 25 % of rabbit fiber generated a significant difference on these parameters. And Spandex was blended with cotton or polyester to improve the moisture management property the textile.²⁶

2.2.2 Surface modification of the textiles

Tailoring the hydrophobic fibers and making them more hydrophilic via surface modification is another effective strategy to improve the water transport. For instance, Masuduzetal²⁷ modified the surface of polyester textile by applying a hydrophilic surface finishing agent that contains nanocrystalline cellulose, leading to improved water wettability (the contact angle reduces from 132° to 42°). The enhancement of the water wettability of PP fibers by surface adsorption of different soybean proteins has also been

reported. A shift in the contact angle from 128° to completely wettable surfaces ($\approx 0^\circ$) is observed and confirmed by imaging experiments conducted with fluorescence tags. Furthermore, the results from wicking tests indicate that hydrophobic PP nonwovens absorb a significant amount of water after protein treatment, i.e., the PP-modified surfaces become completely hydrophilic.²⁸ Also, tailoring the hydrophilic fibers more hydrophobic via surface modification is used by some researchers. For example, the water absorption capability reduction of cotton can be achieved by chemical treatments. Resins, such as common wrinkle resist type chemistries, can reduce the water absorption capability of cotton on the order of 15-20% or more. Resins reduce the amount of water held inside the fiber, thus better water transport property is achieved.¹³

2.2.3 Design of dual-side textiles

Many strategies to modify a single layer of natural hydrophilic fibers or synthetic hydrophobic fibers have been mentioned above, and there are some researchers trying to improve the moisture management property by fabricating dual-side textile. Usually, the dual-side textiles are fabricated from a hydrophobic inner layer and a hydrophilic outer layer by weaving, wrap or circle knitting technologies,²⁹ and the sweat could transport through the hydrophobic inner layer to the hydrophilic outer layer by the force induced from the large hydrophobicity difference (the sweat will be pulled from the hydrophobic layer to the hydrophilic layer if the two layers have very different hydrophobicity) between the two layers, which is defined as push-pull effect.²⁸ Since the inner hydrophobic layer could prevent or reduce the accumulation of sweat on the skin, the micro-climate gap between skin and textile could allow sweat to evaporate and make the skin feel drier and cooler.³⁰ For example, double face fabrics composed of cotton and PP layers were produced on circular knitting machine, and it is proved that the double face composed of a cotton layer as outer face and a PP layer as inner face could successfully transport the water away to the outer face.³¹ Also, Troynikov³² produced double face fabric composed of wool and polyester or bamboo using circular knitting machine. And compared with wool fabric, the double face fabric could decrease the wetting time more than 80% and the moisture can spread in the double face fabric several times faster than in the wool fabric. Thus the improved

moisture management property was verified.

A typical method to fabricate a dual-side textile is introduced as below. The first step in the method is to knit a three dimensional knit fabric which has a first fabric layer, a second fabric layer and a plurality of yarns that interconnect the two layers. The three dimensional knit fabric is prepared using a conventional double needle bar warp knitting machine. Then, the yarn connecting the two layers is cut, resulting in two pieces of fabric having a velvet surface on one side, and a flat knit surface on the other. The flat knit surface is then raised by a conventional process such as napping, in order to form a pair of double face fabrics, each with a first velvet surface and a second fleece surface. In another method to fabricate the dual-side textile, people need to prepare two different yarns and a knot yarn, and then produce the textile by simultaneously weaving the two yarns, and linking them with knot yarn. Thus, the fabrication of dual-side jacquard textile is complicated, and how to make sure the well assignment of outer and inner lay weaves and well match of outer and inner lay yarns are still under research. It is also noted that the two layers are fairly thick due to the fabrication process, therefore the inner layer could not be fairly hydrophobic to make sure the moisture could pass through the inner layer, thus the push-pull effect will be weakened by the smaller hydrophobicity difference of the two layers. Following the design concept of dual-face textile, if the two layers could be made of electrospinning nanofibers with large specific surface area, which could facilitate both the capillary motion and effect of surface modification and incorporation of functional materials, the dual layers textile may have much better moisture transport property and other desired functions (such as low friction with skin, antibacterial and anti-UV property).

2.3 Friction between skin and textile

2.3.1 The friction between skin and textile and the friction tester

The friction between skin and the textile also directly influence the skin sensorial wear comfort. The friction is generated when the textile slide over skin, and usually, the easy

gliding textiles with lower friction is preferred due to the enhanced skin sensorial wear comfort and reduced skin irritation.³³ For example, for sock fabrics that come in direct contact with the foot, friction between skin and sock due to cyclic relative movements can cause friction blisters.³⁴ The friction is defined as the force, or resistance, experienced along the tangent of the common boundary between two sides when they move, or tend to move, relative to each other.^{35, 36} If the two sides are dry, the force of the friction is composed of the adhesion at the interface and the deformation of the softer side as the harder side passes over it, and can be expressed as:

$$F_{\text{friction}} = F_{\text{adhesion}} + F_{\text{deformation}}^{35}$$

And the coefficient (μ) is defined as the ration of tangential force of friction (F) to the normal force (N) pressing the body together, which can be shown as:

$$\mu = F/N$$

According to the studies, the skin with lower hydration has lower friction coefficient, and with the increase of the amount of sweat on the skin, the friction on skin also rises (the friction between wet skin and socks (48 AU) could be three times higher than that of dry skin and socks (16 AU))³⁷, which could also verify the importance of moisture management of the textile.³⁸

Usually, in the experiments, the friction in the dry environment is tested and studied. The material of the textile, as well as the surface roughness of the skin, the hydration and other conditions could directly influence the friction coefficient.³⁹⁻⁴¹ A typical friction tester is shown as Figure.2.2.

Figure 2.2 Principle of the textile friction analyzer.

As shown in Table.2-1, some researchers have reported that⁴², compared with bamboo viscose, cotton and polyester (PET), Polytetrafluoroethylene (PTFE) shows lower friction coefficient due to the lower surface energy which may influence the adhesion between the material and the skin. As shown in the Table 2.1, the friction coefficient is almost age independent and gender independent, and the mean friction coefficient of all textiles are significantly different from each other. The PTFE shows much lower friction coefficient than other textiles.

Table2.1 Friction coefficients of Bamboo viscose, PTFE and Cotton/PET.⁴²

Group and sub-group	Friction coefficients of		
	Bamboo viscose	PTFE	Cotton (50%) PET (50%)
Young	0.38±0.03	0.29±0.03	0.43±0.04
Aged	0.37±0.05	0.30±0.05	0.43±0.05

Female	0.38±0.04	0.29±0.04	0.43±0.04
Male	0.38±0.04	0.30±0.04	0.42±0.04
Female/young	0.38±0.04	0.30±0.04	0.43±0.04
Female/aged	0.37±0.04	0.30±0.05	0.43±0.04
Male/young	0.38±0.03	0.29±0.02	0.42±0.03
Male/aged	0.38±0.05	0.31±0.05	0.42±0.04
All	0.38±0.04	0.30±0.004	0.43±0.03

2.3.2 The use of fluoropolymers to reduce the friction

PTFE shows lower friction with skin due to the lower surface energy, and for the same reason, usually fluoropolymers have very low coefficients of friction and low adhesion to most substances.⁴³⁻⁴⁴ Surface energy is the fundamental parameter determining the tribological properties, including coefficient of friction of a material. The effect of the surface energy on the coefficient of friction can be explained by the formation and breakage of the adhesive bonds between the rubbing surfaces. When a surface is rubbed by another surface, some micro- or nano-junctions may be formed between the opposing asperities on the contacting surfaces. When the load applied to the contacting asperities is high enough, they deform into each other, creating adhesive bonds. When the bonds break, portions of the material are transferred to the counter surface. This process involves disappearance of a portion of the interfacial surface and creation of a new surface.⁴⁵⁻⁴⁷ Thus lower surface energy reduces the energy consumed in the friction process, leading to lower coefficient of friction. Furthermore, some fluoropolymers could form a low-friction surface layer on by themselves. PTFE chains, for instance, can be drawn out to form an extended chain crystal structure on the surface, which results in low shear and hence low friction.⁴⁸

Thus, fluoropolymers, either in semi-crystalline or fully amorphous nature, have been widely used for various lubrication applications such as O-rings and lubricants.⁴⁹ For

example, Bertaux⁵⁰ investigated the friction of socks made of different types of fibers, and found that the socks containing PTFE have lower friction and are more comfortable. Indeed, Frederick⁵¹ fabricated double layer sock made of conventional garment material and fluoropolymer material, and the layer to layer interface embodies a low coefficient of friction that enables the different layers to easily move relatively against each another. Simone Cazzaniga⁵² also pointed out that fluorine-synthetic fiber socks are more comfortable and healthy.

However, to lower the friction between the skin and the textile, both the chemical structure of the textile and the hydration of the skin should be considered. Since usually the fluoropolymers are quite hydrophobic, the introduction of fluoropolymers will reduce the capillary motion, thus will affect the water management property of the textile. Therefore, how to achieve lower friction between the skin and textile as well as keep good moisture management property of the textile should be studied.

2.4 Antibacterial property of textiles

Nowadays customers and producers are paying more attention to the antibacterial property of textile due to rapid increasing of hygienic awareness.⁵³⁻⁵⁴ Usually, the sports textile in contact with skin is a very good substrate for the growth of micro-organisms, due to the moisture and heat induced from the increasing of metabolism during sports, especially for the people live in tropical countries, who will suffer excessive perspiration. Although a broad range of micro-organisms lives in the human body, a rapid increase of microbes will result in many serious issues.⁵⁵⁻⁵⁶ For example, the increasing number of microbes could accumulate on the textile and stain the cloth, foster the degradation of fibers, which will increase the cost of life (people need to buy more cloth), and release unpleasant odor. Also, the contact between skin and a large amount of micro-organisms may increase the potential health risk.⁵⁷

2.4.1 The antibacterial agents

The conventional textiles do not have any antibacterial property, and the wearers are faced with innumerable bacterial during sports activities.⁵⁸ In the last decades, controlling of the serious problems caused by the uncontrolled growth of bacterial has attracted the attention of public and an increasing number of researchers. They have focused on the anti-bacterial modification of textiles and many related papers are published.⁵⁹ As the antibacterial agent, the nano-structured materials are preferred due to their higher surface-to-volume ratio.⁶⁰

Among all the above nano-structured materials, Zinc Oxide (ZnO) nanoparticles are one of the most important ones due to its multifunctional properties and low cost. As a wide-band-gap n-type semiconductor, ZnO nanoparticles could be used for photocatalytic material, antibacterial agent, solar cells, mechanical actuators and piezoelectric sensors. Although many people have investigated the antibacterial mechanism of ZnO nanoparticles, it is still not quite clear now. Some people believe that ZnO nanoparticles could release zinc ion⁶¹⁻⁶³ or reactive oxygen⁶⁴ to kill the bacteria and it is also reported that the ZnO nanoparticles could mechanically destruct the cell membrane of bacterial.⁶⁵ Besides ZnO, silver is another popular antibacterial agent, because silver nanoparticles can effectively destroy a broad spectrum of Gram-negative and Gram-positive bacteria and are active against strains resistant to antibiotics.⁶⁶⁻⁶⁸ Compared with other antibacterial agents, ZnO is biocompatible and nontoxic to humans. And even at neutral pH, ZnO displays antimicrobial activity.⁶⁹

2.4.2 The introduction of the antibacterial nanoparticles

Since the antibacterial property of the nanoparticles is depend on the shape and size of particles, which are determined by the preparation route, there are so many routes have been reported on the introduction of antibacterial nanoparticles to the textiles. For example, Meilert et al⁷⁰ attached TiO₂ nanoparticles on the textile with the help of polycarboxylic acids, and the SEM pictures confirmed the immobilization of the nanoparticles on the fabric surface that remain after 10 washing cycles; Plasma treatment was

used to introduce active groups to the surface to be attached with TiO₂ nanoparticles, and the results showed that increasing the amount of nano TiO₂ leads to improved degradation of stains on the treated fabric.;⁷¹ Wang et al.⁷² grafted nanoparticles on wool by argon plasma, and the results showed that antibacterial activity increased with the increasing concentration of the composite antibacterial agent and the antibacterial wool fibers grafted 4.3% of composite antibacterial agent was highly effective in killing test bacteria; Yuranova et al.⁷³ attached nanoparticles on the surface with was treated by plasma firstly, and by elemental analysis it was found that levels of Ag loading > 0.118% (w/w) for the vacuum-UV samples lead to complete inhibition of bacterial growth; Won et al.⁷⁴ introduced nanoparticles in the polymeric matrix by reducing corresponding salts under UV light, and then it could be used as optically, electrically and magnetically functional materials..

Compared with the above methods, the introduction of ZnO nanoparticles by sol-gel reaction is simple and effective. The cost of raw materials and equipment is low, and the reaction temperature is low (could be lower than 100° C). The size and shape of the ZnO nanoparticles also could be accurately controlled and ZnO nanoparticles could be attached on kinds of substrates. However, since the nanoparticles have larger specific surface and higher reactivity, they may bring some potential health risk with human exposure. Skin exposure to nanoparticles may cause the nanoparticles into the stratum cornea. It is reported that the nanoparticles could move in the human body, go through the cell membranes and damage the genetic material.^{75, 76}

Thus, compared to loading the NPs inside the fabric, the introduction of ZnO nanoparticles by sol-gel reaction could let nanoparticles directly touch the bacteria and may provide more efficient antibacterial property; however, the durability of the attachment of the nanoparticles must be strong enough if the nanoparticles are located on the surface of the fabrics and exposed.

2.5 Multi-functional textiles

Another trend of the sports textile is combining more than one function on one textile to fabricate multi-functional textile. For example, now the UV protection of the textile is another important issue for the sake of health consideration. Nowadays there are a lot of reports on the deterioration of the ozone layer of earth, and more and more people have realized that the more UV radiation reached on the earth could bring several serious unfavorable effects on the human health.⁷⁷ Since the UV radiation triggers the free radicals, the effects of long term exposure skin to the radiation from the atmosphere or working environment includes erythema, skin aging, and the risk of skin cancer. Also, the UV radiation could lead to some degrading effects to the textiles such as color fading and decrease in tensile strength.⁷⁸⁻⁷⁹

Usually, the common textiles themselves can provide the wearers some protection against the UV radiation, and the UV protection property of the common textiles is determined by the chemical structure, the yarn style, the thickness and the dyes on the fabric. However, the UV protection property of the common fabrics is poor, and additional UV protective materials should be incorporated on the fabrics. ZnO nanoparticles were incorporated into textile by Y. Chen and after treatment average transmissibility of fabrics to UVA,UVB decreased from 34.4%, 25.5% to 5.3%, 4.3%,and the UPF value of the fabrics also enhanced from original 6.2 to 24.6⁸⁰⁻⁸¹

ZnO is a well-known inorganic UV, which absorbs UV radiation via process of electron excitation called band-gap absorption, and shows no degradation under UV exposure. Since ZnO is very stable under UV exposure and is well known as a non-toxic material, it is widely used as UV filter. With the rapid development of nano-technology, the nano-size UV filters are commonly used because they are significantly more effective than traditional bulk materials due to the larger surface area to volume ratio. For example, the improvement of UV protection property of the ZnO nanoparticles attached cotton is verified by many researchers.⁸²

As mentioned before, the incorporation of ZnO can also impart the textile antibacterial property. Therefore, the ZnO is widely used as a multifunctional material to render the antibacterial property as well as UV protection property to the textile. By now, usually the multi-functional textiles are fabricated by the introduction of multifunctional materials like ZnO nanoparticles, or introduction of more than one agents together in the same substrate,⁸³⁻⁸⁵ and how to combine the good moisture transport property with antibacterial property or achieving lower friction between skin and the textile in the same textile still need to be studied.

2.6 Textiles made from microfibers and nanofibers

2.6.1 Textiles made from microfibers

Recently, the fabrics made from microfibers are investigated by various researchers to improve the wear comfort, and such fabrics are already widely used for cleaning cloth in hospital.^{86, 87} Microfibers is defined as synthetic fibers that measure less than 1 denier, and most common microfibers are made from polyester and nylon.⁸⁸ Compared with common cotton fibers, the microfibers have approximately 40 times more surface area. Therefore, the cleaning cloths made from microfibers have much better cleaning and decontamination properties than common cloth.⁸⁹⁻⁹¹

As mentioned before, since the size of empty voids between fibers is determined by the diameter of the fibers, the capillary motion of the textile depends on the diameter of capillary and the surface energy of the inside face of the textile. Thus on one hand, the microfibers with finer diameter, possess better moisture wicking, from the results of a water drop test shown as Table 2.2⁹², we can see the microdenier fibers can absorb the water faster than normal denier. Also due to the larger surface area, the water release property of the microfibers could also be better, as shown in Table 2.3⁹². On the other hand, the larger surface area render the microfibers great potential to be modified

efficiently, thus the hydrophilization of the microfibers via surface modification and the introduction of covalently bonded antibacterial and UV protection materials will be more effective.⁹³ Therefore, the fabrics made from microfibers have good potential to achieve good moisture management and better wear comfort, and is a perfect substrate to incorporate functional materials on it.

Table2.2 Results of water drop test of microdenier and normal denier.

Particular	Microdenier	Normal denier
Height of burette tip=10cm	17s	22.3s

Table2.3 Drying rate of microdenier and normal denier.

Particular	Microdenier	Normal denier
Initial drying rate (g/hm ²)	414.3	369.2

2.6.2 Textiles made from nanofibers

Compared with microfibers, the nanofibers possess finer diameters and smaller pores between the fibers. Thus nanofibers could also be used as the substrate of antimicrobial non-woven textile due to the large surface area,⁹⁴ and are suitable for wound dressing because the small pores between the nanofibers could protect the wound from bacteria.⁹⁵ Also due to the high surface to volume ratio and the fairly small pores between the nanofibers, the nanofibers are widely used in filtration and drug delivery.^{96, 97}

The nanofibers have great potential in the applications for sports textiles because of the large specific surface area and high surface area to volume ratio from interpenetrating pores both inside and between the nanofibers.⁹⁸⁻¹⁰⁰ This facilitates both the capillary motion and the efficiency of surface modification/incorporation of functional materials. However, the low mechanical strength of nanofibrous mats is usually of great concern, which makes it difficult to be applied as an exclusive freestanding support for sports textile. The fairly small thickness of the nanofibrous mat, nevertheless, offers reasonable

possibility to combine the mat with traditional fabrics to strengthen the mechanical property while maintain its own advantages. Moreover, fairly thin hydrophobic nanofibrous inner layer is preferred in order to transport moisture quickly. Thus, in my PhD study, the dual-layer nanofibrous mats are used as model systems to verify the design concepts introduced in Chapter 1.

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Chapter 3

Experimental Methodology

In this chapter, the rationale for selection of materials and synthesis of materials will be elaborated. The underlying principles of the electrospinning, self-polymerization of dopamine as well as the sol-gel reaction will be discussed to understand their functionality and feasibility for the fabrication of dual-layer electrospun nanofibrous mats as a model system in this research. Also, the moisture management test, friction coefficient test, antibacterial test and anti-wash test will be introduced to demonstrate the multi-functionality of the mats. Following this, the mechanism of the characterization techniques used in this PhD work, including scanning electron microscope, transmission electron microscope, Fourier transform infrared spectrometer, X-ray photoelectron spectroscopy and X-ray Diffraction will be introduced.

3.1 Rationale for selection of key materials

In my PhD work, polyacrylonitrile (PAN), polystyrene (PS), Cellulose Acetate (CA) and Poly (vinylidene fluoride-co-hexafluoropropene) (P(VDF-HFP), denoted as PVDF in the thesis for simplicity) were used as the main materials to fabricate the nanofibrous mats, and polydopamine (PDOPA) was used to tailor the surface hydrophilicity of the nanofibrous mats. Zinc oxide (ZnO) was used as antibacterial agent to render the textiles antibacterial property.

PAN is a commonly used textile material and is hydrophilic¹, thus PAN nanofibrous mats are chosen as the outer layer in the dual-layer system to draw the moisture out. PS is a common hydrophobic polymer with low price, and the PS electrospun nanofibers could be both porous and solid with different parameters during electrospinning.² Thus, PS nanofibrous mats are chosen as the inner hydrophobic layer. To study the mechanism of capillary effect, the water transport behavior of porous PS nanofibers and solid nanofibers are investigated and compared.

PDOPA is a mussel-inspired biomimetic polymer that could adhere to various types of material surfaces, and also widely used due to its hydrophilic, biocompatible and multifunctional groups.³ In the experiment, PDOPA is used to tailor the hydrophilicity of the PS mats because the very thin coating of PDOPA could strongly increase the hydrophilicity of the surface of the mats, and the hydrophilicity of the surface of the mats could be precisely controlled by adjusting the coating time of PDOPA.

PVDF is a hydrophobic polymer with quite low surface energy, thus it has the potential to form core-shell structure as the shell part. Also, as one of the typical fluoropolymers, PVDF has low friction with other surface.⁴ Therefore, PAN and PVDF are electrospun together to fabricate nanofibers with a core (PAN-rich) shell (PVDF-rich) structure which is used as inner layer. The PVDF-rich shell could provide lower friction and the PAN could enhance the water transport property of the blend fibers. However, since the PVDF-rich shell is hydrophobic, the water transport property of the composite mats are

very poor, thus the PAN outer layer cannot provide enough pull force to draw the moisture out and another material which is more hydrophilic and absorbent than PAN should be used as the outer layer. Therefore, CA is chosen as the outer layer. CA could be converted into cellulose gradually with the increasing of base-treated time, and cellulose is the main content of cotton, which is quite hydrophilic and absorbent. Thus, base-treated CA is used as outer layer in the study to provide enough force to draw the moisture out.

ZnO is a wide-band-gap n-type semiconductor, and widely used as an antibacterial agent mainly because its nontoxicity, biosafety and low cost.⁵⁻⁶ In my following experiments, ZnO nanoparticles will be covalently bonded on the functionalized PVDF to prevent the detachment of them.

3.2 Electrospinning method and apparatus

In our design, the model textiles are fabricated by electrospinning. I chose electrospun nanofibers because they have large specific surface area due to a lot of interpenetrating pores both inside and between the nanofibers, which could facilitate both the capillary motion and effect of surface modification and incorporation of functional materials. Also, to let the moisture transport away fast, fairly thin hydrophobic inner layers could be achieved by electrospinning because it could control the thickness accurately.⁷⁻⁹

The history of electrospinning is traced back to 1902 based on Cooley pattern and Morton. John Zeleny had reported that in 1914 he was working on treatment of liquid drop at the end of iron capillaries. During this study, he tried found a mathematical model of liquids under electrostatic forces. In the 1930s, Formhals tried to produce electrospun fibers. Although it had some disadvantages such as drying system (due to distance between nozzle and collector), he modified the device and improved it in 1940. Sir Geoffrey Ingram Taylor had generated the electro-spinning theoretical underpinning between 1964

and 1969. His research has helped to upgrade the electrospinning by modeling the hopper form which liquid drops were formed by electric field. Also his collaboration with JR Melcher led to expand the “leaky dielectric model” for conducting liquids. After that in the 1990s Reneker used high voltage to charge the polymer dispersion to produce fibers with diameter of less than 5 μm .⁸⁻⁹

The electrospinning set up and the schematic diagram are shown in Figure.3.1. The setup is usually composed of a high voltage supplier, a plastic tube with a metal needle and a collector. During electrospinning, the polymer solution was charged by the high voltage. With the increase of the intensity of the electric field, the repulsive electrostatic force increases, and the solution in the tip of tube is elongated. When the voltage reaches a critical value, the electrostatic force could overcome the surface tension of liquid, and the solution is ejected from the tip of tube to the collector. During this process, the solvent is evaporated, and the polymer could be collected as nonwoven nanofibrous mat on the collector which is grounded. In some cases, the melt polymer could be introduced into the tube instead of the polymer solution.¹⁰

Figure 3.1 The electrospinning set up and the schematic diagram.

There are many parameters including the properties of solution, the ambient parameters, and the set up parameters that could influence the process of electrospinning and the

morphology as well as other properties of the as electrospun nanofibrous mats.¹¹⁻¹³ The properties of solution, such as the viscosity, elasticity and conductivity, could be controlled by the concentration of solution, the molecular weight of the polymer and the chosen solvent. The ambient parameters including the temperature, humidity, air velocity in the chamber of the electrospinning process could also be adjusted by additional heater, dryer and other apparatus. The set up parameters, such as the voltage applied on the solution, the flow rate of the solution, the distance between the tip of the tube and the collector, could directly influence the electrospinning and should be corrected in the process of electrospinning if necessary.^{14, 15}

For high quality nonwoven nanofibrous mat, the surface of the nanofibers should be defect-free and the diameter of the nanofibers should be consistent and controllable. The diameter of the nanofibers is primarily affected by the viscosity of the polymer solution which could influence the solution jet size during the electrospinning, and for the selected polymer and solvent, the viscosity of the solution is determined by the concentration of solution. Thus, the diameter of the nanofibers could be controlled by adjusting the concentration of the solution.¹⁶⁻¹⁸ For example, in this research, PAN solutions with different concentration (6% wt, 8% wt and 10% wt) were electrospun on the aluminum foil. The morphology of the PAN nanofibers is observed by FESEM and shown in Figure 3.2. The diameter of PAN nanofibers electrospun from 6% wt solution, 8% wt solution and 10% wt solution is around 180 nm, 350nm and 650 nm respectively.

Figure 3.2 FESEM micrographs showing the morphologies of the as-spun PAN nanofibers with 6% wt solution (a), 8% wt solution (b), and 10% wt solution (c).

Also, the applied voltage, could also affect the size of the solution jet, thus could influence the diameter of the nanofibers. The defect-free surface morphology of the nanofibers is also primarily influenced by the viscosity of the polymer solution. With higher applied voltage, there are fewer beads on the surface of the nanofibers, and some researchers reduced the beads on the surface of the nanofibers by reducing the surface tension or adding some filler into the polymer solution.¹⁹⁻²¹

In the experiment, both porous and solid PS nanofibers were fabricated to compare their water transport behavior. The pore formation in the PS nanofibers is significantly determined by the environmental humidity. At high humidity, normally > 50 H%, the moisture in the surrounding air diffuses into the formed nanofibers during their solidification with the used solvent, N, N-dimethylformamide (DMF) in this case, evaporates out. The immiscibility of moisture and polymer, as well as the miscibility of moisture and DMF causes rapid phase separation, creating inter-connected nanochannels, i.e., pores. The morphology of the porous PS nanofibers is shown in Figure 3.3, and the application of the porous nanofibers will be discussed in Chapter 4.

Figure 3.3 SEM images showing the morphology (a) and cross-section (b) of porous PS nanofibers.

The core-shell nanofibers were also fabricated using a straightforward single-spinneret electrospinning. Compared with conventional electrospinning technique that used to prepared core-shell nanofibers, i.e., co-axial electrospinning, which requires strict combination of the two polymers and the corresponding solvents, the single-spinneret

electrospinning is much more simple and inexpensive. Utilizing the quite low surface energy of PVDF and induced phase separation, the PAN/PVDF solution could be fabricated into core-shell nanofibers directly without any further treatment required. The morphology of the core-shell nanofibers is shown in Figure 3.4, and the application of the core-shell nanofibers will be discussed in Chapter 5.

Figure 3.4 SEM (a) and TEM (b) image of the core-shell (PAN: PVDF=1:1) nanofibers

3.3 Synthesis of materials

3.3.1 Hydrophilic surface modification

PDOPA coating is used to tailor the hydrophilicity of the surface of the nanofibers. PDOPA adhesive coatings can be easily prepared on a wide range of substrates by self-polymerization which is driven by the oxidation of the catechol to a quinone as shown in Figure 3.5, and the catechol groups in PDA can facilitate adhesion of PDA to various types of material surfaces such as metals, oxides, semiconductors, ceramics and polymers.²²⁻²⁵ In this work, instead of normal flat solid substrates where self-polymerization only occurs on the flat surface, porous nanofibrous mat was used as the one for coating of PDOPA. Due to the large specific surface area and high porosity, the self-polymerization occurs both on the outer surface and within the inner wall of nanofibers, achieving highly hydrophilic and functionalized surface for further usage.

Figure 3.5 The polymerization of dopamine.

3.3.2 Sol-gel reaction

To render the textile antibacterial property, in our dual-layer textile design, ZnO nanoparticles are covalently incorporated onto the inner layer by sol-gel reaction. The sol-gel reaction is simple and effective, and the cost of raw materials and equipment is low. The size and shape of the ZnO nanoparticles which could directly influence the antibacterial property also could be accurately controlled in the sol-gel reaction.²⁶ Also, comparing with the approach of loading nanoparticles into the fibers, the attachment of ZnO nanoparticles on the surface of the textiles by sol-gel reaction can increase the direct contact area of the antibacterial agent with the surrounding media, providing a more efficient antibacterial function. The covalent bonding between the nanoparticles and the nanofibers can prevent the detachment of the nanoparticles, leading to a more durable antibacterial property while also overcoming the potentially harmful effect of the nanoparticles in contact with skin.²⁷⁻²⁸

To let the ZnO nanoparticles be covalently distributed in the PVDF nanofibers, the PVDF nanofibers were reacted with amine-terminated silane firstly. As nucleophiles, amines can

react with PVDF and creat C=N double bond due to the strong polarity of C-F bond. The grafted ethoxysilane groups can facilitate the incorporation of ZnO via sol-gel reaction²⁹. Zinc salts and alkali are used to prepare a sol. Thereafter, the sol evolves gradually towards the formation of a gel-like network. After the reaction, white precipitate was formed.

3.3 Lamination of the electrospun mats

Lamination is the technique for manufacturing a material in multiple layers. A laminate is usually permanently assembled by heat, pressure, welding, or adhesives. In this research, to get dual-layer nanofibrous mats, two pieces of nanofibrous mats are combined by a paper laminator (PRO BiO 320) at 70°C and rolling speed of 50 rpm. The laminator is shown in Figure 3.6. After passing through the laminator, the two pieces of mats adhere to each other and become one piece of mat, and there are no changes of the morphology of the fibrous mats after lamination.

Figure 3.6 The paper laminator (PRO BiO 320).

3.4 Moisture transport related tests

3.4.1 The water absorption test

To study the interaction between the water and the mats, the water absorption test was

conducted. In this research, the rectangle-shaped mats with area of 20 cm² were immersed in DI water for 48 hrs. Their weight was measured before and after immersion in the water. Water absorption is defined as the weight ratio of the absorbed water to the dry sample.

3.4.2 Time-dependent contact angle

The time-dependent contact angle test is another method to study the interaction between the water and the mats.^{30, 31} In the experiments, the contact angles of the PS and PAN cast films and apparent contact angles of the nanofibrous mats were measured using a contact angle tester (Analytical Technologies, FTA32) via drop shape (6 μ m DI water) analysis as shown in Figure 3.7.

Figure 3.7 The contact angle tester.

The contact angle of the nanofibrous mat is recorded every second to investigate the hydrophilicity and the water transport behavior of the mats. A typical time-dependent contact angle result is shown in Figure 3.8. It can be seen that after 1 second, about half of the droplet penetrated into the mat, and after 4 seconds, the whole droplet penetrated into the mat, and the mat shows very fast moisture transport.

Figure 3.8 The time-dependent contact angle of PAN nanofibrous mat.

3.4.3 Moisture management tester

Fabric liquid moisture transport properties in multi-dimensions, so called moisture management properties influences the human perception of moisture sensations significantly. In this research, moisture transport behaviors of the mats were characterized using a Moisture Management Tester (MMT, SDLATLAS).

Moisture Management Tester (MMT) is an instrument to measure the dynamic liquid transport properties of textiles such as knitted and woven fabrics. In order to simulate sweating, a special solution was prepared, by using one liter of distilled water and approximately 9 g of sodium chloride to achieve 0.2 mS of solution conductivity, and dropped onto the fabric's top surface. During the test, the same quantity of solution (0.15 g) was applied onto each specimen's top surface automatically by the instrument. The test liquid is dropped from the top part of the instrument to the top surface of the fabric, which is designed as an inner surface that will be in touch with the human skin. When moisture is transported in the test fabric, the contact electrical resistance of the fabric changes. Usually, the electrical resistance of dry textiles is very large when placed in a closed circuit. When a fabric is wet or contains a certain quantity of moisture, the resistance will be reduced. In MMT, the resistance of a fabric sample could be measured on two surfaces of the fabric with sensors. The resistance depends on two factors: the composition of the liquid and the liquid content of the fabric.³² When the liquid composition is fixed with synthetic sweat the measured electrical resistance is only dependent on the water content of the fabric. Thus the water contents on the two surfaces

of the fabric can be obtained by correlating them to the corresponding resistance values using the built-in software in MMT. Based on the values, the typical curves of water content changes versus time on the fabric's top and bottom surfaces can be obtained, which will be introduced in the next paragraph (Figure 3.10). When moisture transports in a fabric, the electrical resistance at different locations of the fabric will change and such change can be used to interpret moisture transport behaviors of the fabric. Thus, with this MMT, we can measure dynamic liquid transfer in a fabric in three directions in one step.³²⁻³⁴ The liquid used in the tests was 0.15 M sodium chloride aqueous solution. The mechanism of the MMT is shown in Figure 3.9.

Figure 3.9 The schematic diagram of Moisture management tester.

Figure 3.10 The MMT results showing good moisture transport (a) and poor moisture transport (b).

The MMT results with good moisture transport and poor moisture transport are shown in Figure 3.10, where the green lines indicate the water content of the inner side of the sample, and the blue lines indicate the water content of the outer side of the sample. For Figure 3.8 (a), the value of green line and blue line increase initially before stabilization shortly and the value of green line is always higher than that of the blue line. It means that the water could pass the mat very quickly and finally there is more water in the inner side than the outer side. While for Figure 3.8 (b), the value of blue line keeps at zero all the time, indicating no water transport through the mat, which means that the moisture transport property of the sample (b) is quite poor. The results suggest that the water can pass through the sample (a) much more easily than sample (b). During the MMT test, the test solution is put on the sample. The transport direction is the same as gravity. Since the results show that even with the gravity force, the test solution still cannot pass the sample (b), whereas for sample (a), there is more water on the top surface, we believe the gravity does not show significant influence on the MMT results.

3.5 The friction coefficient test

The friction coefficient of the nanofibrous mats was measured from a Tribometer (CSM

Instruments). During the test, a Polydimethylsiloxane (PDMS) film was used to simulate the skin and was slid over the surface of the nanofibrous mats and cotton fabric.³⁵⁻³⁷ The tangential force of friction (F) to the normal force (N) pressing the body together is recorded by the Tribometer, and then the coefficient (μ) is calculated by $\mu = F/N$. The scheme of the Tribometer is shown as Figure 3.11.

Figure 3.11 The schematic diagram of Tribometer.

3.6 The Antibacterial test

To demonstrate the antibacterial property of the mats, zone of inhibition test was conducted. Compared with other laboratory antibacterial tests, such as time-kill test and flow cytometric methods, the zone of inhibition method is fast, low-cost, and well suited for textiles.³⁸ Thus, zone of inhibition test is widely used and is chosen in this experiment. The zone of inhibition test is based on the following principles. An inhibition zone is formed when a disc of the paper or board sample is placed directly onto an inoculated nutrient medium and releases water-soluble antimicrobial constituents. The antibiotic diffuses, creating a radial decreasing gradient of the drug around the disk. The susceptibility of the organism to the antibiotic is indicated by a zone of growth inhibition, i.e. “a clear zone” around the disk. The diameter of the inhibition zone is related to the extent of the release of the inhibitor, combined with its potency. Therefore, the limitation of zone of inhibition test is that in the case of antibacterial agents that can leach out of the

textile and diffuse into the aqueous agar matrix, the result is normally better than those antibacterial agents which stay affixed to the textile or are not water-soluble. Moreover, this method is not classically quantitative. Therefore, scanning electron microscope (SEM) is also used to observe the test surface of the textiles more precise comparison.^{39, 40} The related equipment are shown in Figure 3.12. In my zone of inhibition test, the bacterial cultures of *E. coli*-K12 (Wild Type) were prepared in 100ml LB Broth, Miller, inoculated and incubated at 37 °C overnight. LB Agar plates were seeded with 1ml of overnight culture. Discs of test material were placed onto plates and incubated at 37 °C overnight. The inhibition zones of the samples are checked and the morphology of the samples is obtained from FESEM. For example, the inhibition zone of two samples is shown in Figure 3.13. There is substantial amount of bacteria in sample (a), which means that the sample has poor antibacterial property. For sample (b), there is no bacterial on the surface, and there is an area with no bacteria around the sample, which is called inhibition zone. Thus, sample (b) has much superior antibacterial property to sample (a). In the experiment discussed in Chapter 6, *E.coli*, which is the most widely used bacteria due to the low cost and the only choice in many labs (including my lab) was used as the microorganisms.

Figure 3.12 The equipment for antibacterial test.

Figure 3.13 The inhibition zone of the sample with poor antibacterial property (a) and the sample with good antibacterial property (b).

3.7 Characterization methods

3.7.1 Scanning electron microscope

To study the relationship among the morphology, structure and property, the surface morphology need to be observed. In this experiment, the nano-scale pores and ZnO nanoparticles on the nanofibers could be clearly observed by Scanning electron microscope (SEM). In the experiment, electrons interact with atoms in the sample, producing signals containing information about the sample's surface topography (the surface features of the samples) and composition (the elements that the sample is composed of and the relative amounts of them).⁴¹⁻⁴³ The schematic diagram of SEM is shown as Figure 3.14.

Figure 3.14 The schematic diagram of SEM.

As one of the most widely used equipment to observe the morphology of the nano-scale materials, SEM has high magnification (from 10 to 500000 times) and good resolution (less than 1nm). Normally, to get a better resolution, the secondary electrons mode is used as the standard mode. And normally, energy dispersive x-ray spectroscopy (EDS or EDX) is equipped with the SEM to characterize the elemental composition of the samples imaged in the SEM.⁴⁴⁻⁴⁶

3.7.2 Transmission electron microscope

To check the core-shell structure of a single nanofiber, the nanofibrous mats are assessed by transmission electron microscope (TEM), in which a beam of electrons is transmitted through the mat, interacting with the mat as it passes through it. The beam of electrons is generated from the electron emission source, and is focused into a very narrow beam by the condenser lens and condenser aperture. After the beam strikes the sample, depending on the thickness and electron transparency of the samples, part of them could be transmitted and then focused by the objective lens into an image on the screen.⁴⁷⁻⁴⁹ The mechanism of TEM is shown in Figure 3.15.

Figure 3.15 The schematic diagram of TEM.

The core-shell structure of the nanofibers is verified by TEM, with abrupt change in brightness between the shell and core observed due to the asymmetric distribution of elements.

3.7.3 X-ray photoelectron spectroscopy

In X-ray photoelectron spectroscopy (XPS), an incident X-ray photon interacts with a core electron in a solid, often resulting in its excitation from the atom and escaping into the surrounding material. As these core electrons are in unique electronic environments depending upon the atomic species the electron is bound to, XPS provides a detailed method for probing the composition of a material.⁵⁰⁻⁵²

The detection depth of XPS is normally less than 12 nm, thus the XPS only investigates the composition of the near surface of the nanofibers. Since the XPS results show that PVDF is rich in the surface of the nanofibers, the core-shell structure of the nanofibers could be further verified.

3.7.4 X-ray Diffraction

Diffraction occurs when a collimated beam of electromagnetic waves with a wavelength comparable to interatomic distances interacts with the periodic array of molecules in a crystal. In X-ray diffraction, the incident beams with wavelengths of ~ 0.1 nm are generated by x-ray sources (photons), and the elastically scattered photons are measured to reveal the information on the electron distribution in the material. The positions of the diffracted beams with respect to the incident X-ray beam are largely governed by the positions of atoms in the unit cell of the crystal, which is the smallest structural unit that can be repeated by simple translations to generate the entire crystal. The relationship among the spacing between diffracting planes (d), the incident angle (θ), and the wavelength of the beam (λ) is determined by Bragg's law: $2d \sin\theta = n\lambda$.⁵³⁻⁵⁵ The mechanism of XRD is shown in Figure. 3.14.

Figure 3.16 The mechanism of XRD.

The main target of X-ray diffraction by crystals is to know the particular condition in which the scattered X-rays from atoms and the incident X-rays are completely in phase and reinforce each other to produce a detectable diffraction beam. The intensity of diffracted X-rays depends on not only the atomic arrangement but also the atomic species. Since the nucleus of an atom is relatively heavy compared with an X-ray photon, it does not scatter X-rays. The scattering ability of an atom depends only on electrons, their number and distribution.

To verify the attachment and the durability of the zinc oxide nanoparticles on the PVDF nanofibers, XRD tests were conducted on XRD-6000 Shimadzu. In the test, the nanofibrous mats (after long time washing) were cut into small pieces ($1\text{cm} \times 1\text{cm}$) and

put onto slides. Then the slides with small pieces of mats were put into XRD-6000 Shimadzu. The incident angle varied from 10° to 90° and the speed is $2^{\circ}/\text{minute}$. When the incident beams reacted with the sample, the appearance of characteristic peaks of ZnO could be evidence of the existence of ZnO nanoparticles, hence prove the durability (anti-wash property) of the ZnO nanoparticles on the nanofibrous mats.

3.7.5 Fourier Transform Infra-red spectroscopy

Fourier Transform Infrared Spectrometer (FTIR) is widely used in organic chemistry, because it could easily identify the presence of certain functional groups in a molecule. During the test, when the sample is exposed to infrared radiation, the molecules selectively absorb radiation of specific wavelengths which causes the change of dipole moment of sample molecules. Consequently, the absorption peak will appear in the FTIR spectrum. The schematic diagram of FTIR is shown in Figure. 3.17. In this research, FTIR results were recorded on PerkinElmer spectrometer.⁵⁶⁻⁵⁸

Figure 3.17 The schematic diagram of FTIR.

In my experiments, the nanofibrous mats were cut into small pieces ($1\text{cm} \times 1\text{cm}$) and then fixed on the sample holder of tester, and the transmission mode was selected. The wave length was from 500 to 4000 (resolution 8). At the first time, no sample was fixed on sample holder and the background was scanned. Then the

small pieces of mats were scanned one by one to examine the chemical structure of the mats respectively.

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Chapter 4

Tailoring surface hydrophilicity of porous electrospun nanofibers to enhance capillary and push-pull effects for moisture wicking

In this chapter, the work on the dual-layer mats composed of a thick layer of hydrophilic PAN nanofibers and a thin layer of hydrophobic PS nanofibers with and without interpenetrating nanopores, respectively, is reported. PDOPA is coated on the mats with different time to adjust the hydrophilicity of the PS nanofibers. According to the results, the porous PS nanofibers show a stronger capillary motion than the solid PS nanofibers due to a large number of nanochannels. The capillary effect in the porous PS nanofibers could be further improved by the surface modification with PDOPA while keeping the large hydrophobicity difference between the two layers, which can induce a strong push-pull effect to draw the moisture from the inner layer to outer layer.

*This section published substantially as reference 1 in this chapter.

4.1 Introduction

As mentioned in the background, water transport property is a critical issue of sports textile because it could primarily affect both thermo-physiological comfort and skin sensorial wear comfort of the wearers. Nowadays, single layer sports textiles made from modified synthetic fabric are widely used because they have good water release property²⁻⁴

In the literature review, the dual-layer textiles were introduced and explained the reason that the dual-layer structure can enhance the water transport property were explained.⁵It is the difference of hydrophobicity between the inner layer and outer layer that induces the push-pull effect, and the moisture could be pulled out quickly by this structure. The mechanism of capillary effect is also introduced in the literature review. Based on the mechanism, theoretically, the capillary motion can be controlled by tailoring the size of pores in the textiles and the surface hydrophilicity of the textiles. Thus, decreasing the pore size and increasing the hydrophilicity will enhance the capillary motion.

In chapter 3, the electrospinning technology has been introduced, and the reasons that why electrospinning is used to fabricate the model textiles in my experiments were also elaborated.⁶⁻¹⁴It is already reported that nanopores could be created in electrospun nanofibers by controlling the temperature and humidity.¹⁵⁻¹⁷ Also, various surface modification processes have been used to adjust the surface hydrophilicity of electrospun fibers,^{18, 19} although these opportunities to improve the capillary motion have not been explored.

In this work, PAN, PS and PAN-PS dual-layer nanofibrous mats are fabricated by electrospinning to study the moisture transport behaviors through the electrospun mats. The key materials, such as PAN, PS and PDOPA, and the surface modification of the nanofibers by self-polymerization of dopamine, have been introduced in chapter 3.²⁰⁻²²The influence of morphology and surface hydrophilicity of nanofibers on the water transport of the electrospun mats is herein reported. The possibility of improving the

push-pull effect in dual-layer mats by controlling the structure and morphology of the inner layer is also demonstrated.

4.2 Experimental Methods

4.2.1 Chemicals and materials

PAN ($M_w = 150000$), PS ($M_w = 350000$), dopamine hydrochloride (DOPA) and tris(hydroxymethyl) aminomethane (Tris) were supplied by Sigma-Aldrich Chemistry (USA). Dimethylformamide (DMF) and tetrahydrofuran (THF) were supplied by Tedia Company Inc (USA). Ethanol is purchased from Merck KGaA (Germany).

4.2.2 Preparation of PAN, PS nanofibers and PS-PAN dual-layer mats

PAN solution in DMF (8 wt% PAN), PS solution in DMF (15 wt% PS) and PS solution in DMF/THF (DMF/THF weight ratio =1:1, 15 wt% PS) were prepared by dissolving PAN or PS powder in the corresponding solvent(s) at 60 °C under continuous magnetic stirring. All solutions were fabricated into nonwoven nanofibrous mats by electrospinning. During the electrospinning, a Precision Inc., Matsasuda Gamma high voltage power supply (AV-30PI-L (200 V)) was utilized to supply the high operating voltage. To ensure continuous and homogenous delivery of polymer solution to the spinneret orifice, a digital infusion syringe pump (SP100iZ) from World Precision Instruments, Inc. was used. The polymer solution was electrospun into fiber mats under the working voltage ranging from 10kV to 20 kV and the needle tip-to-substrate distance was 15 cm. The type of the spinneret used was 27^{1/2} G with inner diameter of 200 μm . The flow rate was between 0.3 and 0.4 ml/h. The mats were collected on aluminum foil. The spinning time for PAN/DMF, PS/DMF and PS/DMF/THF solutions were 3hrs, 25 min and 25 min, respectively. PAN-PS double-layer mats were prepared via electrospinning of PS/DMF or PS/DMF/THF solution for 25 min followed by electrospinning of PAN/DMF solution for 3hrs on aluminum foils. All the mats were dried in vacuum at 60°C for 24 hrs and then went through a paper laminator (PRO BiO

320) at 70°C and a rolling speed of 50 rpm.

4.2.3 Preparation of PDOPA coating

The mechanism of PDOPA coating on the electrospun mats by self-polymerization was introduced in chapter 3. The electrospun mat was immersed in 500 mL 1.21 mg/mL Tris buffer aqueous solution, and 150 mg DOPA (0.3 mg/mL) was then added into the solution. The polymerization was conducted at room temperature for 15 and 90 min, respectively, under continuous magnetic stirring. All PDOPA-coated mats were rinsed with deionized (DI) water for three times and dried in vacuum at 60°C for 24 hrs. Solution-casted solid PAN and PS films were also coated with PDOPA following the same procedure. The films were casted from the PAN/DMF and PS/DMF/THF solutions and dried in a vacuum oven at 80 °C for 24 hrs.

4.2.4 Characterization

Morphologies of the mats were observed using a field-emission scanning electron microscope (FESEM, JEOL 7600F). To evaluate the durability of the mats, the samples are immersed in detergent aqueous solution (0.15 g/100 ml), and vigorously shaken by shaker for 24 hours or longer time followed by shaken in water for 1 hour, and then dried in vacuum at 60 °C for 4 hrs. The contact angle and moisture management test were introduced in chapter 3.²³ An aqueous blue ink was used to stain the PS-pNF/PAN-sNF and PS-pNF-15/PAN-sNF dual-layer mats to visually observe their liquid transport behavior.

4.3 Results and Discussion

4.3.1 Morphologies and surface modification of the electrospun nanofibrous mats

In this work, to study the morphology and surface hydrophilicity of nanofibers influence on moisture transport through nanofibrous mats, three kinds of nanofibrous mat

composed of PAN, solid and porous PS nanofibers were fabricated by electrospinning and the surfaces of the nanofibers were coated with PDOPA with different time.

To facilitate the discussion below, the morphological and surface features of the mats are indicated in the sample names. For instance, PS porous nanofibers without PDOPA coating are denoted as PS-pNF, while PS solid nanofibers with PDOPA coating of 15 min are denoted as PS-sNF-15. The reference samples are denoted in a similar way except that NF (nanofiber) is replaced by FM (film). For example, PS-FM-15 denotes the cast PS films with PDOPA coating of 15 min.

Figure 4.1 shows the morphology of the three types of nanofibers. It can be seen that the diameter of all the three types of nanofibers is less than $0.8\ \mu\text{m}$. Although the diameters of the three kinds of nanofibers are different, such moderate differences will not strongly influence their water transport behaviors. For example, as shown in Figure 4.2, the PAN nanofibers with different diameter exhibit quite similar moisture transport behaviors shown in MMT results. The solid nature of PAN-sNF and PS-sNF is verified by the high-magnification SEM images, and the high porosity of PS-pNF is also confirmed. The mechanism for the formation of porous PS nanofibers is explained in chapter 3.¹⁷

Figure 5.1 SEM images showing the morphologies of the as-spun (ai and aii) solid PAN (PAN-sNF), (bi and bii) solid PS (PS-sNF) and (ci and cii) porous PS nanofibers (PS-pNF)

Figure 4.2 SEM images showing the morphologies of the as-spun PAN of 6% concentration (a1), PAN of 8% concentration (a2), PAN of 10% concentration (a3), (b) The MMT results of PAN of 6% concentration (b1), PAN of 8% concentration (b2), PAN of 10% concentration (b3)

The high porosity of PS-sNF can be observed more clearly from the cross-sectional SEM image (Figure 4.3a). The nanopores inside the fibers are actually inter-penetrating nanochannels with size of less than 100 nm. Such nanochannels render the porous nanofibers much higher specific surface area (SSA) than the solid nanofibers. Moreover, the nano-sized channels and their inter-penetrating nature may strongly enhance capillary motion, thus improve water transport.

Figure 4.3 High-magnification FESEM images showing the morphologies of (a) the as-spun porous PS nanofibers (PS-pNF), and (b) the porous PS nanofibers coated with PDOPA for 90 min (PS-pNF-90). (c) The cross-sectional FESEM image of PS-pNF-90.

As mentioned in literature review, the hydrophilicity of fibers plays an important role in determining the moisture wicking of sports textiles. In this work, the surface hydrophilicity of the PS nanofibers is adjusted by the coating of PDOPA. As shown in Figures 4.3b and 4.3c, after 90 minutes' PDOPA coating, the inter-penetrating nanopores in the porous PS fibers are still distinguishable. Actually, as shown in Figure 4.4, for all the nanofibers, the morphology kept the same after 90 minutes' PDOPA coating.

Figure 4.4 FESEM images showing the morphologies of (a) PAN nanofibers coated with PDA for 90 mins and (b) solid PS nanofibers coated with PDA for 90 mins, indicating that the nanofibrous morphology remains after coating.

The successful coating of PDOPA was proven by FTIR results. To show the surface structure evolution with coating time more clearly, the results from solid film samples are listed here. As shown in Figure 4.5, compared with the spectrum of PS-FM, the spectra from PS-FM-15 and PS-FM-90 show characteristic peaks of PDOPA at about 3300 cm^{-1} (-OH stretch) and 1260 cm^{-1} (C-O vibration of phenolic moieties), and a shoulder at 1120 cm^{-1} .²⁴ With the increased coating time, the intensity of these peaks become stronger, meaning that more PDOPA is coated on the surface of films. The FTIR results of the nanofibrous mats are shown in Figure 4.6, which indicates a similar trend with the spectrum of solid film samples.

Figure 4.5 FTIR spectra of PS-FM, PS-FM15 and PS-FM90.

Figure 4.6 FTIR spectra of the solid PS nanofibrous mat and the one coated with PDA for 90 mins, confirming the successful PDA coating.

4.3.2 Effect of capillary effect on liquid moisture transport behavior

To investigate the moisture transport behavior of the nanofibrous mats, understanding the interaction between the mats and water is very important. Therefore, time-dependent contact angles of the nanofibrous mats and solid films were tested to characterize the water wettability and spreading capability of the surfaces. For the nanofibrous mats, the results are dependent on both the surface properties and the rate of water penetration into the mats. To further study the moisture transport behavior through the nanofibrous mats, the samples are also measured by MMT. The mechanism of MMT was elaborated in chapter 3.

Firstly, to investigate the intrinsic water wettability of PAN and PS, and the effects of the PDOPA coating on their surface hydrophilicity, contact angles of the cast PAN and PS solid films before and after PDOPA coating were measured. In figure 4.7, it could be seen that the PAN film shows smaller contact angle and hence is more hydrophilic than the PS film. Moreover, water can spread on the PAN film in all directions uniformly, thus the contact angle decreases quickly within 1 minute, while water cannot spread on the PS film (no significant contact angle change in 1 minute), indicating the hydrophobic nature of PS. For the PAN film, the coating of PDOPA does not apparently change the contact angle, indicating that both PAN and PDOPA surfaces are fairly hydrophilic. While, after the coating a PDOPA layer on the PS film, the contact angle of the film reduces slightly, which is more apparent for PS-FM-90, verifying that the PS surface has been successfully modified by PDOPA. However, after the PDOPA coating, the contact angles of PS-FM-15 and PS-FM-90 do not decrease significantly within 1 minute, indicating that the surfaces are still quite hydrophobic because of the fairly short coating times and hence deposition of relatively small quantities of PDOPA on the PS thin films. Note that with the slightly reduced contact angle, the gravity force for further spreading will be smaller. Moreover, it is possible that since the coating time is long enough, the PDOPA layer cannot totally cover the surface of the film.

Figure 4.7 Contact angles of the solid films (a) PAN-FM, PAN-FM-15 and PAN-FM-90, and (b) PS-FM, PS-FM-15 and PS-FM-90.

Figures 4.8 a, b and c show the apparent contact angles of the PAN nanofibrous mats. The results of PAN-sNF, PAN-sNF-15 and PAN-sNF-90 are very similar. However, it could be seen that, compared with the corresponding cast films, the contact angles of the nanofibrous mats are much smaller. Although PAN has very limited water sorption ability due to its highly crystalline nature, with the assistance of surface nitrile groups, moisture on the top surface of the mats could spread along or across the nanofibers very fast, penetrate into the pores in the mats and reach the bottom surface of the mats. Therefore, the apparent contact angle decreases to zero very fast and the test water disappears in less than 4 seconds. The water transport behaviour is further studied by the MMT results shown in Figure 4.8 d. The solid green line indicates the water content of the top surface where the test water drops are sprayed initially, while the dashed blue line indicates the water content of the bottom surface. For PAN-sNF, the water contents of both surfaces rise very quickly initially and reach a plateau very fast, and the water content of the bottom surface is always lower than that of the top surface, showing that although moisture could pass the mat very fast, once a certain water content gradient is established, the water transport will be slowed down. The PDOPA coating on the PAN nanofibers exerts no distinct influence on the water transport behaviour.

Figure 4.8 Apparent contact angles of (a) PAN-sNF, (b) PAN-sNF-15 and (c) PAN-sNF-90 measured at (i) initial state, and after water touching the mats for (ii) 1 s and (iii) 4 s. (d) The MMT results of (i) PAN-sNF, (ii) PAN-sNF-15, (iii) PAN-sNF-90.

Figures 4.9a-4.9c show the apparent contact angles of PS-sNF, PS-sNF-15 and PS-sNF-90. In contrast to that of PAN-sNF, which shows much smaller apparent water contact angle than the cast PAN film, the apparent water contact angle of PS-sNF is much larger than the cast PS film because for hydrophobic materials, a rough surface at submicron scale can strongly increase water contact angle due to the lotus effect.²⁵ Moreover, the value keeps the same for fairly long, i.e. in 3 minutes (Figure 4.10), showing that the test neither spread along/across the nanofibers nor penetrate into the pores in the nanofibrous mats. However, after PDOPA is coated on PS-sNF for 15 minutes, the water contact angle drops very fast and decreased to 0 in less than 4 seconds, which means that the test moisture can penetrate through the mat. For the sample coated with PDOPA for 90 minutes, the surface is much more hydrophilic and the test water can thus penetrate through the mat even faster. The contact angle results are in good agreement with the MMT results shown in Figure 4.9d. It can be seen that for PS-sNF, the blue line keeps at zero all the time, which means that no test water can transport through the mat. PS-sNF-

90 shows much faster water transport and higher relative water content on the bottom surface than PS-sNF-15. Different from PAN-sNF-90, for PS-sNF-90, the water contents on both sides are almost the same, due to the much smaller thickness of the PS mats ($\sim 20\mu\text{m}$) than the PAN mats ($\sim 120\mu\text{m}$).

Figure 4.9 Apparent water contact angles of (a) PS-sNF, (b) PS-sNF-15 and (c) PS-sNF-90 measured at (i) initial state, and after water touching the mats for (ii) 1 s and (iii) 4 s. (d) The MMT results of (i) PS-sNF, (ii) PS-sNF-15, (iii) PS-sNF-90.

Figure 4.10 Apparent water contact angles of PS-sNF measured at (1) initial state, and after water touching the mats for (2) 1 minute and (3) 3 minutes.

As introduced in literature review, the nanochannels in porous PS nanofibers can in principle enhance the capillary effect. Based on the mechanism, decreasing the pore size will enhance the capillary motion. Since the size of the interpenetrating pores in the porous PS nanofibers is much smaller than the inter-fiber spaces, which are micrometers and above in size, the interpenetrating pores could probably more strongly enhance the capillary motion. However, compared with the apparent contact angle of PS-sNF (Figure 4.9a), the apparent water contact angle of PS-pNF (Figure 4.11a) is only slightly smaller, and the value does not drop with time very fast because these two mats have similar hydrophobic surface and submicron-scale roughness that make test moisture very difficult to spread on the nanofibers or penetrate into the nanofibrous mats. After PDOPA is coated on the porous PS nanofibers for 15 minutes, the apparent water contact angle of PS-pNF-15 is much smaller than that of both PS-pNF and PS-sNF-15, indicating improved capillary motion. Furthermore the apparent contact angle of PS-pNF-15 drops with time much faster than that of PS-sNF-15, showing faster moisture transport in PS-pNF-15. This proves that appropriate water wettability (hydrophilicity) is a precondition for effective capillary motion. The enhanced water transport of PS-pNF and PS-pNF-15 in comparison with that of PS-sNF and PS-sNF-15 is also verified by MMT results, as shown in Figure 4.11d. PS-pNF shows detectable water content, albeit small, on the bottom surface, which indicates that even without the PDOPA coating the capillary motion could be improved due to the presence of nanochannels. The surface of PS-pNF-90 is very hydrophilic because of much longer PDOPA coating time and hence the test moisture can be transported through the thin mat, similar to that of PS-sNF-90. PS-sNF-90 and PS-pNF-90 thus give similar MMT results. To facilitate the understanding of the changes on apparent contact angle of different sample are summarized in Table 4.1

Figure 4.11 Apparent water contact angles of (a) PS-pNF, (b) PS-pNF-15 and (c) PS-pNF-90 measured at (i) initial state, and after water touching the mats for (ii) 1 s and (iii) 4 s. (d) The MMT results of (i) PS-pNF, (ii) PS-pNF-15, (iii) PS-pNF-90.

Table 4.1 Summarizing the results of apparent contact angle of the samples with different times

Sample/time	Initial state	1 second	4 seconds	1 minute	3 minutes
PAN-FM	$68^{\circ} \pm 1^{\circ}$			$61^{\circ} \pm 1^{\circ}$	
PAN-FM-15	$66^{\circ} \pm 2^{\circ}$			$60^{\circ} \pm 1^{\circ}$	
PAN-FM-90	$65^{\circ} \pm 1^{\circ}$			$60^{\circ} \pm 2^{\circ}$	
PS-FM	$79^{\circ} \pm 1^{\circ}$			$78^{\circ} \pm 2^{\circ}$	
PS-FM-15	$76^{\circ} \pm 2^{\circ}$			$76^{\circ} \pm 1^{\circ}$	
PS-FM-90	$72^{\circ} \pm 1^{\circ}$			$71^{\circ} \pm 1^{\circ}$	
PAN-sNF	$30^{\circ} \pm 2^{\circ}$	$20^{\circ} \pm 1^{\circ}$	0°		
PAN-sNF-15	$32^{\circ} \pm 3^{\circ}$	$22^{\circ} \pm 2^{\circ}$	0°		
PAN-sNF-90	$33^{\circ} \pm 2^{\circ}$	$19^{\circ} \pm 2^{\circ}$	0°		
PS-sNF	$106^{\circ} \pm 1^{\circ}$	$106^{\circ} \pm 2^{\circ}$	$106^{\circ} \pm 1^{\circ}$	$106^{\circ} \pm 1^{\circ}$	$105^{\circ} \pm 2^{\circ}$
PS-sNF-15	$102^{\circ} \pm 3^{\circ}$	$82^{\circ} \pm 4^{\circ}$	0°		
PS-sNF-90	$44^{\circ} \pm 3^{\circ}$	$32^{\circ} \pm 3^{\circ}$	0°		
PS-pNF	$103^{\circ} \pm 2^{\circ}$	$103^{\circ} \pm 2^{\circ}$	$103^{\circ} \pm 1^{\circ}$		
PS-pNF-15	$90^{\circ} \pm 3^{\circ}$	$42^{\circ} \pm 4^{\circ}$	0°		
PS-pNF-90	$40^{\circ} \pm 4^{\circ}$	$28^{\circ} \pm 3^{\circ}$	0°		

4.3.3 Liquid moisture transport behaviors of PAN-PS dual-layer nanofibrous mats

The dual-layer structure is introduced in the literature review, which is composed of a hydrophobic inner layer and a hydrophilic outer layer. Push-pull effect could be induced by this structure to draw the water to outer layer,⁴ thus textiles with a dry inner layer will make people feel more comfortable. The PS-pNF/PAN-sNF dual-layer mats were fabricated by electrospinning of PS first followed by electrospinning of PAN on top of the PS nanofibers. The morphology of the cross-sectional of the dual-layer mats were observed by SEM. In Figure 4.12, it can be seen that in the interfacial area, the PS nanofibers (thicker ones) are entangled with the PAN nanofibers (thinner ones), providing good adhesion between the two layers, which can enhance the water transport from the inner to outer layer. The MMT results of the dual-layer mats composed of a PS

top layer and a PAN bottom layer are shown in Figure 4.13. The results show that for the mats with either PS-sNF or PS-pNF top layer without the coating of PDOPA, water can hardly wet the bottom surface due to the hydrophobic nature of PS; the adhesive force with test water is too small to trigger the capillary effect and hence hinders the push-pull effect. Even though, the PS-pNF/PAN-sNF dual-layer mat still performs slightly better than its PS-sNF/PAN-sNF counterpart as evidenced by a slight increase in relative water content of the bottom layer of PS-pNF/PAN-sNF over time (the blue line in Figure 4.13(bi)). This verified that the capillary motion can indeed be improved by creating nanopores in the nanofibers.

Figure 4.12 A cross-sectional FESEM image of the PS-pNF-15/PAN-SNF dual-layer nanofibrous mat. It is shown that the PS porous nanofibers are entangled with PAN solid nanofibers in the interfacial area, providing good adhesion between the PS layer and PAN layer.

Figure 4.13 MMT results of the dual-layer mats with PAN-sNF as the bottom layer, and (ai, aii and aiii) PS-sNF as the top layer and (bi, bii and biii) PS-pNF as the top layer. The samples include the mats not coated with PDOPA and those coated with PDOPA for 15 and 90 mins, respectively.

After the coating of PDOPA on the mats, moisture could be effectively pushed into the pores in the top layer with capillary motion and then pulled out by the hydrophilic bottom layer. Such distinct push-pull effect can be seen in Figures 4.13(aii-aiii) and 4.13(bii-biii), where the two lines in each figure cross over after some time, i.e., the water content of the top surface becomes clearly lower than that of the bottom surface, showing that most moisture is successfully drawn out from the relatively hydrophobic top layer to the hydrophilic bottom layer. As shown earlier, compared with PS-sNF-15 and PS-sNF-90, the interpenetrating nanopores in PS-pNF-15 and PS-pNF-90 lead to slightly stronger capillary motion (slightly smaller apparent contact angles). It is striking to see that the nanopores enhance the push-pull effect in the corresponding double-layer mats strongly.

For PS-pNF-15 and PS-pNF-90 top layers, the water content difference between the top and bottom layers of the dual-layer mats is distinctly larger than that of the mats with the PS-sNF-15 and PS-sNF-90 top layers, i.e. the stronger capillary effect makes the top layer much drier. As shown in figures 4.13(bii) and 4.13(biii), it is quite clear that for the mat with the PS-pNF-90 top layer the crossover of the two lines occurs within 1 minute, whereas for the mat with PS-pNF-15 top layer, the crossover occurs after 3 minutes, which indicate that the former shows more quickly water transport rate than the latter. This is due to the stronger capillary motion induced by the more hydrophilic surface in PS-pNF-90.

Figure 4.14 further verifies the effect of capillary motion on water transport behavior of the dual-layer mats. Without the PDOPA coating, an aqueous blue ink droplet placed on the PS-pNF top layer can neither spread out nor penetrate into the mat in 50 seconds (Figure 4.14a), thus no ink stain can be observed on the backside of the dual-layer mat. While, the other ink droplet placed on the PAN bottom layer (on the folded half in Figure 4.14a) spreads out very fast. After 50 seconds, a very pale blue spot can be observed on the backside, i.e., the PS-pNF top layer. This means that the droplet is trapped in the PAN layer, further verifying that although water can wet the PAN layer easily, it is difficult to pass through the hydrophobic PS layer without the PDOPA coating. As shown in figure 4.14b, after the coating of PDOPA, the ink droplet placed on the PS-pNF-15 top layer can penetrate into the mat very fast and spread on both the top and the bottom layers, leaving ink spots on both sides of the mat. Since the color of the spot on the bottom surface is much darker, it can be concluded that the bottom surface has more water content than the top surface. It demonstrates that with the assistance of nanochannels, a slight increase in hydrophilicity of the PS nanofibers surface can strongly enhance capillary motion, while by adjusting coating time a large hydrophilicity difference between the two layers can be retained to give enough driving force to draw the moisture out.

Figure 4.14 Pictures showing water spreading and transport abilities of (ai, aii, aiii and aiv) a PS-pNF/PAN-sNF dual-layer mat without PDOPA coating and (bi, bii, biii and biv) a PS-pNF/PAN-sNF dual-layer mat coated with PDOPA for 15 min.

The anti-wash property of the PDOPA coating was also tested by comparing apparent contact angles of the PS-pNF-15/PAN-sNF dual-layer mat before and after washing. The apparent contact angle keeps the same after washing, as shown in Figure 4.15, indicating that the PDOPA coating on the nanofibers can survive after washing.

Figure 4.15 Apparent water contact angles of a PS-pNF/PAN-sNF dual-layer mat coated with PDOPA for 15 min before (ai and aii) and after (bi and bii) laundry treatment.

4.4 Conclusions

In summary, in the work, the good water transport potential of electrospun nonwoven mats is verified experimentally for the first time using double-layer PAN-PS electrospun nanofibrous mats with PDOPA coatings. It is demonstrated that by significantly decreasing the size of the moisture transport channels through using the nanofibers with interpenetrating nanopores and slightly enhancing the hydrophilicity of the surface of nanofibers, the capillary motion in the hydrophobic nanofibrous mats can be strongly improved. Since the nanochannels only require very low hydrophilicity to trigger the capillary motion, in the dual-layer system the hydrophilicity difference between the top layer and bottom layer can be quite large to induce strong push-pull effect, leading to a much drier inner layer. It is believed that the approach demonstrated in this work has great potential to be extended to other base polymer systems, possibly in combination with other surface modification methods, for development of advanced sportswear and work wear. The porous electrospun nanofibers may also be used to modify conventional textiles to enhance their water transport capability.

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Chapter 5

Materials design towards sport textiles with low-friction and moisture-wicking dual functions

In the work reported in this chapter, dual-layer nanofibrous mats were designed and fabricated to achieve low friction between the inner layer and skin as well as good water transport property. In the dual-layer structure, PAN-core/PVDF-shell nanofibers were used as the inner layer, and base-treated CA nanofibrous mats were used as the outer layer. The large hydrophilicity difference between the two layers can provide enough driven force to draw the moisture out, at the same time the shell part of the inner layer is rich in PVDF, which can lower the friction between the inner layer and skin.

*This section published substantially as reference 1 in this chapter.

5.1 Introduction

As mentioned in background, both the moisture transport^{2,3} and low friction with skin are very important properties for sports textile. In the textile industries, fluoropolymers which have very low coefficients of friction have been used to lower the friction between skin and textile.⁴⁻⁶ However, the highly hydrophobic nature of fluoropolymers will impede the moisture transport.

As introduced in literature review, the moisture transport property and low friction with skin are two key issues of the sports textile which could directly influence the wear comfort. By now, usually the multi-functional textiles are fabricated by the introduction of multifunctional materials like ZnO nanoparticles, or introduction of more than one agents together in the same substrate.⁷⁻¹⁰ However, how to achieve low friction between the inner layer and skin as well as good water transport property still need to be studied

In chapter 4, we showed that dual-layer textile have good moisture management property due to push-pull effect, and is of great potential to achieve multifunctional textile.¹¹ Thus, we plan to use fluoropolymers which are highly hydrophobic as the inner layer to fabricate a dual-layer moisture-wicking textile with low friction, and just the same as chapter 4, electrospun nanofibers are still used as a model system to verify our design concept.¹²⁻¹⁶

In previous work reported in chapter 4, the good water transport property of dual-layer mats composed of a PS inner layer and a PAN outer layer has been demonstrated. In this work, PAN-core/PVDF-shell nanofibers were fabricated by single-spinneret electrospinning with the aid of phase separation and used as the inner layer to lower the friction between the inner layer and skin without sacrificing water transport property. The PVDF which is rich in the shell part could induce lubricating effect to ensure low friction, while although PAN is rich in the core part, a small amount of PAN on the shell part can enhance the capillary motion in the inner layer. The effectiveness of our design in providing both low friction and good water transport properties is verified experimentally.

5.2 Experimental Methods

5.2.1 Chemicals and materials

PVDF and CA were supplied By Sigma-Aldrich Chemicals, PAN and DMF were introduced in chapter 4.

5.2.2 Preparation of nanofibrous mats

PAN solution, PVDF solution, PAN/PVDF solution in DMF(5 wt% PAN-5 wt% PVDF, 6wt% PAN-2wt% PVDF and 6wt% PAN-1wt% PVDF) and CA solution in DMF/Acetone (13wt% CA, DMF/Acetone-1/1 by weight)were prepared following the same procedures mentioned in chapter 4. The electrospinning setup and conditions used were also the same as those mentioned in chapter 4 (Coaxial needles were not used.).The spinning time for PAN/DMF, PVDF/DMF and PAN/PVDF/DMF solutions was 25 minutes, while CA solutions were spun for 12 hours. After electrospinning, the CA mat was soaked in 0.05MNaOH aqueous solution for 16 hours and rinsed with DI water to convert CA into a cellulose mat. Base-treated CA-PAN/PVDF dual-layer mats were prepared by electrospinning of PAN/PVDF/DMF (5 wt% PAN-5 wt% PVDF) solution for 25 minutes onto base-treated CA matsfollowed by going through a laminator.To facilitate the discussion below, the dual layer is denoted as D-CA-PAN/PVDF. All the mats were dried and laminated as mentioned in chapter 4. Solution-cast solid PVDF, PAN, PVDF/PAN blend and CA films were also prepared. The films were cast from the corresponding solutions and dried in a vacuum oven at 80°C for 24 hrs. CA films were soaked in 0.05MNaOH aqueous solution for 4, 8, 12, 16, 20, 24hours and rinsed with DI water to convert CA into cellulose to different extents.

5.2.3 Characterization

Morphologies of the mats were observed by SEM and TEM. The composition of the PAN/PVDF blend nanofibers is tested by XPS. FTIR, water transport and contact angle were measured using the same instruments and experimental conditions as chapter 4, and tests of water absorption and friction coefficient were introduced in chapter 3.

5.3 Results and Discussion

5.3.1 PAN-rich core/ PVDF-rich shell blend nanofibers as the inner layer

In our design, to trigger a push-pull effect, the inner layer of the dual-layer structure should be fairly hydrophobic, and it is also expected to provide low friction between the textile and skin. Thus, PVDF is chosen as the inner layer material. Since the water can hardly pass the PVDF layer because of its poor wettability, PAN was used to enhance the wettability of the inner layer.

Firstly, the morphology of the PAN/PVDF core-shell nanofibers at a weight ratio of 1/1 was observed by SEM and TEM. The typical morphologies of the blend nanofibers is shown in Figure 5.1 (a). The nanofibers are solid and beadless, and the diameter of nanofibers is uniform. As shown in TEM image (Figure 5.1(b)), a distinct core-shell structure can be observed within the blend nanofibers, because there is an abrupt change in brightness between the shell and core due to the asymmetric distribution of elements, indicating phase separation during electrospinning. The reason of the formation of core-shell structure is that the surface energy of PVDF is much lower than that of PAN, thus PVDF prefers to stay at the surface of the nanofibers, forming the shell.¹⁷

Figure 6.1 SEM (a) and TEM (b) images of the blend (PAN: PVDF=1:1) nanofibers.

To further verify the core-shell structure of the blend nanofibers, the blend nanofibers were also fabricated at a PAN to PVDF weight ratio of 3/1 and 6/1, and then XPS analysis was conducted (Figure 5.2), and the theoretical atomic content of fluorine (F) in uniform blend nanofibers is calculated based on the feed compositions. As a reference, the composition of neat PVDF nanofibers was calculated and tested by XPS analysis. As shown in Figure 5.3, by comparing the F contents, calculated value with the measured surface F content, it can be seen that the calculated F content is much lower than the measured value for the blend nanofibers. As introduced in chapter 3, the detection depth of XPS is normally less than 12 nm, and the elemental F only comes from PVDF, thus it can be concluded that the shell of the blend nanofibers is rich in PVDF. Therefore, the PAN-core/PVDF-shell configuration for the PAN/PVDF blend nanofibers is further verified. Owing to the hydrophobic nature of PVDF, the shell-rich PVDF can produce a hydrophobic surface on the blend nanofibers. This is reflected by the quite similar contact angles of neat PVDF and the blend nanofibers with different ratios shown in Figure 5.4.

Figure 5.2 XPS results of elemental fluorine in the pure PVDF nanofibers (a), and blend nanofibers with PAN/PVDF ratios of 1/1 (b), 3/1 (c) and 6/1 (d).

Figure 5.3 Content of fluorine in PVDF nanofibers, blend nanofibers with PVDF/PAN ratios of 1/1, 1/3 and 1/6 measured by variable angle XPS and calculated values based on the feed ratio of the nanofibers.

Figure 5.4 Apparent contact angle of PVDF nanofibers (a), blend nanofibers with PVDF/PAN ratios of 1/1 (b), 1/3 (c), 1/6 (d) and PAN nanofibers (e)

The MMT results of PVDF, PAN and PVDF/PAN blend (PVDF/PAN ratio=1/1) nanofibrous mats are shown in Figures 5.5 (a), (b) and (c). The MMT method has been introduced in chapter 3 and chapter 4.¹⁸ The MMT result for PAN mats is shown in

Figure 5.5(a), the moisture can pass the hydrophilic PAN very soon. While as shown in Figure 5.5(b), moisture cannot pass through the hydrophobic PVDF mat and wet the bottom surface, thus the value of the blue line remains at zero in the test. The Figure 5.5(c) shows the water transport behavior of the blend mat. At the beginning, the water content of the bottom surface keeps at zero because the water cannot pass through the mat easily due to the presence of shell-rich PVDF. Also, as shown in Figure 5.5 (c), after a while, the water content of bottom layer gradually increases although it keeps much lower than that of the top layer. For the PAN/PVDF blend nanofibrous mats, the surface of the mats is hydrophobic due to the PVDF-rich shell. However, the existence of a small amount of PAN in the shell part of the blend nanofibers can slightly enhance the water wettability of the surface, which could facilitate the capillary motion and thus let the test water pass through the blend nanofibers very slowly. This is because the small amount of PAN in the shell of the blend nanofibers can improve the wettability of the surface of mat. Therefore, as it can be seen in Figure 5.5 (c), the water transport capability of the blend nanofibrous mat is better than that of pure PVDF mat.

Figure 5.5 The moisture management results of as-spun PAN (a), PVDF (b) and blend nanofibers with PVDF/PAN ratio of 1/1(c).

5.3.2 Base-treated CA nanofibers as outer layer

As discussed above, the PAN/PVDF blend electrospun mat is more wettable than the neat PVDF mat and could allow water to pass through it. At first, as the same with method reported in chapter 4, we used electrospun PAN mats as the outer layer of the dual-layer mats. However, since the PAN/PVDF blend mats are much more hydrophobic than

PDOPA coated PS mats, the PAN mats as the outer layer cannot provide enough pull force to draw the moisture out, thus the push-pull effect could not be achieved. Thus, we have to choose a more hydrophilic and absorbent outer layer. Cellulose, which is the main component of traditional cotton fabric, was selected and proved to be qualified outer layer material due to its highly hydrophilic and absorbent nature.

To fabricate the outer layer, CA nanofibers were electrospun^{19,20} followed by soaked in NaOH aqueous solution for 16 hours to remove acetylgroups.²¹ To check the effect of deacetylation reaction time on the moisture transport behavior, cast CA films were immersed in NaOH aqueous solution for different times and their apparent angle and water absorption were measured. In figure 5.6, it can be seen that the cast CA film becomes more hydrophilic with the rise of treatment time. However, since the CA mats will be fragile with fairly long reaction time, the CA nanofibrous mats were immersed in NaOH aqueous solution for 16 hours to partly convert CA into cellulose.

Figure 5.6 Apparent contact angles and water absorption of CA mat and CA mat soaked in NaOH for 4, 8, 12, 16, 20 and 24 hrs.

To make it more clear, the apparent contact angle of PAN/PVDF composite mats and CA mats soaked in NAOH for different times with standard deviation are summarized in Table 5.1.

Table 5.1 Summarizing the results of apparent contact angle of PAN/PVDF composite mats and CA mats soaked in NAOH for different times

sample	PVDF	PVDF/PAN(1/1)	PVDF/PAN(1/3)	PVDF/PAN(1/6)
contact angle	$115^{\circ} \pm 1^{\circ}$	$116^{\circ} \pm 1^{\circ}$	$116^{\circ} \pm 1^{\circ}$	$116^{\circ} \pm 1^{\circ}$
sample	PAN	CA	CA (soaked 4h)	CA (soaked 4h)
contact angle	$37^{\circ} \pm 4^{\circ}$	$62^{\circ} \pm 3^{\circ}$	$59^{\circ} \pm 2^{\circ}$	$49^{\circ} \pm 3^{\circ}$
sample	CA (soaked 8h)	CA (soaked 12h)	CA (soaked 16h)	CA (soaked 24h)
contact angle	$47^{\circ} \pm 4^{\circ}$	$42^{\circ} \pm 4^{\circ}$	$40^{\circ} \pm 3^{\circ}$	$38^{\circ} \pm 3^{\circ}$

The CA nanofibrous mats with 4, 8 and 16hours' treatment were tested by FTIR. In Figure 5.7, the characteristic peaks of CA become weaker while those of cellulose become more significant with the increase of treating time. Thus converting CA into cellulose in the reaction is demonstrated.

Figure 5.7 FTIR spectra of CA mat and CA mat soaked in NaOH for 4, 8 and 16 hrs.

Moreover, the contact angle and water transport results for a CA nanofibrous mat after 16 hours' base treatment is shown in Figure 5.8, which indicate that the moisture can pass through the mats very fast, proving that the mat is a suitable outer layer material. The morphology of CA nanofibers and base-treated CA nanofibers are shown in Figure 5.9, which indicates that there is no apparent morphological variation after the treatment.

Figure 5.8 Apparent contact angle (a) and moisture management result (b) of CA mat soaked in NaOH for 16 hrs.

Figure 5.9 SEM images of CA nanofibers and CA nanofibers soaked in NaOH for 16 hrs.

5.3.3 Base-treated CA-PAN/PVDF dual-layer mats

The double-layer mats were prepared by electrospinning of PAN/PVDF/DMF solution onto base-treated CA mats followed by going through a laminator to improve the interlayer adhesion. In Figure 5.10(a), schematic structure of the dual-layer mat is explained, which illustrates that the water can be drawn out efficiently from the inner layer to outer layer by push-pull effect. The water transport behaviour is demonstrated by MMT results shown in Figure 5.10(b). In the figure, the green and blue lines cross over at around 300 seconds, and then the value of green line keeps much lower than that of blue

line, indicating that most water is pulled out to the bottom hydrophilic surface (outer surface), which is quite similar with the results of dual-layer mats reported in chapter 4.

Figure 5.10 Schematic diagram (a) and moisture management results of D-CA-PAN/PVDF mats (b).

5.3.4 Friction coefficient of the inner layer

The moisture transport property of the dual-layer mat has been verified above. Then the friction coefficients of PAN, PVDF and PAN/PVDF blend nanofibrous mats were also measured, and the cotton fabric is used as a reference. The results of the test is summarised in Figure 5.11. It can be seen that the nanofibrous mats all exhibits lower value than that of cotton fabric, which is of micron size, and PVDF and PAN/PVDF mats have lower friction coefficient than PAN mat due to the fluorine component. To further demonstrate the contribution of the fluorine component, the friction coefficients of PAN, PVDF and PAN/PVDF blend cast films were measured and the results are also shown in Figure 5.11, which indicate the same trend as the nanofibrous mats. Also, it can be seen in Figure 5.11, the friction coefficients of the cast films are higher than those of the electrospun mats. The thickness of the cast film is usually not quite uniform due to the process of the evaporation of the solvent, which could make the coefficients of the cast films higher. According to the results listed above, the neat PVDF mats and PAN/PVDF blend mats exhibit quite similar friction coefficients because of the PVDF-rich shell structure of the blend nanofibers. Thus it is demonstrated that the blend nanofibrous mats as inner layer can provide low friction with skin as well as a better wettability compared with neat PVDF.

Figure 5.11 The friction coefficients of cotton, PAN, PVDF and PAN/PVDF blend (at the ratio of 1/1) mats and cast films.

5.4 Conclusions

In this work, dual-layer nanofibrous mats composed of a piece of base-treated CA mat as outer layer and a piece of core-shell PAN/PVDF nanofibrous mat as inner layer were designed and fabricated. The PAN in the blend nanofibrous mats can enhance the capillary motion in the inner layer, thus improve the water transport property of the dual-layer mats, and the water transport property could be further improved by the combination of a base-treated CA outer layer due to push-pull effect. Moreover, the PVDF-rich shell of the inner layer may provide a lubricating effect to enhance the wear comfort.

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Chapter 6

Electrospundual-layer mats with covalently bonded ZnOnanoparticles for moisture wicking and antibacterial textiles

In this work, to improve the water transport behavior, dual-layer nanofibrous nonwoven mats composed of a hydrophilic PAN outer layer and a PVDF inner layer are fabricated by electrospinning. The distinct difference in surface hydrophobicity between the inner and outer layers induces a push-pull effect to transport water from the inner to the outer surface efficiently. To render an antibacterial property, ZnO nanoparticles are covalently attached to the PVDF nanofibers. The good anti-wash properties and anti-bacterial function of the ZnO-PDVF/PAN dual layer mats are demonstrated.

6.1 Introduction

As mentioned in background, antibacterial properties of the sports textiles is a critical issue for comfort and well-being.¹⁻⁵ Since conventional fabrics do not have antibacterial properties, a variety of antibacterial agents have been loaded into fabrics, or attached directly onto the surface of the fabrics to render textiles antibacterial.⁶⁻¹⁴ For example, by simultaneous sonochemical dyeing and coating, antibacterial metal oxide nanoparticles have been coated onto fabrics.¹⁵ To achieve antibacterial properties, polylactide /zinc oxide nanocomposite filaments have been fabricated by a melt-spinning process.¹⁶ Zinc oxide (ZnO) is widely used as an antibacterial agent because it is nontoxic, biosafe and has low cost.¹⁷⁻²¹

In chapter 4, using electrospun nanofibrous mats as model systems, we have proved that the use of dual-layer textiles composed of a hydrophobic inner layer and a hydrophilic outer layer is an effective strategy to achieve good moisture transport property as well as low friction between skin and textile.

It is also worth noting that moisture transport and antibacterial properties are closely related. Textiles with good moisture management properties could provide a drier environment between skin and textiles, and hence lower the speed of bacterial growth. Thus novel design strategies are needed to address both moisture transport and antibacterial issues. In this chapter, for the first time, antibacterial properties are introduced into a push-pull dual-layer mat, which is composed of a thick hydrophilic polyacrylonitrile (PAN) nanofibrous layer and a thin hydrophobic polyvinylidene fluoride (PVDF) nanofibrous layer, by covalent attachment of ZnO nanoparticles onto the PVDF nanofibers. Compared with the approach of loading nanoparticles into the fibers, this approach can increase the direct contact area of the antibacterial agent with the surrounding media, providing a more efficient antibacterial function. Also the covalent bonding between the nanoparticles and the nanofibers can prevent the detachment of the nanoparticles, leading to a more durable antibacterial property while also overcoming the potentially harmful effect of the nanoparticles in contact with skin. More importantly, this

design can give the dual-layer mat both good moisture transport and antibacterial functions. In this chapter, the unique structure and morphology of the hybrid nanofibrous mats are reported, and the resultant good antibacterial, anti-wash, and moisture management properties of the mats are demonstrated.

6.2 Experimental Methods

6.2.1 Chemicals and materials

PAN, PVDF and DMF were introduced in chapter 4 and chapter 5, zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2$), hexamethylenetetramine (HMTA), zinc acetate dihydrate ($\text{Zn}(\text{Ac})_2$), (3-aminopropyl) trimethoxysilane (APTES), 1,3-diaminopropane (DAP), acetone, and ethanol were purchased from Aldrich Chemical Company Inc(USA).

6.2.2 Preparation of cross-linked PVDF nanofibrous mats

Cross-linked PVDF nanofibrous mats were prepared according to the procedure reported by Zhou et al.²² DAP was added into PVDF DMF/acetone solution, followed by magnetic stirring for 1 hour. The solution was electrospun into nonwoven nanofibrous mats on aluminum foil. Electrosinning was carried out for 5 minutes for standard mats and for 3 hours for thick mats. Then the mats were cured in an oven at 120 °C for 1 hour. The mats are denoted as PVDF and PVDF-thick, respectively.

6.2.3 Preparation of ZnO-attached PVDF nanofibrous mats and dual-layer mats

It has been reported that silane-functionalized PVDF nanofibers provide a versatile platform for covalently attaching inorganic oxide nanoparticles (such as SiO_2 , TiO_2 and Al_2O_3) on PVDF nanofibers.¹⁹ In this work, the reported procedure was modified for covalently attaching ZnO. In the first step, PVDF and PVDF-thick were immersed into 10 wt% APTES ethanol solution for 10 hours at 70 °C, to allow the silane group to be grafted on to the surface of the fibers. The resultant fibers are denoted as Si-PVDF and

Si-PVDF-thick. In the second step, the Si-PVDF, PVDF and Si-PVDF-thick fibers were immersed into $\text{Zn}(\text{Ac})_2$ and NaOH blend ethanol solution (0.01 mol/L $\text{Zn}(\text{Ac})_2$ and 0.02mol/L NaOH) for 30 minutes at 60°C, then annealed at 120°C for 10 minutes, and are denoted as seed-Si-PVDF, seed-PVDF and seed-Si-PVDF-thick. In the third step, seed-Si-PVDF and seed-PVDF were immersed in the $\text{Zn}(\text{NO}_3)_2$, and HMTA blend solution(0.05mol/L ZnNO_3 and 0.05mol/L HTMA) for 1hour, then rinsed and dried at 60°C for 2hours, and are denoted as ZnO-PVDF and ZnO-PVDF-no Silane. Using the same route, seed-Si-PVDF-thick were immersed in the $\text{Zn}(\text{NO}_3)_2$, and HMTA blend solution (0.05mol/L ZnNO_3 and 0.05mol/L HTMA) for 0.5hour, 1hour and 3hours, then rinsed and dried at 60°C for 2hours.They are denoted as 0.5-ZnO-PVDF-thick, 1-ZnO-PVDF-thick and 3-ZnO-PVDF-thick.

PAN solution in DMF (7 wt% PAN) was prepared by dissolving PAN powder in DMF under continuous magnetic stirring. Then the PAN solution was electrospun into nonwoven nanofibrous mats for 1.5 hours, using the setup mentioned above. The ZnO-PVDF was peeled off from the aluminum foil, and the PAN mats were collected on the front side (on which the ZnO NPs were attached), backside of ZnO-PVDF fibers and on aluminum foil (denoted as PAN) respectively. Then the double-layer mats consisting of PAN nanofibrous mat (around 80 μm) and ZnO-PVDF (around 5 μm) were laminated using a paper laminator (PRO BiO 320) at 70°C and a rolling speed of 50 rpm. These are denoted as PVDF-ZnO/PAN (PAN eletrospun on the front side of ZnO-PVDF) and ZnO-PVDF/PAN (PAN electrospun on the backside of ZnO-PVDF) respectively.

6.2.4 Characterization

Morphologies of the samples were observed using a field-emission scanning electron microscopy (FESEM, JEOL 7600F) mentioned in chapter 4. XRD tests were conducted using a XRD-6000 Shimadzu diffractometer. Moisture transport ability of the samples was measured using a Moisture Management Tester. FTIR spectroscopy was recorded using a PerkinElmer (Frontier) spectrometer. Contact angles of the samples were measured using a contact angle tester (dataphysics, OCA 15 PRO). The procedures of

anti-washing are introduced in chapter 4. To test the antibacterial property of the mats, the bacterial cultures of *E. coli*-K12 (Wild Type) were prepared in 100ml LB Broth, Miller, inoculated and incubated at 37 °C overnight. LB Agar plates were seeded with 1ml of overnight culture. Discs of test material were placed onto plates and incubated at 37 °C overnight. Then, the plates were taken out for observation. The inhibition zones of the samples are checked and the morphology of the samples is obtained from FESEM.

6.3 Results and Discussion

In this work, both PAN and PVDF nanofibers were prepared by electrospinning, while ZnO nanoparticles were covalently attached onto the surface of the electrospun PVDF nanofibers to form hybrid mats through a sol-gel-based process, as shown in Figure 6.1. The PVDF nanofibrous mats were cross-linked in order to improve their structural integrity for facilitating the sol-gel reaction. The combination of the hybrid and PAN mats by a simple laminating process gave ZnO-PVDF/PAN dual-layer mats. In order to illustrate the properties of the ZnO-PVDF/PAN dual-layer mats, some reference samples were also prepared. The sample preparation conditions and their names are summarized in Table 6.1.

Figure 7.1 Preparation of ZnO-PVDF/PAN dual-layer mats.

Table 6.1 The sample names and their preparation conditions

Sample Name	Polymer	Spinning time	Silane attachment	Seeding	Sol-gel time	Single/ Dual-layer
PVDF-thick	PVDF	3 hr	No	No	-	Single layer
Si-PVDF-thick	PVDF	3 hr	Yes	No	-	Single layer
seed-Si-PVDF-thick	PVDF	3 hr	Yes	Yes	-	Single layer
0.5-ZnO-PVDF-thick	PVDF	3 hr	Yes	Yes	0.5 hr	Single layer
1-ZnO-PVDF-thick	PVDF	3 hr	Yes	Yes	1 hr	Single layer
3-ZnO-PVDF-thick	PVDF	3 hr	Yes	Yes	3 hr	Single layer
PVDF	PVDF	5 min	No	No	-	Single layer
ZnO-PVDF	PVDF	5 min	Yes	Yes	1 hr	Single layer
ZnO/PVDF-no silane	PVDF	5 min	No	Yes	1 hr	Single layer
PAN	PAN	1.5 hr	No	No	-	Single layer
ZnO-PVDF/PAN	PVDF	5 m + 1.5 h	Yes	Yes	1 hr	Dual-layer
PVDF-ZnO/PAN	PVDF	5 m + 1.5 h	Yes	Yes	1 hr	Dual-layer

6.3.1 Structure and morphology of the PVDF nanofibrous mats with covalently attached ZnO

To confirm the successful preparation of ZnO-PVDF hybrid mats, following the preparation route, the morphologies of the nanofibrous mats were observed step by step. As shown in Figs. 6.2a-c, the morphology of the mats does not show any obvious change after the attachment of silane, and the coating of the ZnO seed layer. The attachment of silane groups and the seeding layer were confirmed by FTIR (Fig. 6.3). After the sol-gel reaction, a large amount of ZnO nanoparticles are attached onto the nanofibers. With the increase of the sol-gel reaction time, the ZnO nanoparticles gradually grow into nanorods. The EDX results in Table 6.2 show the increases of both Zn and O contents with the reaction time, corroborating the SEM observation.

Figure 6.2 FESEM micrographs showing the morphologies of (a) PVDF-thick, (b) Si-PVDF-thick, (c) seed-Si-PVDF-thick, (d) 0.5-ZnO-PVDF-thick, (e) 1-ZnO-PVDF-thick and (f) 3-ZnO-PVDF-thick mats.

Figure 6.3 FTIR spectra of PVDF-thick, Si-PVDF-thick and seed-Si-PVDF-thick mats.

Table 6.2 EDX results of 0.5-ZnO-PVDF-thick, 1-ZnO-PVDF-thick and 3-ZnO-PVDF-thick mats

Samples	Zn	Atomic (%)	Zn/F	O/F
0.5-ZnO-PVDF-thick		0.82	0.02	0.06
1-ZnO-PVDF-thick		1.94	0.04	0.06
3-ZnO-PVDF-thick		24.20	0.92	0.90

Since the overgrowth of ZnO nanorods may block pores in the hybrid mats, hindering moisture wicking in the mats, in the following experiments, the time for the sol-gel reaction was fixed at 1 hour. After 1-hour reaction time, the PVDF fibers are fully covered by the ZnO nanoparticles, and the pores between the nanofibers are not blocked by the nanoparticles. The XRD analysis of 1-ZnO-PVDF-thick mats was also conducted and the result is shown in Figure 6.4. In the XRD pattern, all of the characteristic peaks of ZnO can be observed, verifying the presence of ZnO nanoparticles on the PVDF mat.

Figure 6.4 XRD result of 1-ZnO-PVDF-thick mat.

6.3.2 Anti-bacterial properties of the hybrid mats

To investigate the effectiveness of this approach in bringing about anti-bacterial property, we firstly fabricated thick PVDF nanofibrous mats (about 150 μm thick) and attached ZnO nanoparticles onto the mats by suspending the mats in sol-gel solution for different times. The antibacterial properties of Si-PVDF-thick, 0.5-ZnO-PVDF-thick, 1-ZnO-PVDF-thick and 3-ZnO-PVDF-thick mats are shown in Fig. 6.5. Three samples of each condition have been analyzed. The zones of the three samples in the same condition are similar. It can be seen that without ZnO attachment, the PVDF mat does not show any antibacterial property, and there are plenty of bacteria on the surface of the PVDF mat. With the attachment of ZnO nanoparticles, bacteria are not visible on the surfaces of the hybrid mats, and the inhibition zone becomes larger with the increase of the ZnO content. This indicates that the surface-attached ZnO nanoparticles are an effective anti-bacterial agent.

Figure 6.5 Inhibition zone of (a) Si-PVDF-thick, (b) 0.5-ZnO-PVDF-thick, (c) 1-ZnO-PVDF-thick, (d) 3-ZnO-PVDF-thick mats.

In our design, the ZnO-attached PVDF mats are used as the hydrophobic inner layer of the dual-layer mat, and the hydrophobic layer should be fairly thin in order to let the moisture pass through it quickly. Thus, thin hybrid mats (ZnO-PVDF, about 5 μ m thick) were fabricated. In order to prevent folding of the mat and achieve uniform attachment of the ZnO nanoparticles on the PVDF mat in the sol-gel reaction, the mats collected on aluminum foils were directly suspended in the sol-gel solution for reaction for 1 hr. The side that is fully exposed to the reaction solution is denoted as the front side, while the side stuck to the aluminum foil is denoted as the backside. The morphologies of the front side and the backside of ZnO-PVDF are shown in Figs. 6.6a and 6.6b. It can be seen that on the front side, the ZnO nanoparticles are uniformly attached on the nanofibers, while on the backside there is almost no ZnO nanoparticles on the fibers, implying that although the thickness of mat is fairly small, the reaction solution cannot effectively reach the backside of the mat. Thus, the properties of the two sides will be different. As shown in Figs 6.6c and 6.6d, for both the front and back side, the inhibition zone is not

very clear because the amount of ZnO present in this very thin modified layer is very small. In addition, different from other types of antibacterial agents, herein the ZnO nanoparticles are covalently bonded to the mats, so very little ZnO could diffuse into the culture medium. Nevertheless, these mats are distinctly different from the neat PVDF mat because no bacterium is visible on either the front or the back sides of the ZnO-PVDF mat. Thus, to further confirm the anti-bacterial property of the ZnO-PVDF mat, the surfaces after the antibacterial test were observed under FESEM to check the presence of bacteria, and the results are shown in Figs. 6.6e and 6.6f. It can be seen that there are no bacteria on both sides of the ZnO-PVDF mats, indicating that a very thin ZnO-attached PVDF nanofibrous layer is effective to prevent bacterial growth on the mat. In the experiment, the nanofibrous mats are observed by FESEM without washing after the antibacterial test. The surface of the nanofibers is largely covered with the residues of the culture in the test. Therefore the ZnO nanoparticles on the nanofibers are not obvious after the test.

Figure 6.6 FESEM micrographs showing the morphologies of (a) front side of ZnO-PVDF, (b) backside of ZnO-PVDF, inhibition zone of (c) front side of ZnO-PVDF, (d) backside of ZnO-PVDF, and the morphologies of (e) front side of ZnO-PVDF and (f) backside of ZnO-PVDF after antibacterial test.

6.3.3 Anti-washing property

Since detachment of ZnO nanoparticles from the mats would reduce the antibacterial properties of the mats, and the detached nanoparticles may also give rise to potential health risks, a good anti-wash property is one of the key criteria for textile applications. In this study, ZnO is covalently attached onto silane-functionalized PVDF to enhance the anti-wash property. To verify the effectiveness of this method, the ZnO-attached silane-functionalized PVDF (ZnO-PVDF) and ZnO-coated unfunctionalized PVDF (ZnO/PVDF-no silane) mats were washed for 20 hours and 40 hours, respectively, and then observed using FESEM. As shown in Fig. 6.7, the ZnO nanoparticles attached onto the silane-functionalized PVDF can survive well during a 40-hour wash in a detergent solution with continual shaking. However, for the ZnO/PVDF-no silane mat, although ZnO nanoparticles initially cover the whole surface of the nanofibrous mat, they are washed away after 20-hr of washing and almost disappear completely after 40-hr of washing, presumably due to the lack of strong covalent bonds between the nanoparticles and nanofibers. With severe washing in the detergent solution, the PVDF nanofibers also aggregate together, forming big lumps (Fig. 6.7c), after the ZnO layer was lost.

Figure 6.7 FESEM micrographs showing the morphologies of (a) ZnO/PVDF-no silane, (b) ZnO/PVDF-no silane after washing for 20 hrs, (c) ZnO/PVDF-no silane after washing for 40 hrs, (d) ZnO-PVDF, (e) ZnO-PVDF after washing for 20 hrs, and (f) ZnO-PVDF after washing for 40 hrs.

The good anti-wash property provided by the covalent bonding is further verified by the XRD results shown in Fig.6.8. Compared with the results shown in Fig. 6.4, most characteristic peaks of ZnO, except (101), are not visible due to the very thin nature of the ZnO-PVDF mat. After washing for 20 and 40 hours respectively, the weak (101) peak of ZnO can still be observed, again suggesting the strong bonding between the nanoparticles and nanofibers. Thus, this robust thin hybrid mat was used to fabricate ZnO-PVDF/PAN (back side next to PAN layer) and PVDF-ZnO/PAN (front side next to PAN layer) dual-layer mats.

Figure 6.8 XRD patterns of ZnO-PVDF before washing, after washing for 20 and 40 hrs, respectively.

6.3.4 Properties of the dual-layer mats

To study the moisture transport properties of the dual-layer nanofibrous mats, the wettability of the mats and their components should be investigated first. Thus the time-dependent apparent contact angles of these samples were tested first. Usually, the time-dependent contact angle is determined by both water spreading on the testing surface and penetrating into the pores of the mats. The images in Figure 6.9a show the changes of the apparent contact angles with time, and the test results are summarized in Figure 6.9b. The neat PVDF mat is very hydrophobic. During the test, although a small amount of water could penetrate into the PVDF mats very slowly and hence the volume of the droplet decreases slightly, the droplet cannot spread on the surface of the PVDF mat at all (Fig. 6.9a(i)) owing to the high hydrophobicity of PVDF. The apparent contact angle of the PVDF mat is almost a constant in the test period of ten minutes. By contrast, PAN is hydrophilic and hence the water could both spread on the surface and penetrate into the mats, causing it to disappear in less than 3 seconds (Fig. 6.9a (ii)). As already mentioned,

the thin ZnO-PVDF mat has two distinctly different sides, one consists of PVDF nanofibers fully covered with ZnO nanoparticles (ZnO side) while the other consists of neat PVDF nanofibers (PVDF side). The ZnO side is more hydrophilic, and the water droplet could penetrate into the mat in 100 seconds (Fig. 6.9a(iii)). When a PAN layer is added at the bottom to form a ZnO/PVDF/PAN dual-layer mat, the water could penetrate into the mat faster due to the push-pull effect induced by the difference in hydrophilicity of the two layers. This is evident from the quicker reduction in volume of the water from the surface (Fig. 6.9a(iv)). However, the time dependent behavior of the apparent contact angle of the dual layer mat is almost identical to that of the ZnO-PVDF single-layer mat with the ZnO side on top (Fig. 6.9b). By contrast, the wettability of the ZnO-PVDF single-layer mat with the PVDF side on top is close to that of the neat PVDF film, i.e., the droplet penetrates into the mats very slowly (in nearly 7 minutes, Fig. 6.9a(v)). In addition, when a PAN layer is added at the bottom to form a PVDF-ZnO/PAN dual-layer mat, the time dependent behavior of the apparent contact angle of this dual layer mat is quite different from that of the ZnO-PVDF single-layer mat with the PVDF side on top; the water could penetrate into the PVDF-ZnO/PAN mat much faster, in only 140 seconds. It means that after combination with a hydrophilic PAN mat, the push-pull effect induced by the difference in hydrophilicity of the two layers becomes more significant.

Figure 6.9 Time-dependent contact angle of front side and backside of ZnO-PVDF, PVDF, PAN, PVDF-ZnO/PAN and ZnO/PVDF/PAN.

However, the apparent contact angle measurements cannot thoroughly show the water

transport behaviour, because for a hydrophobic surface like PVDF, as shown in Figure 6.9a, as a part of the water penetrated into the mats, the droplet on the surface shrunk but the contact angle remained the same. Thus, the MMT tester is needed to further study the water transport property of the dual-layer mats.

Figure 6.10 MMT results of (a) ZnO/PVDF/PAN and (b) PVDF-ZnO/PAN mats. For both, PAN is the bottom layer.

The MMT results of the ZnO/PVDF/PAN and PVDF-ZnO/PAN dual-layer mats are shown in Fig. 6.10. For the ZnO/PVDF/PAN mat, since the top surface has reasonably good wettability owing to the attachment of ZnO nanoparticles on PVDF, water could wet the surface quickly. The bottom layer is made of PAN nanofibers, which are more hydrophilic than the top layer. Water can hence be pulled from the top to the bottom layer quickly. Therefore, the water content of the bottom surface is much higher, demonstrating the push-pull effect. For the PVDF-ZnO/PAN mat, since the top surface is mainly made of PVDF which is more hydrophobic than ZnO, water could not penetrate into the mats very quickly due to the poor wettability and the lotus effect. As a result, the water content of the top surface is fairly high at the beginning. After around 80 seconds, water penetrates into the mats and the water content of the top layer starts to reduce, until the water content of the top layer is much lower than that of the bottom layer. The MMT results are consistent with the results of time-dependent contact angle measurements, indicating that the ZnO/PVDF/PAN mats have better moisture transport properties than the PVDF-ZnO/PAN mats. Thus, for dual-layer mats, antibacterial tests were only

conducted for ZnO-PVDF/PAN mats.

The antibacterial properties of ZnO/PVDF/PAN dual-layer mats were tested with neat PVDF and PAN mats as controls. The inhibition zone of the dual-layer mats could not be observed clearly, as found for the corresponding single-layer ZnO/PVDF mats (Figs. 6.6c and 6.6d). Thus, to verify the antibacterial properties of the dual-layer mats, they were observed under FESEM after the antibacterial tests. As shown in Figs. 6.11a and 6.11b, the surfaces of neat PVDF and PAN mats are completely covered by bacteria after the antibacterial tests, showing that they do not have any antibacterial property. By contrast, there are no bacteria on both sides of the ZnO-PVDF/PAN mat (Figs. 6.11c and 6.11d). The E.Coli is elliptical, and the size is around $0.5\text{ }\mu\text{m} \times 1\text{ }\mu\text{m}$ to $0.5\text{ }\mu\text{m} \times 3\text{ }\mu\text{m}$, and is closely stacked on the nanofibrous mats which are not boned with antibacterial agent. Thus, it can be observed in SEM image. Another SEM image with lower magnification showing the morphology of the bacteria at different area of neat PVDF nanofibrous mat is shown in Figure 6.12, in which the bacteria can be observed more clearly. The observations indicate that the ZnO-PVDF/PAN mats exhibit reasonably good antibacterial properties.

Figure 6.11 FESEM micrographs showing the morphologies of (a) PVDF, (b) PAN, (c) ZnO-PVDF/PAN (PVDF side), (d) ZnO/PVDF/PAN (PAN side) mats after antibacterial test.

Figure 6.12 FESEM micrographs showing the morphologies of PVDF mats after antibacterial test.

6.4 Conclusions

In this work, dual-layer nanofibrous mats composed of a thick hydrophilic PAN nanofibrous layer and a hydrophobic PVDF nanofibrous layer with covalently attached ZnO nanoparticles are designed and fabricated. The antibacterial property of the dual-layer mats rendered by the surface-located ZnO nanoparticles is verified, and it is found that the hybrid mats with covalently bonded ZnO nanoparticles have good anti-wash properties. The dual layer mats also show good moisture transport properties and

therefore could provide a drier environment between the skin and textile, which can enhance the wear comfort and reduce the growth of bacteria.

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Chapter 7

Conclusions and Future Work

In this chapter, the threads of the whole thesis are drawn together by summarizing the results obtained. The main findings are discussed with respect to the hypotheses. It is found that: (1) the capillary motion in the mats is significantly facilitated by decreasing the pore size or increasing the surface hydrophilicity of the mats, and the water transport property of the mats are further enhanced by push-pull effect; (2) core-shell nanofibers with a PAN-rich core and a PVDF-rich shell as the inner layer could lower the friction between the textile and skin, at the same time keep good water transport property of the mats; (3) ZnO nanoparticles could be covalently introduced into dual-layer system as an effective and durable anti-bacterial agent. Thus, the hypotheses raised in chapter 1 are verified. Based on the results and verified hypotheses, future research directions are suggested.

7.1 Result summary and validation of hypotheses

In this PhD research, model sports textiles are designed and fabricated as testbed to achieve dual-functionalities, i.e., good moisture transport property with low friction with skin or antibacterial property. To achieve the objectives, dual-layer textiles which consist of a thin hydrophobic electrospun inner layer and a thick hydrophilic electrospun outer layer are fabricated. In our hypotheses, the hydrophobic inner layer ensures low water absorption and transmission of sweat via capillary motion, while the hydrophilic outer layer draws the sweat out from the inner layer and facilitates evaporation to the surrounding environment. In our design, the model textiles are fabricated by electrospinning, because the electrospun nanofibers have large specific surface area due to a lot of interpenetrating pores both inside and between the nanofibers, which could facilitate both the capillary motion and effect of surface modification and incorporation of functional materials. Also, to let the moisture transport away fast, fairly thin hydrophobic inner layers could be achieved by electrospinning because it could control the thickness accurately. Therefore, the electrospun nanofibrous mat is a perfect substrate to achieve good moisture transport property and dual-functions.

7.1.1 The enhancement of moisture transport property of the textile

The first hypothesis was that the moisture transport property of the textile could be improved by facilitating the capillary motion in the textile. According to the mechanism of capillary motion, it could be facilitated by decreasing the pore size or increasing the surface hydrophilicity.

To validate the hypothesis and enhance the capillary motion in the textile, dual-layer mats composed of a thick layer of hydrophilic PAN nanofibers and a thin layer of hydrophobic PS nanofibers with and without interpenetrating nanopores are fabricated respectively. Then the mats are coated with PDOPA to different extents to tailor the water wettability of the PS layer. The water transport behavior of the mats is observed and compared.

It is found that with a large quantity of nanochannels, the porous PS nanofibers exhibit a

stronger capillary effect than the solid PS nanofibers. The capillary motion in the porous PS nanofibers can be further enhanced by slight surface modification with PDOPA while retaining the large hydrophilicity difference between the two layers, inducing a strong push-pull effect to transport water from the PS to the PAN layer. Thus the first hypothesis in the PhD. researches is validated.

7.1.2 The lower the friction between the skin and textile

The second hypothesis was that the good moisture transport property of the textile and the lower friction between the textile and skin could be achieved at the same time. Since the friction between the textile and the skin is also influenced by the hydration of the skin, the textile with good moisture transport property could provide a drier environment between skin and textile to lower the friction.

To validate the hypothesis, in our design, both of the hydration of the skin and the chemical component of textiles are modified. Core-shell nanofibers with a PAN-rich core and a PVDF-rich shell are fabricated by single-spinneret electrospinning and used as the inner layer of the dual-layer mats, and the moisture transport property and the coefficient of friction of the textile are measured. The results show that the dual-layer textile has good moisture transport property and the inner layer of the textile has lower friction with the skin, because the PAN in the inner layer could increase the wettability of the layer, thus improve the capillary effect, and the PVDF-rich shell could lower the friction between the textile and the skin. The synergistic combination of a considerably hydrophobic PAN/PVDF inner layer and a highly hydrophilic CA outer layer induces a strong push-pull effect, resulting in efficient moisture-wicking. Thus, the second hypothesis in the PhD. researches is validated.

7.1.3 The introduction of antibacterial property to the textile

The third hypothesis was that the good moisture transport property and antibacterial property of textile could be achieved at the same time by incorporation of antibacterial

nanoparticles agent, and the exposed nanoparticles have good anti-wash property due to their covalently attachment with the textile.

To validate the hypothesis, dual-layer nanofibrous nonwoven mats that composed of hydrophilic PAN outer layer and hydrophobic ethoxysilane-functionalized cross-linked PVDF inner layer were fabricated, and zinc oxide (ZnO) NPs were covalently attached on the surface of PVDF. According to results of related tests, the dual-layer mats have good moisture transport property, and the antibacterial property of the dual-layer mats rendered by the surface located and exposed ZnO NPs is also verified. The covalently bonded ZnO NPs show good anti-wash property, thus the potential health risk caused by the detachment of the NPs could be avoided. So, the third hypothesis in the PhD. researches is validated.

7.1.4 Overall conclusion

In my PhD study, the electrospinning-derived nanofibrous mats are used as model dual-layer sports textiles. The capillary motion in the mats is significantly facilitated by decreasing the pore size or increasing the surface hydrophilicity of the mats, and the water transport property of the mats are further enhanced by push-pull effect. Core-shell nanofibers with a PAN-rich core and a PVDF-rich shell as the inner layer could lower the friction between the textile and skin, at the same time keep good water transport property of the mats. Also, ZnO nanoparticles could be covalently introduced into dual-layer system as an effective and durable anti-bacterial agent. Thus, the hypotheses raised in chapter 1 are verified.

7.2 Implications of the work

In the PhD study, for the first time dual-layer electrospinning-derived nanofibrous mats have been fabricated to investigate liquid moisture transport behaviors through the electrospun mats. The work presented in this thesis proves that the moisture transport property of the mats could be enhanced by both improving the capillary motion in the

mats and inducing push-pull effect between the two layers, and the capillary action in the mats could be significantly enhanced by creating nanopores inside the electrospun nanofibers and improving the surface hydrophilicity of nanopore surface. This design concept has great potential to be applied to ticker textile fibres for development of advanced moisture wicking sports textile.

The results of our study also show that core-shell nanofibers with a PAN-rich core and a PVDF-rich shell have low friction with skin and will not hinder the moisture transport. Again, this is readily applicable strategy for fabricating low-friction textiles with thicker fibers because some degree of migration of PVDF to fiber surface is expected in conventional fiber spinning process as well.

Also, ZnO nanoparticles could be covalently attached on silane-functionalized PVDF nanofibers and be used as an effective and durable anti-bacterial agent. The method may be used to create antibacterial sports textiles or antibacterial porous mat for other applications.

7.3 Suggested future work

7.3.1 Introduction of polymer nanofibrous mats onto conventional fabrics

In these PhD researches, dual-layer textiles composed of a thin hydrophobic electrospun inner layer and a thick hydrophilic electrospun outer layer are designed and fabricated. By now, the research is focus on the design and the surface modification of the inner layer material next to skin. Theoretically, the double layered structure composed of an electrospun hydrophobic mat as inner layer and a hydrophilic conventional fabric as outer layer is expected to have better moisture transport capability, because the conventional hydrophobic fabrics can be much more hydrophilic and thicker than the electrospun hydrophilic mat and induce higher power to pull moisture out. Such double layer is also supposed to have better mechanical property due to the thicker fabric layer.

In order to obtain PVDF and fabric double layered structure, wet phase inversion process³⁻⁷ and lamination are normally used. In the preliminary work, the lamination of a PVDF layer and a cotton fabric layer was attempted but failed. The two layers could not adhere to each other well. Therefore, the PDOPA-assisted lamination will be attempted in the future work. Mussel-inspired surface modification has been developed as a facile method for coating of various organic and inorganic substrates. This method is based on oxidative polymerization of dopamine into PDOPA, and non-covalent bonds, such as hydrogen bonding and p-p stacking between the PDOPA and the matrices.⁸⁻¹¹ PDOPA coatings can generate a highly stable adhesive polymer layer on the surface of a broad range of materials, including metal, metal oxide, polymer, ceramics, and biological cells. It is also reported that the introducing of PDOPA could impressively enhance the UV resistance of the material owing to the radical scavenging capability of the polydopamine.¹²

PVDF nanofibers will be firstly coated with PDOPA thin layer via self-polymerization of dopamine. The adhesion capability of PDOPA-coated PVDF layer onto fabric layer as well as the moisture transport of the formed double layers will be investigated. The mechanical, friction and UV resistance properties of the multi-layer textile will be measured as well. It is expected that a multi-functional textile with good moisture transport property, good mechanical property, lower friction to skin and low UV penetration may be obtained due to strong affinity of PDOPA to solid surfaces, UV blocking function of PDOPA layer, as well as possible effect of PDOPA's hydrophilicity on the moisture transport of the system.

7.3.2 Melt-electrospun porous microfiber

As mentioned in Chapter 2, recently, the fabrics made from microfibers are investigated by various researchers to improve the wear comfort, and such fabrics are already widely

used for cleaning cloth in hospital,^{13, 14} and also have been used in sports textile industries. Due to the high surface to volume ratio. Also, the fabrics made from microfibers have stronger capillary motion than normal fabric and could release the moisture faster, which makes them fabrics with good moisture transport property. Also, compared with nanofibers used in my PhD study, the microfibers have better mechanical property, thus the microfibers have great potential to be fabricated as freestanding sports textile.

In my PhD study, porous nanofibers are fabricated by solution electrospinning. While, the porous microfibers could be fabricated by melt electrospinning. In the melt electrospinning process, the polymer is heated in a chamber until the polymer melts or softens. The viscosity of the melt polymer must be low enough for the electrospinning to form microfibers from the Taylor cone.^{15, 16} Compared with solution, there are much less polymers could be melt electrospun into fibers, thus the research on melt electrospinning is not as much as on solution electrospinning. However, the melt electrospinning possesses its own advantages. On one hand, during the electrospinning, the viscosity of the melted polymer is higher and the surface charge of the melted polymer is lower, the diameter of the fibers is much thicker. Thus, the melt electrospun microfibers do not need to be combined with other traditional fabrics. On the other hand, melt electrospinning enables better control of topography compared to solution electrospinning.¹⁷⁻¹⁹ Therefore, the pores could be more uniformly created on the melt electrospun fibers, and the hydrophilization of the microfibers via surface modification and the introduction of covalently bonded antibacterial and UV protection materials will be more effective.²⁰

In conclusion, the melt electrospun porous microfibers have good potential to achieve good moisture management property as well as good mechanical property, and could be perfect substrates to incorporate functional materials on it.

7.3.3 The fabrication and application of oriented nanofibers

In typical solution electrospinning experiment, the nanofibers are collected disorderly to form a non-woven mat on the collector. Recently, some researchers have focused on the

fabrication of electrospun nanofibers with good orientation. It has been reported that the aligned nanofibers not only have better mechanical strength, but also can increase the sheet resistance for opto-electronics²¹, enhance sensitivity for sensors²² and improve conductivity for fuel cell membranes.²³ In my project, the aligned nanofibers may enhance the water transport by faster water spreading in the hydrophobic inner layer, and several methods have already been used to fabricate the nanofibers with good alignment.

In the first route, the nanofibers were collected on a uniaxially aligned rotating drum. The preliminary results show that the nanofibers are better-aligned at a higher rotating speed of the drum. The morphology of the nanofibers deposited on the drum rotating at 50rpm is shown in Figure 7.1.

Figure 8.1 Nanofibers deposited on the rotating drum.

In the second route, the nanofibers were collected on two pieces of iron sheets. The preliminary results show that the nanofibers are better-aligned when the distance between the two pieces of iron sheets is shorter. The morphology of the nanofibers deposited between the iron sheets with a distance of 10cm is shown in Figure 7.2.

Figure 7.2 Nanofibers deposited between two pieces of iron sheets.

In the third route, the nanofibers were collected in swirl of the stirred water. The rotating speed of the stir bar was adjusted to make the swirl stable and let the nanofibers deposited on the swirl. The morphology of the nanofibers is shown in Figure 7.3.

Figure 7.3 Nanofibers deposited on the swirl.

In our preliminary results, it seems that the nanofibers deposited on the swirl shows better alignment than others, and it is believed that the influence of the aligned nanofibers exert on the mechanical and moisture transport property of the textile is worth to be studied in the future research.

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Publication List

1. Y. Dong, J. Kong (discusses the experiment results with Y. Dong and revised the manuscript), S. Phua (discusses the FTIR experiment with Y. Dong), C. Zhao (discusses the SEM experiment with Y. Dong), N. L. Thomas(co-supervisor, checked the language and revised the manuscript)and X. Lu(supervisor, helped to design the route, analyze the results and revised the manuscript), “Tailoring Surface Hydrophilicity of Porous Electrospun Nanofibers to Enhance Capillary and Push–Pull Effects for Moisture Wicking”, *ACS Applied Materials & Interfaces*, 2014, 6(16), 14087-14095.
2. Y. Dong, J. Kong(discusses the experiment results with Y. Dong), C. Mu, C(discusses the friction test with Y. Dong). Zhao, C(discusses the SEM experiment with Y. Dong). N. L. Thomas(co-supervisor, checked the language and revised the manuscript)and X. Lu(supervisor, helped to design the route, analyze the results and revised the manuscript), “Materials Design towards Sport Textiles with Low-Friction and Moisture-Wicking Dual Functions”, *Materials & Design* 2015, 88, 82-87.
3. Y. Dong, N. L. Thomas (co-supervisor, checked the language and revised the manuscript), X. Lu(supervisor, helped to design the route, analyze the results and revised the manuscript), Electrospun Dual-Layer Mats with Covalently Bonded ZnO Nanoparticles for Moisture Wicking and Antibacterial Textile, *Materials & Design* 2017, 134, 54-63.
4. C. Zhao, J. Kong, X. Yao, X. Tang,Y. Dong, S. Phuaand X. Lu, “Thin MoS₂Nanoflakes Encapsulated in Carbon Nanofibers as High-Performance Anodes for Lithium-Ion Batteries”, *ACS Applied Materials & Interfaces*,2014, 6(9). 6392-6398