Superhydrophobic coating and directional water transport fabrics

by

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Submitted in fulfilment of the requirements for the degree of

Doctor of Philosophy

Deakin University

April, 2016
I am the author of the thesis entitled

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PUBLICATIONS ARISING FROM THIS THESIS

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Abstract

Fabrics with directional water transport ability show intriguing science underpinning the phenomena and exciting applications. However, the fabrication, theoretical understanding and applications of those fabrics have very limited study. This overall aim of this PhD project was to develop directional water transport fabrics through turning the surface wettability using a single-side coating technology. The experimental works consisted of three main parts. In this first part, a coating material was identified to prepare hydrophobic fabrics. A commercial photoresist (SU-8) was chosen to prepare coating solution. When a coating solution comprising SU-8, a fluorinated alkyl silane and silica nanoparticles, it can make hydrophilic fabric such as cotton fabric, have superhydrophobic surface, and the hydrophobicity had a very low contact angle hysteresis (water contact angle as high as 163° and a sliding angle as low as 2°). The coating was durable enough to withstand 100 cycles laundry. It also had excellent stability against long hour immersion in organic solvents, and acid and base solutions.

In this second part, directional water transport fabrics were prepared and the water transport mechanism was examined. A novel method was developed to apply SU-8 on one side of a hydrophilic fabric. Factors such as the loading capacity of SU-8 on fabric, the coating layer thickness and wettability changes after coating were examine to understand their effect on directional water transport property. The results shown that coating thickness is a critical factor deciding water transport mode. By adjusting the SU-8 loading capacity, the coating thickness and wettability would be changed. The fabric with different SU-8 coating thickness could show bidirectional, unidirectional, or non-permeable features to water. A possible mechanism of this directional water transport phenomenon has been proposed.
In this last part, heat transport properties of the SU-8 treated directional water transport fabric was studied. Since the directional water transport fabric showed different wettability on the two fabric sides, the SU-8 layer had a significantly influence on moisture transport ability of the treated fabric, and the heat transport showed a dramatic difference between dry and wet conditions. When the treated fabric is dried, the heat transfer through the coated fabric layer is faster than that through the uncoated layer due to the effect of SU-8. And the loading capacity of the coated layer only has a small influence on the heat transfer speed. When the fabrics were per-loaded with a small amount of 37 °C water, the heat transfer property was further enhanced.

This thesis consists of seven chapters. Chapter 1 describes the aims, subject and significance of this PhD research project. Chapter 2 reviews the research progress in superhydrophobic coatings, directional liquid transport fabrics and the moisture and heat transport ability of fabrics. Chapter 3 introduces the materials, characterisation methods and the procedures for preparing coating solutions and fabric coatings. Chapter 4 detailed results about the preparation of durable superhydrophobic fabrics using a negative photoresist. Chapter 5 reports on the preparation of fabrics with unidirectional water transport ability using a single-side electro-spraying technology. The directional water transport mechanism is also elucidated in the chapter. Chapter 6 describes the heat transfer properties of the directional water transport fabric under dry and wet states. Chapter 7 summarises the conclusions obtained from this research work. Suggestions for future research in this area are also proposed.
Chapter 1

Introduction

1.1 Significance and research questions

Superhydrophobic surfaces with high water repellency and low contact angle hysteresis (typically $< 10^\circ$) often have a bio-mimicking self-cleaning property. Fabrics with such a self-cleaning ability are very useful for making water-proof garments, fire-retardant clothes, personal protection clothing, soldiers’ uniform garments and work wears. The majority of self-cleaning, superhydrophobic fabrics are prepared by forming nano-/micro-scaled rough surface and by decreasing the surface free energy. There are many techniques including wet-chemical coating (e.g. dip-coating, sol-gel process and spin-coating), surface deposition (gas phase deposition, plasma, electrostatic assembly and magnet-induced assembly), and electrospinning for making superhydrophobic fabrics, however, wet-chemical coating is the most widely used because of the low cost, good homogeneity, and easy preparation on large scale. Also for practical and some industrial applications, washing durability, chemical stability and solvent resistance are vital.

Directional water motion (also referred to as “one-way” water motion) guided by structure and/or surface feature has been observed in nature on plants and insects. Recently, fabrics capable of unidirectionally transporting water across the thickness have been reported. Two main strategies have been developed to prepare directional water transport fabrics:

1) Creating a hydrophobicity-to-hydrophilicity gradient through fabric thickness, and
2) Combining a layer of hydrophobic fibres with a layer of hydrophilic fibres.

However, most of the studies only reported the qualitative results of directional water transport. The lack of quantitative measure makes it hard to assess directional water transport.
quality. In addition, washing durability is an important feature for practical applications of functional textiles, but little is reported on the directional water transport fabrics. Apart from experiment development, theoretical understanding of directional water transport fabrics has not been clear. Directional water transport through fabrics is ascribed to isotropic wettability along the fabric thickness. Directional water transport fabrics show difference in water breakthrough pressure on the two fabric sides. However, the lack of effective technique to precisely control the coating layer thickness has confined the study on the role of hydrophobic layer thickness in forming directional water transport on conventional fabrics. Nevertheless, the relationship and the mechanism between the directional water transport phenomenon and the hydrophobic layer thickness has not been clear.

Heat and moisture transfer in textiles is of growing interest for researchers as they are of extreme importance for active wears, sportswear and summer clothing design. It is therefore important to optimize the properties of fabrics so as to maximized the sweat transmission through the skin surface and minimize the metabolic heat loss of human body. However, the mechanisms of heat and moisture transfers in porous media are complicated. Heat transfer theory often involves three main routes—heat transfer by conduction, heat transfer by convection; and heat transfer by radiation, and it is generally accepted that heat transfer via conduction is more significant than the other two methods. Multifunctional fabrics having both directional sweat/moisture transfer ability and reduced heat loss from the body are highly desired but have not yet been explored so far.

The research question about this PhD project has been to investigate new techniques to produce functional fabrics based on the sudden-changed wettability; the mechanism understanding of directional water transport phenomenon of fabrics and its heat and moisture transport ability. Specifically, two main functional fabrics including 1) superhydrophobic
fabric, 2) directional water transport fabric; two theoretical models used to explain the directional water transport property and its heat and moisture transfer ability were developed.

1.2 Special aims of the PhD project

Fabrics with superhydrophobicity are very useful for both practical and industrial applications, however, functional fabrics are often required to be durable enough against repeated wash, to be stable enough against strong acid/alkali attack and to be resistible against different organic solvents. SU-8 is an epoxy-based and chemically inert photoresist widely used for electronic industries. Previous study in our group has reveal that silica nanoparticles can generate rough surface on various substrates and fluorinated alkyl silane (FAS) can decrease the surface energy. By combining with SU-8, FAS and FAS functionalized silica nanoparticles is expected to realize durable superhydrophobic coatings on fabrics. Upon exposure to UV, SU-8 crosslinks to form a highly crosslinked structure. The silane head of FAS is hydrolysable and can condense to form insoluble macromolecules. These make the coating highly stable in organic solvents and can withstand chemical damage. Therefore, the 1st specific aim of this PhD project is:

Special Aim 1: Using SU-8, hydrophobic silica nanoparticles and fluorinated alkyl (FAS) to prepare new fabric providing excellent superhydrophobicity, durability to repeated wash, stability to acid/alkali and resistance to solvents.

The directional water transport is ascribed to isotropic wettability along the fabric thickness. However, the lack of effective technique to precisely control the coating layer thickness confined the study on the role of hydrophobic layer thickness on directional water transport ability of conventional fabrics. Electro-spraying is a simple technique to prepare a functional coating on solid surface. It involves atomization of liquid under a strong electrical field. Liquid
drops split into tiny droplets before depositing on the substrate. Since the deposition rate can be controlled through adjusting the flow rate of liquid, electro-spraying offers opportunities to control the coating depth on fabric, which is useful for making directional water fabrics. Nevertheless, the mechanism of directional water transport has not been clear. Therefore, the 2nd special aim is:

**Special Aim 2: Using SU-8 based on electro-spraying technique to create new fabric coating system that can possibly make fabrics have a durable, directional water transport ability. And the theoretical understanding of the directional water transport phenomenon of this fabrics.**

Previous work done by our group has indicated that a hydrophilic fabric after being electro-sprayed with controllable thickness of a hydrophobic layer on one fabric side shows a directional water transport ability. Fabrics with such property shows a great potential applications on active wears, sportswear and summer clothing design, however, very few is studied the heat transfer process on such fabrics during dry and wet status. Therefore, the 3rd special aim of this PhD project is:

**Special Aim 3: Study the heat transfer behaviour of the directional water transport fabric under dry and wet status.**

### 1.3 Thesis outline

This thesis consists of seven chapters as outlined below:

- Chapter 1 is the brief introduction of the whole thesis.
Chapter 2 is the review summary of the background knowledge and research progress in wettability; the superhydrophobic surfaces in natural and artificial area; the technologies; and the directional water transport fabrics.

Chapter 3 introduces the materials and characterisation approaches, and the procedure to prepare the fabric coating solutions.

Chapter 4 is a research chapter revealing detailed results about the preparation of superhydrophobic fabrics using a negative photoresist nanocomposite coating. The surface wettability and morphology of the treated fabric have been characterised. The durability against repeated wash, stability against strong acid/alkali, organic solvents resistance and the self-cleaning property are reported.

Chapter 5 provides detailed results on a new coating method involving electro-spraying technique to prepare fabrics with an asymmetric wettability from hydrophobic to hydrophilic across the fabric thickness, and a novel directional water transport property caused by this hydrophobic/hydrophilic combination. The theoretical understanding of the mechanism of the directional water transfer phenomenon was studied, the influences of coating conditions and the hydrophobic layer thickness on the directional water transfer effect were examined.

Chapter 6 reports on the heat transfer behaviour on the directional water transport fabrics. The fabrics were prepared based on our previous study. The thermal conductivity of the directional water transport fabrics was measured and the heat transfer behaviours via conduction and radiation through the directional water transport fabrics under dry and wet status were studied.

Chapter 7 summarises the main conclusions obtained from this research work. Some suggestions for future work in this area are also provided.
Chapter 2

Literature Review

This chapter reviews the recent literatures on wettability, superhydrophobicity, directional water transport fabrics and heat transfer through fabrics. Techniques of preparation and potential applications of superhydrophobic and directional water transport fabrics are also summarized.

2.1 Fundamental understanding of wettability

2.1.1 Definition of contact angle

Wetting is one of the most common phenomena that can be widely observed in the world. It can be defined as the ability of a liquid to freely contact with a solid surface. In general, the static wettability of a surface can be evaluated by a contact angle (CA). The basic laws for CA calculations were firstly established for ideal solid surfaces, which are both flat and chemically homogeneous. As explained by Young and Laplace, the cohesion of the underlying solid or liquid phase can be reflected by a specific energy, the so-called surface tension, carried by surfaces. Here, we denoted the surface energy simply as $\gamma_{IJ}$ for an interface between phases $I$ and $J$ (below the indices are $S, L, V$ for solid, liquid and vapour, respectively). The equation 2.1 gives the relationship among wettability, surface tension and contact angle of a solid surface:

$$\frac{(\gamma_{SV}-\gamma_{SL})}{\gamma_{LV}} = \cos(\theta)$$

(2.1)
Here $\gamma$ refers to the surface tension; $SV$, $SL$ and $LV$ denote the solid-vapour, the solid-liquid and the liquid-vapour interface respectively (Figure 2.1).

![Figure 2.1. Surface tension forces on the three interfacial surface lines of a drop on a solid surface in equilibrium.](image)

The Young equation has evaluated the interfacial energies at the solid-vapour ($SV$), solid-liquid ($SL$) and liquid-vapour ($LV$) interface through contact angle $\theta$. However, it is suitable only for inert and non-volatile liquid on an ideal surface, i.e. on a rigid, smooth, homogeneous, nonporous surface. Natural surfaces cannot meet these requirements, due to their heterogeneity and roughness. This can lead to contact angle hysteresis and irregular drop shapes. The difference between an advancing and receding angle of a drop occurring at the contact line is defined as contact angle hysteresis. Dynamic contact angles can be obtained from the major and minor observable contact angle values respectively.

### 2.1.2 Definitions of superhydrophobicity and superhydrophilicity

According to the contact angle, the wetting performance of a solid surface to liquid can be classified into two main states: non-wettable and wettable.
Alternatively, these are referred to as hydrophobicity (CA > 90°) and hydrophilicity (CA < 90°). Two extreme states, which are superhydrophobicity (CA > 150°) \(^8,^9,^10\) and superhydrophilicity (CA < 5°), \(^11\) have also been defined. The term superhydrophobicity was introduced by Reick in 1976 to describe a hydrophobic particle coating which is composed of hydrophobic fumed silicon dioxide, where the shape of the water drop is almost spherical and the force of adhesion is almost negligible. \(^7\) Lotus leaves and duck feather have superhydrophobic surfaces and excellent water repellency. Water drop can easily fall off from a superhydrophobic surface and contact angle hysteresis is used to evaluate the liquid-surface adhesion of superhydrophobic surfaces. \(^12\) On the other hand, the term of superhydrophilic surfaces was introduced after the boom of research on superhydrophobic surfaces. \(^13\) Generally, a superhydrophilic surface is defined as a surface with a water apparent CA is less than 5° or 10°. \(^11\) Some researchers even believed that a superhydrophilic surface should have a CA of 0°. \(^2\) They are ubiquitous both in nature and our daily life. For example, paper, sponges and plants, such as the Nepenthes pitcher plant, have a superhydrophilic surface and exhibit strong water absorbing ability. Moreover, Drelich and Chibowski suggested to refer to superhydrophilic surfaces only for the surfaces with a roughness factor \(r\) (defined by a Wenzel equation) larger
than 1 (on which water can spreads completely). Thus, superhydrophilic surfaces cannot be obtained without manipulation of surface roughness on hydrophilic materials. 13

The contact angle $\theta$ and $\gamma_{LV}$ of Young’s equation (2.1) can be measured experimentally, leaving $\gamma_{SV}$ and $\gamma_{SL}$ unknown. However, when $\theta$ is larger than 20°, it is assumed that $\gamma_{LV} \approx \gamma_L$ and $\gamma_{SV} \approx \gamma_S$. 14 Therefore, the Young equation can be reformulated as:

$$\frac{\gamma_S - \gamma_{SL}}{\gamma_L} = \cos(\theta)$$

(2.2)

The thermodynamic work of adhesion has been explained by the Dupre equation:

$$W_{SL}^a = \gamma_S^a + \gamma_L^a - \gamma_{SL}^a$$

(2.3)

Since the thermodynamic work of adhesion ($W_{SL}^a$) is also called the free energy of adhesion ($\Delta G_{SL}^a$), the free energy of adhesion is formulated as:

$$\Delta G_{SL}^a = \gamma_{SL}^a - \gamma_S^a + \gamma_L^a$$

(2.4)

By combining equation (2.2) and (2.3), the Dupre-Yong equation is obtained as follows:

$$W_{SL}^a = \gamma_S^a + \gamma_L^a - \gamma_{SL}^a = \gamma_L^a (1 + \cos \theta)$$

(2.5)

From the Dupre-Young equation (2.5), we know that neither $\gamma_S$ nor $\gamma_{SL}$ exceeds the sum of the others surface energies, 9 which leads to the prediction of complete wetting when $\gamma_S > \gamma_L + \gamma_{SL}$ and no wetting at all when $\gamma_{SL} > \gamma_S + \gamma_L$ (as Figure 2.2 shown).

It is well established that the real textured surfaces will have roughness, which also can be divided into two categories: heterogeneous and homogeneous. Wenzel 15 and Cassie-Baxter 16 explained those two conditions using models they built the Wenzel model and the Cassie-Baxter model as shown in Figure 2.3.
According to the Wenzel model, the apparent contact angle ($\theta_r$) can be described by equation (2.6):

$$\cos \theta_r^W = r \cos \theta$$

Here, $\theta$ is the contact angle obtained from the Young equation as the surface is defined for an ideal surface, and $r$ is the roughness ratio of the wet area to the apparent surface area. It can be clearly seen that when $r>1$, $\theta_r^W$ will decrease with the increase of surface roughness for a hydrophilic surface but will increase with the surface roughness for a hydrophobic surface. The relationship between contact angle and roughness, $r$, is described in Figure 2.4.
However, the Cassie-Baxter model is an extension of the Wenzel model to porous materials. In the Cassie-Baxter model, the liquid sits on the top of the rough surface with air underneath (Figure 2.3b). This interesting phenomenon was described by Cassie and Baxter in 1944 through the equation (2.7):

$$\cos \theta_r^{CB} = r_f \cos \theta + f - 1 \quad (2.7)$$

Where $r_f$ is defined by analogy with the Wenzel model as above and $f$ is the fraction of solid area in contact with the liquid. It is clear that we cannot observe those two states on a surface at the same time due to the impossibility for a surface to have two totally different contact angles with one fluid under the same situation, but it is possible that the two models can transit between each other under special conditions. Compared with the Cassie-Baxter equation (2.6) and the Wenzel equation (2.7), we can see that when $f=1$ and $r_f=r$, the two equations becomes the same.
In brief, the Wenzel and Cassie-Baxter models indicate the two states of liquid contact on a rough surface. The Wenzel model describes how the liquid is completely sucked into the rough surface without air trapping. Yet it is difficult for the droplet to move and roll across the surface due to the large contact area. This is why Wenzel surfaces are called “sticky”. However, for the Cassie-Baxter model, liquid stands on the top of the rough surface the air is trapped underneath, which allows the liquid to easily move and roll, this is described as a “slippy” surface.  

2.2 Examples with Superhydrophobicity

In nature, superhydrophobic surfaces have been found on many plant surfaces and animal furs. Such a surface causes water to bounce and roll off and the surface remains in a dry state. This phenomenon allows these surfaces to clean the dirt through the liquid, which is also known as self-cleaning (Figure 2.5).  

![Figure 2.5. Schematic of self-cleaning property on a superhydrophobic surface.](image)
2.2.1 Plant leaves

2.2.1.1 Lotus leaf

The lotus leaf is one of the most famous examples among natural superhydrophobic examples. The lotus leaf can emerge completely clean even after rain from dust or dirty water. Pictures of a lotus leaf and its surface biological structure are shown below (Figure 2.6):

Figure 2.6. a) An image of lotus leaf, and b) lotus leaf shows self-cleaning properties, and c) SEM image of the two-scaled rough structure of a lotus leaf (a few microns in size).

The lotus leaf surface is covered with many micron-scale protrusions and nano-scale particles underneath on which the so-called epicuticular waxes are imposed. The two factors (high surface roughness and low surface free energy) contribute to the superhydrophobicity of the lotus leaf. A specific name, the “lotus effect”, has been given to the phenomenon due to its remarkable self-cleaning properties.
2.2.1.2 Rice leaf

It is well known that water drops can roll off freely in all directions on the surface of a lotus leaf. On the contrary, the rice leaves show an anisotropic wetting and dewetting ability owing to its unique structure.\textsuperscript{23} Although the micro- and nanopapillae on rice leaves is similar to those of lotus leaf, the arrangement is in one-dimensional order parallel to the leaf edge but randomly in the other directions. Figure 2.7 shows the large-scale SEM images of a rice leaf.

![Figure 2.7](image)

Figure 2.7. a) Large-scale SEM images of the surface of a rice leaf (the insert is a high-resolution SEM image of an individual papilla), b) SEM image of the top view of a rice-like aligned carbon nanotube (ACNT) film.\textsuperscript{23}

Sliding angle is different for water rolling along the direction of the arrow shows in Figure 2.6 (3°-5°) and perpendicular to the arrow (9°-15°). The orientated distribution of the papillae on the rice leaf surface provides a different energy barrier of wetting in these two directions, which creates an anisotropy tendency on the surface. These results are very useful for controlling the wettability of artificial solid surfaces.
2.2.1.3 Red rose petal

Unlike lotus leaves which have a self-cleaning surface, red rose petals normally keep sphere shape water droplets sticking on their surfaces, the phenomenon of which is also defined as “petal effect”. The petal’s surface also exhibits superhydrophobicity with a CA of 152.4° owing to its hierarchically micro- and nanostructures. However, water droplets with the same volume can maintain the sphere shape and stay pinned to the red rose petal surface when it is turned upside down (Figure 2.8b insert image). Similar phenomenon can also be observed on Chinese Kafir lily petal (Figure 2.8 c & d), sunflower petal (Figure 2.8 e & f) and peanut leaf (Figure 2.8 g & h). These superhydrophobic surfaces with high adhesive ability provide an effective method to transport small volume of liquids in microfluidic devices.
Figure 2.8. SEM images of the surface of a red rose petal (a, b), Chinese Kafir lily petal (c, d), sunflower petal (e, f) and peanut leaf (h) with low and high resolutions, respectively, g) water droplets with spherical shape pinned on peanut leaves. The insert images in a), c) and e) shows the photographic images of red rose petal, Chinese Kafir lily petal and sunflower petal, respectively, the insert images in b), d), f) and h) shows the shape of water on the petal’s surface when it is turned upside down.
2.2.1.4 Taro leaf

Besides of the superhydrophobic property, taro leaf also owns itself unique microstructure formed with many uniformly distributed elliptic protrusions in their corresponding nest-like caves. Many uniformly distributed micro-elliptic protrusions and many harmoniously disseminated nano-scale pins can be observed on the whole surface, resulting in a hierarchical structure on its surface, which is similar to the lotus leaf. The taro surface is superhydrophobic, with a CA of $159 \pm 2^\circ$, and a SA of about $3^\circ$.

![Image of Taro Leaf](image_url)

Figure 2.9. a) The photographic image of taro leaf with a few water droplets on its surface, b) ~ d) the SEM images of taro leaf with different magnifications. The insert image in d) is a water droplet on a taro leaf with a value of $159\pm2^\circ$, exhibiting a good superhydrophobicity. The scale bar of b ~ d) are 100 µm, 20 µm and 5 µm, respectively. 26
2.2.1.5 *Salvinia* leaf

A unique combination of hydrophilic patches on superhydrophobic surfaces, which is also called “*Salvinia* effect”, can be observed on the floating water fern *salvinia*. The upper side of a *S. molesta* leaf is densely covered with complex multicellular hairs with an eggbeater-shaped structure on the terminal ends (Figure 2.10). The hairy surface exhibits superhydrophobicity with a bead shape water droplet sitting on the surface, however, the terminal cells are wetted and show hydrophilic owning to the shape of the meniscus of the water droplet. The hydrophilic patches at the tips of the hairs prevent the rupture of the contact, while the hydrophobic hair surface can resist the water from approaching the plant surface. This “Salvinia effect”, i.e., pinning of air-water interface at a predefined level by hydrophilic patches opens an avenue for designing artificial surfaces with long-term air-retaining properties for a wide range of applications on drag reducing ship coatings and low-friction fluid transportation devices.
Figure 2.10. a) Photographic image of the upper side of a salvinia molesta floating leaf surface densely covered with hairs. The surface shows superhydrophobic property as the water droplet keep a spherical shape. b) ~ c) SEM images of the complex hair structure with an eggbeater-shaped structure at the terminal end, d) SEM image shows the densely covered with nanoscale wax crystals on the whole leaf surface (below) with exception of the terminal cells (above). 27

2.2.2 Animal species

2.2.2.1 Butterfly wing

Butterfly wings are one of examples in animal species that display superhydrophobicity with directional adhesive properties. 28 When a butterfly slightly waves its wings, water droplets easily roll off the surface along the radial outward (RO) direction of the central axis of the body, but pin tightly against the RO direction (Figure 2.11). Butterfly wings are covered with a large number of quadrate scales, which overlap each other to form a periodic hierarchy structures along the RO direction. Each quadrate scale is composed of numerous separate ridging nano-stripes, which are stacked stepwise by tilted cuticle lamellae along the RO direction. These highly directional hierarchical structures of butterfly wings strongly affect the wetting behaviours of water droplets.
Figure 2.11. a) A photographic image of an iridescent blue butterfly *M. aega*. The black arrows denote the radial outward direction away from the body’s centre axis. b) ~ c) shows the directional adhesion on the wings: b) water droplet easily rolls off along the RO direction when the wing is titled toward downwards by 9°, c) water droplet is tightly pinned on the wings that is titled upward, even fully upright; d) and e) SEM images of the periodic arrangement of overlapping micro-scale on the wings and fine lamella-stacking nano-stripes on the scales. Scale bars: a) 100 µm, b) 200 nm.
2.2.2.2 Water strider leg

Water striders are insects that reside on the surface of ponds, rivers and the open ocean, which are famous for their ability to freely walk or even jump on water surface. Bush et al. 39 indicated that capillary waves do not play a key role in the propulsion of the water striders, the striders transferred momentum to the underlying fluid through hemispherical vortices shed by its hairy driving legs, which successfully resolved the Denny’s paradox: 30 infant water striders, whose legs are too slow to generate waves, should be incapable of propelling themselves along the water surface. Jiang et al. 31 further revealed that water striders legs are covered with many oriented, needle-shaped hydrophobic micro-setae, arranging at a 20° inclined angle on the surface (Figure 2.12). These unique hierarchical structures can effectively trap air to create an air cushion between the leg and water that endows the leg with robust and durable water repellency ability. This robust and durable water repellency force from just one leg of a water strider is enough to support 15 times of its total body weight. Therefore, the water strider can freely walk or even jump on the water surface even in a violent storm or torrent conditions.
Figure 2.12. a) ~ b) Natural and mechanical water striders. a) An adult water strider *Gerris remiges* stand on the water surface. b) The static strider on the free surface, distortion of which generates the curvature force per unit leg length $2\sigma\sin \theta$ that supports the total body weight of the strider. c) Typical side view of a maximal-depth dimple before the leg pierces the water surface. Insert image shows the water droplet on a leg with a CA of $167.6\pm4.4^\circ$; d) ~ e) SEM images of a leg showing: d) the numerous oriented spindly microsetae and e) the fine nanoscale grooved structures on a seta. Scale bars: a) 1 cm; d) 20 µm; e) 200 nm. 31
2.2.2.3 Mosquito compound eye

It is known that Mosquitoes possess excellent vision even in a watery and dim habitat. Recently, Jiang et al. revealed the secret of the antifogging ability of the mosquito compound eyes. The mosquito eye is a compound structure composed of many uniformly organized microscale hemispheres with a diameter of ca. 26 µm. Each micro-hemisphere was covered with a large number of fine, nanoscale nipples with average diameters of 101.1±7.6 nm (Figure 2.13). The combination of hexagonally non-close-packed (ncp) nipples at the nanoscale and hexagonally close-packed (hcp) ommatidia at the microscale on the surface of mosquito eyes indicate excellent superhydrophobicity to prevents fog drops from condensing on the eye surface, which endows mosquito to have a clear vision even in humid environment.
Figure 2.13. a) A photograph of antifogging mosquito eyes. The surface of the eyes remains dry and clear even they are exposed to moisture. b) SEM image of a single mosquito eye, c) SEM image of an hcp micro-hemisphere (ommatidia), d) two adjacent ommatidia, e) hexagonally ncp nano-nipples covering an ommatidial surface. 33
2.2.2.4 Duck feather

Many natural surfaces inherently possess re-entrant surface texture which enables them to support a composite interface with water and thereby exhibit superhydrophobicity. Duck feather is one of the most famous superhydrophobic surface examples in nature, which enable them to dive quickly in water without wetting by water. SEM image shows that duck feathers are composed of braches with different dimensions, including microscale backbones, trunks and barbules, which is composed of microscale tomenta with nanosized grooves and protuberances. Those multiscale textures of duck feather structure are helpful for highly water repellent properties (Figure 2.14).
Figure 2.14. a) An optical image of a piece of duck feather, insert is a water droplet on a duck feather; b) ~ e) SEM images of multiscale structures of a duck feather: b) scale bar = 200 µm; c) scale bar = 30 µm; d) and e) scale bar = 300 nm. 34
2.2.2.5 Gecko foot

Geckos are famous in nature as they can climb on almost any rough, smooth, vertical, or inverted surface arising from the multiscale structures with microsetae split into hundreds of nanoscale spatulae on their foot. Besides the famous reversible adhesive, gecko feet also exhibit self-cleaning ability and superhydrophobicity with high adhesive force to water. It was firstly discovered by Autumn et al. in 2002 that gecko setae are superhydrophobic with a CA of 160°.

Furthermore, Liu et al. 37 studied the surface wettability of gecko feet and measured the adhesion force between water droplets and superhydrophobic gecko feet. A wide range of adhesive force (10 ~ 60 µN) of gecko feet toward water droplets was measured, which could be attributed to the complex contact condition between water droplets and gecko setae and the conformational changes in the surface proteins of gecko setae when exposed to water.
Figure 2.15. a) Typical digital photographs of a gecko under anesthesia, the insert on the left is the image of a water droplet standing spherically on the irregular surface of gecko foot, the insert on the right shows a water droplet spherically pinned on the gecko setae when the setae was turned upside down, revealing superhydrophobicity and the highly adhesive ability towards water. b) SEM images of the gecko foot under low magnification, c) the setae on the gecko foot and d) a single seta with branched nanoscale spatulae under high magnification. 37
2.2.2.6 Desert beetle

Water uptake is one of the most serious problems for animals in Namib Desert, only a few species can survive in such severe environment. Desert beetles is one of the exception. The desert beetles’ back can collect water from fog-laden wind of saturated or subsaturated air and directionally trickle down the body to the mouth. The ability of water collection and the directional movement of the collected water droplet were come from the unique structure of the back of the beetle. The back of the beetle was composed by hydrophilic smooth “bumps” and superhydrophobic wax-covered valleys (Figure 2.16). When the beetle was exposed in the fog, the small water droplet in the fog locates on the bumps peaks, and the water striking in the hydrophobic slopes will also bounce to the hydrophilic region. The attached water eventually rolls down the tilted back surface until it grows to a big size that can easily detach from the back. Similar water harvesting surfaces with directional water collection ability can also be found on cactus and spider capture silks. These water harvesting surface with directional water collection ability were very helpful for design and construction of fog collection devices for agriculture.
Figure 2.16. a) The water-capturing surface of the desert beetle *Stenocara sp*; b) A “bump” on the elytra, depressed areas of the otherwise black elytra are stained positively with Red O (waxy, coloured), whereas the peaks of the bumps remain unstained (wax-free, black); c) SEM image of textured surface of the depressed area;  

38 d) optical image of a cactus stem covered with well-distributed clusters of spines and trichomes; e) ~ f) SEM images of a single spine with an apex angle ($2\alpha$) on the tip and with gradient grooves on the middle; 39 g) SEM image of periodic puffs and joints surrounding two main-axis fibres under low magnification, h) magnified image of puff composed of countless nanofibrils. 40-41 Scale bars: a) 10 mm, b) 0.2 mm, c) 10 µm, d) 5 cm, e) ~ f) 2 µm, g) 100 µm and h) 200 nm, respectively.

Many researchers have reported that all leaves with self-cleaning and superhydrophobic properties possess an intrinsic hierarchical structure. 42,43 Those interesting structures can provide air pocket formation, which would cause the lowest contact area of an applied droplet
(as shown in Figure 2.17), and then a reduced contact angle hysteresis with adhesive force and tilt angle can be obtained.\textsuperscript{44, 45}

Figure 2.17. Schematic and wetting states of four different surfaces. The contact area between the droplet and the surface is the largest in flat surface, but is reduced from nanostructure and microstructure, and is minimized in surfaces with hierarchical structure.\textsuperscript{44, 45}

### 2.2.3 Preparation of artificial superhydrophobic surfaces

As suggested by Wenzel\textsuperscript{15, 46} and Cassie-Baxter\textsuperscript{16}, surface roughness is a key parameter for surface wettability. If low surface free energy has been found on a rough surface, it will greatly enhance the hydrophobicity. Therefore, a rough surface with low surface free energy has been considered as the basic principle to fabricate artificial superhydrophobic surfaces. The fabrication of superhydrophobic surfaces has been an attractive research area since the mid-1990s. Various techniques have been reported. In general, those methods can be broadly categorised into two groups: chemical methods and physical methods.
2.2.3.1 Chemical methods

Superhydrophobic surfaces can be prepared by chemical methods including chemical deposition, wax solidification, wet chemical reaction, phase separation method, self-assembly, layer-by-layer deposition method and sol-gel method.

1) Chemical deposition (CD)

Chemical deposition (CD) is a technique whereby chemical or gaseous reactants can be deposited onto a suitable surface. According to the deposition condition, CD can be subdivided into chemical solution deposition (CSD), chemical vapour deposition (CVD) and electrochemical deposition. Liquid reactants, low temperature (<100°C) and normal pressure are required for a CSD process. However, gaseous reactants, high temperature (>100°C) and low/high pressure are applied in a CVD process. Using an electrochemical deposition, the micro-/nanostructure surface required for superhydrophobicity can be obtained. Hosono et al. reported a simple CSD technique to create a nanopin film using CoCl$_2$ and NH$_2$CO in water. The resulting film showed a water contact angle as high as 178°.
Figure 2.18. a) – b) are the SEM images of the resulting films observed from the top and side respectively; c) is the TEM image of the resulting film; and d) is a simple model of the resulting film. ⁴⁷

Zhou et al. ⁴⁸ used CVD to prepare superhydrophobic surfaces with significant slippage effects from carbon nanotubes forests (CNTs). The substrate was magnetron sputtered with an ultra-thin ferrocene film as a catalyst and then placed into a furnace with N₂ gas driving the air away in advance. It was followed by heating at 850°C, and CVD started growth by introducing acetylene vapour. The resulting surface had a water contact angle as high as 161° (as seen in Figure 2.19).
Figure 2.19. SEM images of the resulting surfaces with different distance between CNTs clusters. The distance between CNTs clusters is: 1μm a), ~3μm b), and ~10μm c), respectively. Inset: the water contact angles of a water droplet on those surfaces.  

Recently, He et al. 49 reported an electrochemical anodization approach to synthesize ZnO nanostructures using hydrofluoric acid and methanol electrolyte mixture. Different kinds of nanostructures such as nanodots, nanowires and nanoflowers were obtained by controlling the concentration of electrolyte and reacting time (Figure 2.20).
Figure 2.20. SEM images of the resulting nanostructures with different reaction times in a methanol and water mixed solution. The reaction time in each sample is 30s a), 1 min b), 5 min c), 10 min d), 15 min e), 30 min f), respectively. The length of scale bars is 500 nm. 49

2) Wax solidification

As a simple and useful method for fabrication of superhydrophobic surfaces, wax solidification was firstly applied by Shibuichi 50 and Onda 51 in 1996. Alkylketene dimer (AKD) was melted onto the surface of a glass substrate at 90 °C, and then the AKD turns to fractal growth with its solidification at ambient temperature and dry nitrogen gas. AKD is hydrophobic
with a contact angle about 109°. The obtained surface with solid AKD would lead to a superhydrophobic surface.

3) Wet chemical treatment

Wet chemical coating is a simple method to prepare superhydrophobic surfaces on large scale. Hua et al. fabricated a durable superhydrophobic surface on plain weave fabrics (Figure 2.21) with excellent abrasion resistance. This method is useful for developing self-cleaning protective textiles for various applications.
Figure 2.21. a) A schematic of preparation of the coating solution and superhydrophobic fabrics; b) and c) the pictures of dyed water droplets (10μL) on the untreated and treated fabrics; d) and e) SEM images of pure and treated fabrics, respectively. Inset shows higher resolution SEM image of e).

Wang et al 53 prepared hydrophobic surfaces on mechanical stable macroporous silicon films. The coating could meet mechanical requirements for microfluidics applications.

Figure 2.22. FE-SEM images of the resulting films prepared by electrochemical etching under galvanostatic condition: a)-c) 10 mA·cm⁻² (Psi1); d)-f) 60 mA·cm⁻² (Psi2); g)-i) 60 mA·cm⁻², with subsequent ultrasonic cleaning (Psi2'). The insets show the water droplets’ profiles on the surfaces. 53
4) Phase separation method

Phase separation is simple, low cost method widely used to prepare polymer porous membranes for a wide range of industrial applications such as ultrafiltration\textsuperscript{54}, microfiltration\textsuperscript{55}, forward osmosis\textsuperscript{56}, reverse osmosis and sea water desalination\textsuperscript{57}. In general, there are two main phase separation processes for polymeric membrane formation: thermally induced phase separation\textsuperscript{58} and immersion precipitation\textsuperscript{54}. Kato and Sato\textsuperscript{59} prepared superhydrophobic surfaces using a unique UV light-triggered micro/nanofabrication system. By selecting PIPS mixture of appropriate components, such as cross linkable monomers, soluble polymer additives or solvents, the phase separation gave transparent superhydrophobic films and water repellent fabric textiles.
Figure 2.23. Schematic illustration of the present procedure for providing a) superhydrophobic films; b) surface SEM images and static water contact angle ($\theta_{st}$) values of various microtextured polymer films on silanized glass plates.\textsuperscript{59}
Song et al.\textsuperscript{60} prepared durable superhydrophobic films by using a simple method: dropping silyl chitosan (SC) which was prepared by a solid-gel chemical reaction between chitosan, tertbutyldimethyl silyl chloride (TBDMSCl) and imidazole on a glass slide and drying in air at room temperature. The films showed superhydrophobicity across the whole pH range and exhibited three levels of hierarchical structures. Wang et al.\textsuperscript{61} also prepared a superhydrophobic methylsilicone resin film using a phase separation method: methylsilicone resin and europium complex-Eu(BA)\textsubscript{3}Phen (BA=benzoic acid and Phen=1,10-phenanthroline) were dissolved in ethanol, followed by mixture with deionized water to prepare the coating solution. The solution was then dropped on a glass slide to prepare a superhydrophobic film. Figure 2.24 shows the emission spectra of the result films and optical image under UV light.

![Emission Spectra](image1.png)

![Optical Image](image2.png)
Figure 2.24. (a) The emission spectra of methylsilicone resin film with (A) or without (B) Eu(BA)$_3$Phen; (b) Optical image of water drop on the Eu(BA)$_3$Phen methylsilicone resin film under UV light. 

5) Self-assembly (SA) or layer-by-layer (LBL) deposition method

SA or LBL deposition method is an easy, versatile approach to assemble layered aggregates with tailored architecture and composition. Recently, a robust superhydrophobic fabric was reported by Yoo et al.\textsuperscript{62} by depositing two polymer (apoly(1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane) (p(V4D4)) and a poly(1H,1H,2H,2H-perfluorodecylacrylate) (p(PFDA)) through layer-by-layer using the iCVD process. By controlling the operating parameters, a hierarchical structure with highly transparent and durable chemical robustness was obtained.
Figure 2.25. a) A schematic structure of the stacked polymer p (V4D4) and p (PFDA) coated fabric. b) ~ d) and c) are SEM images of the pure polyester surface, the slightly rough and rougher surfaces of the p (V4D4-L-PFDA) stacked polymer coated fabrics, respectively. Inset images show the contact situation between a water drop and a fabric. 62

Du et al 63 reported a one-step method to prepare superhydrophobic coatings based on anionic polymerization of octyl cyanoacrylate in the presence of aqueous ethanol. A stable superhydrophobic coating with strong adhesion with substrate such as glass, wool, steel and plastic could be achieved.
substrates are b) TLC plate, c) acrylic coated cloth tape, d) steel, e) paper, f) polypropylene, g) cotton gauze, h) mesh-like plastic surface, i) curved tube-like surface and j) cotton fibres. Song et al applied an octadecyltrichlorosilane (OTS) self-assembled monolayer (SAM) on silicon substrate with micro/nano-textured structure produced by the aluminium induced crystallization (AIC) of amorphous Si technique. The hydrophobicity of the silicon surface was significantly improved (the water contact angle is 155° and the sliding angle is less than 1°). The combination of AIC and amorphous Si shows potential in micro electro mechanical systems (MEMS). Zhao et al used this method, followed by a fluoroalkylsilane treatment, to prepare superhydrophobic cotton fabrics (Figure 2.27 a ~ c). The superhydrophobic cotton fabric had a WCA of 150° and a contact angle hysteresis >45° for 1 or 3 multilayers. For 5 multilayers or more assembly, the WCA was higher than 150° with contact angle hysteresis <10°. The buoyancy of the resulting superhydrophobic cotton fabric was demonstrated in the paper (Figure 2.27 d and e). A tiny fabric boat exhibited a remarkable loading capacity as it can load 11.6 or 12.2 g with a volume of 8.0 cm³. Moreover, the obtained fabric also showed a reasonable durability being able to withstand at least 30 machine washing cycles.
Figure 2.27. Optical photographs of water drops on a) untreated fabric and b) assembled with multilayers of PAH/SiO2 fabric; and c) being immersed in water of untreated (left) and superhydrophobic cotton fabric (right). d) and e) shown the optical photographs of a loaded superhydrophobic cotton fabric boat floating on water surface from top view d) and side view e). 65

6) Sol-gel method

A sol is typically produced by hydrolysis of the corresponding precursor with the presence of water, catalyst and solvent. After drying, it forms a network structure. The impregnation of a large amount of solvent in the network can also form a gel 66, 67. The sol-gel method was developed in the 1960s for the increased demand for nuclear industry. Hong et al 68 developed a simple superhydrophobic coating solution by combining particle-containing silica sol and a non-hydrolyzable functional group on textile fabrics. The water contact angle of the resultant fabrics is higher than 170° with a sliding angle of less than 10° (Figure 2.28).
2.2.3.2 Physical methods to prepare superhydrophobic surfaces

Physical approaches, such as the lithographic method, template approach, electrospinning and plasma treatment, have been used for making superhydrophobic surfaces.

1) Lithographic method

The lithographic method is a simple but efficient for preparing rough surfaces. To generate superhydrophobic surfaces, photolithography, electron beam lithography, X-ray lithography, and nanoimprinting, “dip-pen” nanolithography have been used. SU-8 is an epoxy-based negative photoresist, which was originally developed and patented by IBM in 1989. It has remarkable properties, such as good viscosity, highly transparency in ultraviolet (UV) region,
good conductivity and cross-linkable after UV exposure, and can be spun over a thickness ranging from <1 micro-meter to >300 micro-meters. It is applied to lithography and fabrication of semiconductor devices for the microelectronics industry \(^{74}\). Zhang et al \(^{75}\) reported the optimization results of SU8 polymerization and its possible uses in microfluidic and MEMS. Near UV lithography technology was used for the optimization of SU8 polymerization. The results showed that prebake time was the key factor to control the quality. Sharma and coworkers \(^{76}\) have used SU8 to fabricate arrays of micro patterned polymeric and carbon nanofiber structures on different substrate. The resulting substrates were highly hydrophobic (water contact angle ~130°) as shown Figure 2.29.

Figure 2.29 SEM images (left) of arrays of different patterned fibrous carbon structures: (a, b) lines; (c, d) 3D pillars and (e, f) connecting squares respectively, and higher magnification images of b and d are shown as insets; g) showed the effect of fibre morphology and chemical treatment on water contact angles. \(^{76}\)

Öner et al \(^{77}\) prepared a series of superhydrophobic surfaces on silicon by using photolithography and hydrophobization with silane. Shiu et al \(^{78}\) used a periodic nanosphere
array for lithography. The apparent water contact angle changed from 132° to 168° (Figure 2.30).

Figure 2.30. SEM images of different size of the modified polystyrene beads and the water contact angle results (insets). The diameters of polystyrene beads and water contact angles are a) 400nm, 135°; b) 360nm, 144°; c) 330nm, 152°; and d) 190 nm, 168°. Scale bar: 1μm.

2) Template approach

Porous membranes with hierarchical micro- and nanostructures on surface can be used as templates to fabricate superhydrophobic surfaces. Sun et al. have mimicked lotus leaf by using this method. As shown in Figure 2.31, PDMS was cast onto a natural lotus leaf surface firstly, and then, a negative replicate of the lotus leaf structure was prepared by lifting off the PDMS. The obtained replication was then used as a master to fabricate a positive lotus leaf replica. The SEM images showed that the positive replica has almost the same surface
morphology as the natural lotus leaf. The positive replica exhibited the same superhydrophobicity as natural lotus leaf. Jiang et al \cite{79} reported a simple extrusion process by using an anodic aluminium oxide membrane as the template to prepare superhydrophobic nanofibers. A polymer precursor of poly(vinyl alcohol) (PVA) was applied to fabricate the aligned nanofibers with different pore diameters by using the same templates \cite{80}.

![Figure 2.31. a) Schematic of the template method to prepare positive PDMS replica by using a natural lotus leaf, and SEM images of b) the natural lotus leaf surface and c) its positive replica surface. \cite{79}](image)

3) Electrospinning techniques

Electrospinning techniques are normally used to produce polymer nanofibres with diameters ranging from nanometre to submicron scale. It is based on an extrusion process where a driving force, originated from the electrical field, is applied between the extrusion nozzle and a grounded collection plate. \cite{81} Polystyrene (PS) is one of the most common polymers for electrospinning. The first paper about superhydrophobic electrospun nanofibrous film was published by Jiang and co-workers in 2004 \cite{82}. The water contact angle can reach 160° by adjusting the concentration of the polymer solution and adding some micro-sized particles within the fibrous matrix (Figure 2.32):
Figure 2.32. SEM images of the PS electrospun film a) and b) magnified part of a); water droplets on a spin-coated PS film and on the film d); and e) SEM images of porous microsphere/nanofiber composite film (PMNCF) and f) 3D network structure of PMNCF; g) surface morphology of a single porous microsphere and h) water drop on PMNCF. 82

4) Plasma treatment

Plasma treatment can cause a significant change in the surface morphology. Plasma treatment is generally used to form rough surfaces and it can also introduce some other chemicals to the surface. 81 Many superhydrophobic surfaces have been prepared using plasma treatment. For example, Minko 83 and Ji 84 used PTFE as a substrate to fabricate self-adaptive surfaces (Figure 2.34). After oxygen etching, the PTFE showed a greater water contact angle (~160°) with a nearly 0° contact angle hysteresis. When grafted with two polymers, carboxyl-terminated poly (styrene-co-2, 3, 4, 5, 6-pentafluorostyrene) (PSF-COOH) and poly (2-vinylpyridine), the prepared surfaces exhibited switchable wettability upon soaking in different solvents.
2.3 Moisture management fabrics

2.3.1 Fabric moisture management through fibre structure

Moisture transfer through fabrics was studied as early as 1960s. Highly water-absorptive fibres were used to enhance the capillary conductivity of fabrics. Capillary pressure is the main force for liquid to move through a fabric. Our body release heat through sweating and evaporation of moisture from skin surface. When fabric can enhance this process, it remains the wearer more comfortable.

The studies on moisture management fabrics have received great interest in recent decades. Hu et al. developed a method and instrument to evaluate moisture management properties in fabric. It can predict subjective perception of moisture sensations in sweating such as clammy and damp. However, there are many factors which affect the moisture management properties.
McQueen et al 88 observed that washing and drying process affected the moisture transport properties, a minimum of five times washing procedure prior to test is recommended. Öner et al 89,90 also tested the moisture management properties of different fabrics. Results show that the material itself and the fabric with float stitches structure have the most significant effect on liquid management, and tightness is the second, and weave type has the weakest effect.

Raul et al 91 evaluated the moisture management performance of functional yarns such as CoolMax® and Finecool® by testing the drying rate. Two different conditions were used to simulate the body skin temperature to measure the drying rate. CoolMax® based fabrics had the best capillarity and the increase in the percentage of wool fibre in the fabrics would decrease the water absorption but would not increase the drying rate. These findings are useful to produce the most suitable combination of wool/functional fibres for commercial use.

Some functional fabric products with moisture management properties shown below can be easily found in the market. Unlike common fabrics which rely on capillary action to draw the moisture and need to be worn next to the skin to generate humidity, Akwatek® 92 polyester can transport moisture induced by electrostatic force and can form a vapour gap between skin and fabric, which enables them to work as a multi-seasonal performance wear. The active layer functions to transfer water molecules and release them to the atmosphere before they condense into liquid.
Figure 2.34. a) Schematic of surface modification of polyester fibre, b) the working principle of the treated fabrics on normal condition, and c) on cold and hot atmosphere conditions; d) TOPCOOL® fibre structure and working principle. The well designed fibre with many slots can draw moisture away from the skin promptly based on the siphon effect it produced; e) CoolMax® fibres are manufactured in either a tetrachannel or hexachannel style. The vast numbers of closely spaced channel can enhance the capillary action to wick moisture out of body and evaporate effectively due to the increased surface area it creates.

TOPCOOL® and CoolMax® can effectively transfer moisture out of body to regulate body temperature, and thereby keep the wearers dry and comfortable as shown in Figure 2.35.
d and e. However, Tactel® \textsuperscript{96,97} is a unique two-layered fabric construction specially designed for strenuous exercises. The moisture absorption of outer layer is better than the inner layer, so the moisture can transfer from the inner layer towards the outer layer where it evaporates efficiently.

Figure 2.35. Size of a Tactel fibre compared with human hair (left); Tactel climate effect (middle) and the surface structure (right). It is well knitted with rip-stop honeycomb pattern and lightly brushed inner face. \textsuperscript{96,97}

### 2.3.2 Directional liquid-transfer fabrics

#### 2.3.2.1 Directional liquid transport fabrics

Directional water motion guided by structure and/or surface feature has been observed in nature on plants or insects. A good example is \textit{Stenocara} beetle’s back which have an incredible ability to collect tiny water from the air for its survival in \textit{Namib} Desert. \textsuperscript{39,98} Spider silk with alternate variations of both hydrophilicity/hydrophobicity and diameter is another example showing water harvesting ability. \textsuperscript{41,99} \textit{Cactus}, \textsuperscript{40} \textit{Strelitzia reginae} leaf, \textsuperscript{100} and rice leaves \textsuperscript{23} also show directional water motion, which is just driven by structural feature. Inspired by these natural examples, advanced water harvesting materials, \textsuperscript{40,98-99,101} microfluidics, \textsuperscript{102-105} filters, \textsuperscript{106-107} condensers, \textsuperscript{108} and oil-water separators \textsuperscript{109-110} have been developed. The research on
superhydrophobic surfaces is driven by various applications, such as superhydrophobic textiles,\textsuperscript{111,52,112} humidity-proof coating for electronic devices\textsuperscript{113} and biological applications. Fabrics having a wettability gradient from hydrophobic to hydrophilic on the two sides show a novel directional water transfer effect: water can penetrate from the hydrophobic side to hydrophilic side but would be blocked from the reverse direction. Although the ability to transfer liquid unidirectionally is common in nature such as in plant structures and human or biological systems, there is currently little published work in the textile industry.

Fabrics with directional water transport across the thickness have been reported. In textile area, directional water transport fabrics can proactively transport sweat from the skin to outer surface, hence strengthening perspiration useful for making sportswear, soldiers’ uniform, summer clothing, and special garment medical and daily life. A few methods have been developed to prepare directional water transport fabrics. They are mainly based on two routes:

1) Creating a hydrophobicity-to-hydrophilicity gradient through fabric thickness,

2) Combining a layer of hydrophobic fibres with a layer of hydrophilic fibres within the fabric matrix.

In 2010, Wang \textit{et al} \textsuperscript{114} first demonstrated a directional fluid transport phenomenon on fabrics induced by asymmetric wettability. A special fabric with different water breakthrough pressures on two sides was developed by combining with the sol-gel coating and UV irradiation process to form asymmetric wettability across the fabric thickness.\textsuperscript{114} A photo catalytic hybrid coating solution was prepared in advance by a sol-gel route from titanium tetraisopropoxide and tetrathylorthosilicate under the exiting of two hydrolysable silanes (hexadecyltrimethoxysilane and 3-trimethoxysilypropanethiol-1) (See Figure 2.39). Later on, the author observed the directional water transport phenomenon on fabrics using the similar method with different coating solution \textsuperscript{115}, indicating a wettability gradient from superhydrophobicity to hydrophilicity on fabric is the key factor to endow the fabric to have a
directional water transport function. A plain weave polyester fabric has been used to
demonstrate the spontaneous, directional water transfer through the fibrous thickness after a
dip-coating process and followed by a finishing treatment with the coating solution. Sol-gel
coating technique is an easy but effective and versatile method to fabricate a surface with
different wettability, and the TiO$_2$ endows the fabric with photocatalytic property and photo
induced superhydrophilicity at the same time. The contact angle can initially reach as high as
170° on both sides. After subsequent UV irradiation from one side, however, it decreased
dramatically to about 30°. The initially superhydrophobic surface was converted into
hydrophilic due to the photochemical reactions catalysed by TiO$_2$. The directional water
transfer phenomenon through thickness was then observed when water droplets were dropped
from different sides. The best irradiation period was determined by measuring the breakthrough
pressure across the asymmetrically modified fabric as it is the key role of this phenomenon.
Figure 2.36. a) Schematic of sol-gel superhydrophobic coating formation, b) the surface CA of the treated polyester fabric with different irradiation periods, c) the minimum pressure required for water to breakthrough the treated fabrics. The samples used for directional water transport test have been marked by * in the figures, d) still frames of a blue ink stained water droplet on the untreated and treated fabrics: (top) dropped on the UV-irradiated fabric surface, and (bottom) dropped on the back side. 114

In 2011, Kong et al. 116 reported a similar technique to prepare directional water transfer fabrics. The similar TiO₂ nanosol was fabricated as the coating solution, and then incorporated within the 3-D textile matrix through a dip-pad-dry process (Figure 2.37a). The coated fabric surface became hydrophobic after a certain period of dark storage. When exposed to solar light or UV irradiation (as shown in Figure 2.37b), the face of the fabric exhibited superhydrophilicity, whereas the back side of the fabric remained hydrophobic. As the absorbed energy of TiO₂ lies within the UV region (350-380 nm), the authors also tested the fabric with different light sources and irradiation periods (Figure 2.37c). As the UV intensity decreased, less UV light penetrated through the fabric.
a) TiO₂ nanosol + fibrous cotton matrix → incorporation

b) Sunlight

- Hydrophilic
- Hydrophobic

Dark

UV or sun light

- UV or sun light irradiation
- Hydrophilic fabric surface
- Surface energy gradient within yarns

- TiO₂ coated cotton fiber
- Cotton yarn
- Capillary channel with gradient wettability within fabric

Hydrophilic face side

Hydrophobic back side

Dark

Hydrophobic fabric surface

Hydrophobicity formed on back side of cotton yarns
Figure 2.37. a) Synthesis of titania nanosol and combination of TiO$_2$ nanosol within the fibrous cotton matrix, b) Schematic of fabric with self-adaptive wettability controlled by “light-and-dark”, c) Schematic of photo-induced superhydrophilicity process of TiO$_2$ coated textile on micro-porous 3D structure: capillaries with gradient wettability formed within the fibrous matrix. ¹¹⁶

Wu et al ¹¹⁷ fabricated an interesting “water diode” film using two different wettability materials based on an electrospinning technique. ¹¹⁷ Similar to the diodes in electric industry, the heterogeneous materials endow different properties. The author designed and fabricated a composite film with heterogeneous wettability through seamless coupling a hydrophobic film (polyurethane) and a hydrophilic film (crosslinked poly vinyl alcohol). The composite fibrous film was fabricated by a two-step electrospinning method. Firstly, a hydrophilic PVA solution was electrospun to form a fibrous film as a base, and secondly, a hydrophobic PU solution was electrospun onto it. After chemically crosslinking PVA using glutaraldehyde, a PU/c-PVA composite film with heterogeneous wettability through thickness was obtained. According to the wettability difference it created, water can penetrate from the hydrophobic side but will block from the hydrophilic side.
Figure 2.38. Schematic diagram of the composite fibrous film through a) electrospinning technique and b) PU/c-PVA composite fibrous film, c) shows the SEM cross-sectional image of PU/c-PVA composite mat including two layers of fibrous film with different thickness, d) e) snapshot of stained water penetration phenomenon from two sides of the composite film. d) Water droplets onto the hydrophobic PU side and penetrates the film spontaneously. e) Water droplets onto the hydrophilic c-PVA side and diffuses rather than penetrates.\textsuperscript{117}

Zhou \textit{et al} \textsuperscript{118} demonstrated a switchable, spontaneous, directional transport ability to both water and oil fluids on fabric materials through a wet-coating and successive UV irradiation treatment as shown in Figure 2.39. The treated fabric showed transport directionality to various liquids depending on the UV irradiation time. Interestingly, the directional transport phenomenon to different liquids can be also observed under different UV irradiation time, just like the same trend of wettability change caused by different UV irradiation time, revealing that changing the UV irradiation time shifts the liquid transport directionality. On 14 hours of UV irradiated fabric, directional transport takes places when the liquid had a surface tension in the range of 29 mN/m to 50 mN/m. Liquids with a surface tension lower than 29 mN/m could penetrate from both sides, while the liquids with a surface tension higher than 50 mN/m were not able to transfer through the fabric from either side (Figure 2.39b). And the transport directionality is switchable from one fluid to another simply by a heating treatment followed by strong UV irradiation for required period time (Figure 2.39 c)
Figure 2.39. a) Photos of 10 µL droplets on the coated polyester fabric before and after 10 hours, 14 hours and 24 hours of UV irradiation (water: blue coloured, hexadecane: red coloured, soybean oil: clear); b) selective transport to different liquid fluids (after 14 hours of UV irradiated fabric); c) switching feature of directional fluid transport on single piece of fabric.  \(^{118}\)

More recently, Barboiu and the co-workers prepared an asymmetric hydrophobic/hydrophilic (HP/HY) dynamic membranes with directional water transport ability using a novel template partial phase segregation method.  \(^{119}\) The generated dynamic membranes under molecular control show an alternative in controlling directional water transport and to go further toward highly selective separation of low mass solutes controlled through molecular diffusion (Figure 2.40a~d).
Figure 2.40. a) Constitutional segregation of the hydrophilic (blue)/hydrophobic (red) elements connected via core-centres (violet) for asymmetric, and the digital photos of b) upside and c) downside of the obtained membrane, d) and e) shows the mechanism of preferential water permeation of d) wettable hydrophilic surface and of e) unwettable hydrophobic surface.\textsuperscript{119}

Wang \textit{et al}\textsuperscript{120} reported a dual-layer electrospun nanofibrous membrane comprising a layer of superamphiphobic nanofibres and a layer of superhydrophobic olephilic nanofibres that has an interesting directional oil-transport ability. This nanofibrous membrane showed an excellent oil-water separation with high diesel-water separation efficiency. Except diesel, other oil fluids with a surface tension in the range of 23.8 mN/m to 34.0 mN/m also showed a similar liquid transport property.
Figure 2.41. a) Schematic illustration of electrospinning setup, b) the digital and SEM images of PVDF-HFP and PVDF-HFP/POSS nanofiber membrane (scale bars = 1 µm), c) digital photos of water and diesel droplets on such membranes, d) still frames taken from digital videos to show red water and clear diesel drops on the two sides of a dual-layer nanofiber membrane, e) the water/diesel separation test. ¹²⁰
2.3.2.2 The mechanism of directional liquid transport fabrics

Apart from preparation, theoretical understanding of directional water transport fabrics has been performed. Effect of fabric wettability on directional water transport ability and breakthrough pressure was reported. Mechanism for directional water transport through fabrics has been proposed, which was mainly ascribed to isotropic wettability along the fabric thickness. The effect of hydrophilic/hydrophobic layer thickness on directional fluid transport has been reported on nanofibrous membranes. However, the role of hydrophobic layer thickness on water transport of conventional fabrics has not been reported. Since nanofibrous membranes have completely different structure, fiber dimension and porous feature to the conventional fabric, the effect of hydrophobic layer on directional water transport property of conventional fabric may follow different trend to that on nanofibrous membrane. Wang et al have proposed two possible mechanisms during the publication: one is the water dragging principle from hydrophobic layers towards the hydrophilic pore section, and the other is the water evaporation and condensation principle from the hydrophobic pore surface and the hydrophilic pore section. To test the relationship between the wettability gradient along the membrane thickness and the anisotropic liquid penetration behaviour, Tian et al used a simple membrane model that composed of spaced microcylinders to explain. The liquid transfer easily from the lyophobic side to the hydrophilic side, while it is blocked from the reverse direction (Figure 2.42 a ~ b). The author further reveal theoretically that the anisotropic penetration resistance to fluid is attributed to the difference in critical breakthrough pressure resulting from the couple effect of local geometrical angle of the cylinder and solid-liquid contact angle on penetration pressure (Figure 2.50 c ~ d ). The anisotropic ratio of critical breakthrough pressure can be increased by either reducing the spacing ratio or increasing the wettability gradient of the cylinder membrane, which provides a clear understanding on anisotropic liquid penetration behaviour of a gradient membrane.
Figure 2.42. Anisotropic liquid penetration phenomenon through a micro-cylinder membrane with a wettability gradient along its thickness. a) The fluid penetrates easily from lyophobic side to hydrophilic side, b) the fluid is blocked in the reverse direction; c) schematic of the liquid-air interface extruded between two cylinders.\(^\text{121}\)

Where the cylinder radius is \(r\), \(\varphi\) and \(\theta(\varphi)\) are local geometrical and CA respectively, \(d_0\) is the inter-distance between two proximal cylinders, \(d\) is the inter-distance between the contact lines, \(r_i\) is the curvature radius of the extruded liquid surface, \(\alpha\) is the extrusion angle. \(\theta_p(\varphi)\) and \(\theta_r(\varphi)\) are local geometrical CA for the cylinder of positive (from lyophobic to hydrophilic...
direction) and reverse wettability gradient respectively, and \( \theta_r(\phi) = \min(\pi - \phi) \). Thus, the tolerable pressure difference \( \Delta P \) can be calculated as:

\[
\Delta P = \frac{\gamma}{r_1} = \frac{2\gamma \sin [\theta(\phi) - \phi]}{d_0 + 2r(1 - \sin \phi)}
\]

when \( \phi \) is larger than \( \frac{\pi}{2} \), the membrane has a negative \( \Delta P_r(\phi) \), indicating a wicking effect which enables the spontaneous penetration of fluids to a certain depth of the membrane, while the fluids cannot permeate the whole membrane due to the positive \( \Delta P_r(\phi) \) when \( \phi \) is lower than \( \frac{\pi}{2} \).

Later on, Kong et al.\(^{116} \) briefly demonstrated the mechanism by taking advantage of the 2D and 3D capillary effects.
Figure 2.43. Schematic of unidirectional transportation of water droplet governed by different dimensions of capillaries from the hydrophobic side to the hydrophilic side within the TiO2 coated cotton.\textsuperscript{116}

The relationship between the thickness of each film and the directional liquid transfer behaviour was examined by measuring the hydrostatic pressure (HP) difference of the composite film in different directions. Wu and the co-workers\textsuperscript{117} tailored the thickness of each film by controlling the electro-spinning time and made some adjustments on the PU film thickness due to the weak uniformed fibrous mat issue.
Figure 2.44. The relationship among electro-spinning time and the thickness of fibrous films and hydrostatic pressure (HP). a) The HP of the composite films rose as thickness of PU fibrous film increased. b) The HP decreased initially with increasing c-PVA film thickness. 

Based on Wang’s mechanism proposals, Wu et al.\textsuperscript{117} described the mechanism of directional water transport behaviour of the electrospun membrane. Three forces are involved: hydrostatic pressures (HP), hydrophobic force (HF) and capillary force (CF) respectively. HP and CF allow liquid to pass through the capillaries of porous materials, while HF resists penetration of the liquid.
Figure 2.45. Mechanism of unidirectional water transport on a heterogeneous composite film. The bearing force status when water is dropped on the upward a) from hydrophobic side (PU) to hydrophilic side (PVA) and b) from hydrophilic side (PVA) to hydrophobic side (PU). \(^{117}\)

HP can be measured by fixing the area of composite film and dripping water slowly through a container while recording the height of the water column when water starts penetrating the film, CF is a constant value related to the surface energy of the material itself and HF is also a constant value for a specific material.

Recently, Zhou et al. \(^{118}\) examined the effect of fabric spatial arrangement, liquid feeding style, liquid viscosity, the initial pressure required for a fluid to break through the fabric and the time required for the directional transport under different temperatures to find out the mechanism behind the directional transport. The results indicated that the directional transport is controlled by surface properties, irrespective of gravity’s effect, the transport became faster at a higher temperature as the surface tension decreased and the saturated vapour pressure increased at a higher temperature; however, the effect of liquid viscosity is much less noticeable in comparison to the surface tension. The novel switchability and selectivity of liquid transport would significantly enhance the applications in several areas including protective clothing, electrochemical or energy devices, healthcare and protection of hazardous liquid chemicals.

In summary, the possible mechanisms for directional liquid transport phenomenon were proposed. The large capillary force generated in the hydrophilic layer of samples was agreed to be the main source for liquid droplets to break through the hydrophobic barrier and spread into the hydrophilic layer. Other reasons include the surface tension of the fluids and the surface properties of the substrates.
Chapter 3

Materials and Characterisation Approaches

In this chapter, materials, experiment details, characterisation methods and instruments used for this PhD project are also introduced.

3.1 Materials and experimental details

3.1.1 Chemicals

Tetraethylorthosilicate (TEOS), ammonium hydroxide (28% in water), 1H,1H,2H,2H-perfluorodecysilane (C\textsubscript{16}H\textsubscript{19}F\textsubscript{17}O\textsubscript{3}Si) (FAS-17), dimethylformide (DMF), ethanol (AR), acetone (AR) and tetrahydrofuran (THF) were supplied by Sigma-Aldrich. Fluorinated alkyl silane (FAS-13, tridecafluorooctyl triethoxysilane Dynasylan F8261) was purchased from Sigma-Aldrich. SU-8 (2075) was obtained from Microchem Corporation. All chemicals were used as received.

The chemical structures of TEOS, FAS-17, FAS-13 and SU-8 2075 are listed in Figure 3.1.
3.1.2 Fabrics

The fabrics used in this project are cotton fabric (plain weave, 160g/m², thickness ≈ 520μm), polyester fabric (plain weave, 168g/m², thickness ≈ 420μm). They were all purchased from the local supermarket. Before coating treatment, cotton fabric was rinsed with acetone and distilled water separately for several times and dried at 100 °C for 30 minutes.

3.1.3 Experimental details

Preparation of hydrophobic silica nanoparticles

Hydrophobic silica particles were prepared using a modified Stöber method developed in our group.\textsuperscript{122} In brief, 1.0 mL TEOS was added into 25.0 mL ethanol to make a homogenous solution. And NH₄OH-ethanol solution was prepared by adding 10 mL ammonia solution (28%) to 25 mL ethanol. And then, the TEOS-ethanol solution was added to the NH₄OH-
ethanol solution at different feed rate through a syringe pump and followed by 5 hours of constant magnetic stirring at room temperature to form silica particulate sol. To form a hydrophobic surface on the silica particles, FAS (1.0 wt%) was added to the as-prepared sol solution. The hydrophobic silica particles were then collected by centrifugation at 7,800 rpm for 15 min, and then washed with distilled water. After three times of centrifugation and washing, the particles were freeze-dried for 12 hours.

**Preparation of SU-8 coating solutions**

Different amounts of commercial SU-8 was added into acetone under magnetic stirring in dark to form homogeneous solutions.

**Preparation of SU-8/FAS/silica particle coating solutions**

SU-8 and acetone was stirred in dark until a homogeneous solution was obtained. FAS and hydrophobic silica particles were added in sequence to the SU-8 solution. After 1 hour of magnetic stirring, the SU-8/FAS/silica particle coating solution was ready for use.

**Hydrophilic treatment of polyester fabric**

A piece of polyester fabric was immersed in 10% NaOH solution at 60 °C for 25 minutes to hydrolyse polyester on fibre surface. The fabric sample was then rinsed in water and 3% acetic acid twice each, and finally dried at room temperature for 24 hours.

**Hydrophobic coating treatment of fabrics**

A dip-coating method was employed for coating treatment. The fabric samples were firstly immersed in the coating solution for 5 minutes, and then dried at room temperature for 30
minutes. The coated fabrics were irradiated by UV light (intensity 80 mW/cm²) for 10 minutes and then further cured at 120 °C for 10 minutes.

**SU-8 Curing**

The coated fabrics were cured by UV irradiation (80 mW/cm²) for 10 minutes, preliminary baked at 120 °C for 10 minutes, and post-baked at 95 °C for 1 minute.

**Acid and base stability tests**

The hydrophobic fabric was immersed in acid and alkali solution (pH = 1, 2, 4, 6, 8, 10, 12, 14) at room temperature for 96 hours. The immersed fabric was then rinsed with water and dried at room temperature for 30 minutes.

**Self-cleaning tests**

The hydrophobic fabrics were cut into 25 mm × 75 mm oblongs and attached on a glass slide which were placed into a plastic box with a small angle. Some dusts were placed uniformly on the coated fabrics surface, and the dust-contaminated surface was cleaned by rinsing with dyed water.

**One side electro-spraying coating process**

A fabric sample was electro-sprayed using a home-made device which could generate a thin SU-8 coating on just one side of the fabric. A SU-8/acetone solution (1.4 wt%) was loaded in a 50 mL plastic syringe. A rubber tube was connected with the syringe and a 21 G steel needle (inner diameter = 0.8 mm) which was fixed on a purposed-built sliding device for electro-
spraying. The solution feeding rate was controlled by a syringe pump (kd Scientific) at 30 mL/h. A high voltage was applied between the needle and the collector using a DC power supply (Gamma High Voltage). The targeted fabric was attached on an aluminium rotating drum (length, 10.5 cm; diameter, 41 cm; rotating speed, 3.8 rpm) connected with a high-speed motor (Baldor Drives) for the electro-spraying treatment. Only the surface which exposed to the nozzle was coated with SU-8. To prepare the fluorescent-labelled samples for confocal microscopy measurement, Rhodamine B (4 wt%) was added into the coating solution.

3.2 Characterisation instruments

3.2.1 Contact angle

Water contact angles were measured using a contact angle goniometer under KSV Model CAM101 (KSV Instruments Ltd, Finland. Figure 3.1). Fabric samples were cut into 1 cm × 2 cm oblongs and placed on a glass slide. Liquid drops of 1.91 mm diameter (~5 µl) were placed on each fabrics surface with a glass syringe (diameter: 0.71 mm) and the image of each drop was captured at a rate of 33 frames per second after deposition onto sample surface. Water droplet pictures were taken by an Olympus DP70 high resolution microscope. 10 images were taken for each plate and the final angle was the average result from 10 images. Each result was the average number of at least 5 times. All tests were carried out in a condition lab (23 ± 2 °C and 65 ± 2% relative humidity).
3.2.2 Sliding angle

Sliding angles were measured using a purpose-made device consisting of a sample holder and a digital angle meter. Fabric samples were cut into 1 cm × 2 cm oblongs and stick on the sample holder. 5 μL of deionized water droplet was dropped on the sample surface. The minimum angle that the droplet can roll off the fabric surface was displayed on a digital angle meter. Each result was the average number of 5 tests. All tests were carried out in the condition laboratory (23 ± 2 °C and 65 ± 2% relative humidity).
3.2.3 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (Supra 55 VP microscope) was used to observe surface morphology. Fabric samples were cut into 0.5 cm × 0.5 cm and placed on sample holders. A thin layer of gold was sputter-coated (Baltec SCD50 sputter coater) on the two sides of the samples before putting into the chamber. To avoid surface charging, a relatively low acceleration voltage (5 kV) was applied with magnification variation from 1000 to 20000 times.
3.2.4 **Fourier transform infrared spectroscopy (FTIR)**

FTIR spectra were measured using a Burker Vetex 70 FTIR spectrometer in Attenuated Total Reflection (ATR) mode. The spectra were obtained under 32 scans at 4 cm\(^{-1}\) resolution. All tests were carried out in a controlled environment (20 ± 2°C and 65 ± 2% relative humidity). The data were analysed using an OPUS 5.5 software.

Figure 3.4. Scanning electron microscopy (Supra 55 VP).
3.2.5 X-ray photoelectron spectrometer (XPS)

X-ray photoelectron spectra (XPS) were collected on a Kratos AXIS Nova spectrometer with a monochromated Al Kα source (1486.6 eV) using samples of ca. 3 mm² in size. The X-ray beam incidence angle is 0° with respect to the surface normal, which corresponds to a sampling depth of ca. 3 mm². The obtained XPS spectra were analysed by the CasaXPS software.
3.2.6 Breakthrough pressure

Breakthrough pressure was measured using a purpose-built testing system consisting of a syringe, a syringe pump, a sample holder, an iron support and a pressure sensor and a computer, as shown in Figure 3.7. Water was fed into the chamber through the syringe and the flow rate was controlled by the syringe pump. A $1 \times 1$ cm$^2$ fabric sample is mounted tightly inside the sample holder. In the test, the pumped water entered the sample holder and reached to contact the fabric. Resisted by the fabric, pressure increased swiftly until water passed through the fabric. The pressure ~ time curve was recorded by the pressure sensor which can be directly transferred to computer through USB cable.

Figure 3.7. Breakthrough pressure test system and its schematic image.
3.2.7 Confocal microscopy

The fabric samples were imaged using a Leica Laser Scanning Confocal Microscopy (LSCM) which was equipped with an optical camera and three laser systems: an Ar-ion (488 and 514 nm), Kr-ion (568 nm), and a He−Ne (632.8 nm). For the purposes of imaging, the 543 nm laser line was used in conjunction with a 10× NA objective. The axial and lateral resolutions provided by Leica are 0.37 and 0.16 μm, respectively. The images were quantified and analysed into fluorescent intensity profiles by using a Leica TCS NT software. The Leica LSCM can be used to image in various scanning modes which include a planar section (xy scan), a vertical section (xz scan), and time-dependent imaging modes. For much of the work reported in this study the images were obtained using the xz-scan, thus providing an optical cross section of the object under study. Each xz-scan data set shown in this study represents an average of four scans and sometimes the averaging was done over eight scans. From the optical cross sections the intensity profile of the fluorophore was converted to a concentration profile of the dye molecules used in the dye diffusion experiments.

Figure 3.8. Leica Laser Scanning Confocal Microscopy system.
3.2.8 Micro-CT

The X-ray micro computed tomography (micro-CT) (Micro XCT XRadia machine, XRadia Inc. USA) was used to take 3D image. The machine is combined with a CCD camera (Andor) and a scintillate system as shown in Figure 3.9. It has a cone beam geometry which permits magnification regulation by adjusting ratio of the distance between the X-ray source and the sample (Z1) to the distance between the X-ray source and the detector (Z2). At the same time, the magnification can also be controlled by magnification lens which are limited from ×0.5 to ×40. The limiting resolution is between 1 and 30μm. The CCD camera is capable of acquiring X-ray images of 2048 × 2048 pixels with a depth of 16 bits per pixel. The samples were wetted with water on the hydrophilic surface. During the test, X-ray source voltage was standardised at 40 kV and beam current at 150 μA from tungsten as a target material. The distances were set 125 mm for Z1 and 20 mm for Z2 in advance. The magnification factor from lens was ×20. The samples were scanned at a rotation step of 0.25 degrees over 180 degrees. Each sample would take about 2 hours to get 10243 voxel tomograms of 1.0 G data and to capture 721 projections of 6.0 G data with a spatial resolution of 1.155 μm and exposure time of 60s/projection.
3.2.9 Air permeability

Air permeability was measured by FX 3300 Air permeability tester according to the Standard (SIST EN ISO 9237-1999) as shown in Figure 3. 10. All values reported represent the mean of 5 measurements.
3.2.10 Washing durability

The washing durability was evaluated by reference of the washing procedure described in the AATCC (American Association of Textile Chemists and Colorists) Test Method 61-2006 test No. 2A. The test was performed using a washing machine equipped with 500 mL (75 mm × 75 mm) stainless-steel lever-lock canisters. The fabric sample (size, 50 mm × 150 mm) was laundered in a 150 mL aqueous solution containing 0.15% (w/w) AATCC standard reference detergent WOB and 50 stainless steel balls. During laundering, the temperature was controlled at 49 °C, and the stirring speed was 40 ± 2 rpm. After 45 minutes of laundering, the samples were rinsed with deionized water, and then dried at room temperature without spinning. This standard washing procedure is equivalent to five cycles of home machine launderings. For
convenience, we used equivalent number of home laundering in this work. The contact angle and sliding angle were then measured.

3.2.11 Abrasion durability

The abrasion durability was tested using the Martindale method according to ASTM D4966. The test was performed under a commercial Martindale abrasion tester (I.D.M Instrument Design & Maintenance) as shown in Figure 3.11. The untreated fabrics were used as abradant 9 kPa of pressure, which is often used to evaluate the coated fabrics for heavy duty upholstery usages, was employed during the test.

![Figure 3.11. Martindale machine for abrasion durability test.](image)

3.2.12 Bending modulus

The softness measurement of fabric samples were tested by the cantilever method using a M003B Shirley stiffness tester (BS 3356 BS 9073 part 7 and ASTM D1388) as shown in Figure 3.12. The bending modulus $Q$ (mg/cm²) was calculated according to the equations below:

$$Q = \frac{12G \times 10^{-3}}{g^3}$$  \hspace{1cm} (1)
\[ G = MC^3 \]  \hspace{1cm} (2)

Where \( g \) is the fabric thickness in centimetres, \( G \) is the flexural rigidity, \( M \) is the mass per unit area of the fabric in g/m\(^2\), and \( C \) is the bending length in centimetre. The thickness of the fabrics were measured using a MES-DAN micrometre for fabrics. Measurements were carried out on samples of fabric 2.5 cm wide and 20 cm long, and cut in the warp and weft directions.

![Figure 3.12. Bending modulus instrument.](image)

### 3.2.13 Fabric thickness

The thickness of fabrics used in this project were measured using a MESDAN LAB micrometre as shown in Figure 3.13. The fabric was placed under a load plate with a loading weight of 1 N. The fabric thickness was displayed on the meter automatically.
3.2.14 Moisture management test (MMT)

A moisture management tester (MMT) was employed to characterize water transport profile on the one-side coated polyester fabrics. Figure 3.14 shows the basic principle (a) and the instrument of MMT (b). A fabric sample was placed horizontally between two arrays of moisture sensors. During testing, a small volume (0.17 g) of saline water (0.9% NaCl in DI water) \(^{87}\) (synthetic sweating, AATCC 15) was dropped from top to the centre of the sample. The areas where were wetted by the saline water increased the local conductivity considerably. Through measuring the conductivity change on the two fabric sides using a computer, the relative water content (unit %) based on the dry state was obtained, which be reported directly by the MMT software.
3.2.15 WL 372 Heat Conduction Unit

For WL372 measurements, the samples were cut into cycles (radius = 25mm). Figure 3.15 shows the setup and the basic principle of the instrument. The heating power was set as 15 W manually with a continuous water cooling flow (1.0 L/h). 2 samples can be measured in one test as the sample can be nipped tightly between sensor 3 and 4 or sensor 6 and 7. To decrease heat lose between the sensors, only one sample which is nipped between the sensors 3 and 4 was applied during the experiment.
Figure 3.15. a) Experimental setup for linear heat conduction with graphical display of the temperature profile, b) 1--heater, 2--measuring object, 3--cooling element; x1-x3, x4-x6, and x7-x9--measuring points.

### 3.2.16 Digital thermometer measurement

For thermometer measurements, a Fluke 289 RMS digital thermometer, a thermocouple probe, a heating source and a Fluke view form 3.3 software were included. The heat source was provided by the Julabo 5EH water circulation bath system, and the thermocouple probe was fixed on the outer wall of the steel cylinder that was in contact with the fabric, which was cut into cycles (radius = 50 mm), and to record the temperature changes when the fabric was heated to 50 °C. All the recorded data were processed with software.
3.2.17 Infrared Camera (IR Camera)

An IR camera (model: IEC thermo tracker IR camera) was used to record the temperature change of the whole fabric. The recorded thermal images were processed with Image Pro II 4.0.6 micron infrared software. The emissivity of all the samples were calibrated by adjusting the camera emissivity to make the temperature measured being the same as using a standard thermocouple. For recording the heat losing process during the hot water attacking, IR thermography video was taken instantly.
Figure 3.17. H2640 Infrared camera.
Chapter 4

Durability Superhydrophobic Fabrics from SU-8 Derived Coating

In this chapter, superhydrophobic fabrics with a very low contact angle hysteresis were prepared using a single-pot coating solution comprising SU-8 (a negative photoresist), a fluorinated alkyl silane and silica nanoparticles. The fabrics were treated by dip-coating technique and subsequently curing under UV light. The coated fabrics showed excellent superhydrophobicity with a water contact angle as high as 163° and a sliding angle as low as 2°. The coating was durable enough to withstand at least 100 cycles laundry. It also had excellent stability against long hour immersion in organic solvents, acid and base solutions.

4.1 Experimental

4.1.1 Synthesis of coating solutions

A commercial SU-8 (1.4 wt%) was magnetically stirred in dark at room temperature for one hour to get a homogeneous solution. FAS and hydrophobic silica particles which were prepared by a modified Stöber method were added in sequence to the SU-8 solution. After 1 hour stirring, the coating solution containing well-dispersed nanoparticles was ready for use.

4.1.2 Coating treatment of fabrics

A dip-coating method was employed for coating treatment. Cotton fabric samples were immersed into the coating solution for 5 minutes, and then dried at room temperature for 30
minutes. The fabric samples were then irradiated by UV light (intensity 80 mW/cm²) for 10 minutes and further cured at 120 °C for 10 minutes.

4.2 Results and Discussion

4.2.1 Preparation of the coating solution

Figure 4.1 illustrates the procedure to synthesise the surface modified silica nanoparticles, the superhydrophobic coating solution for the coating treatment, as well as the chemical structures of the coating materials. Hydrophobic silica nanoparticles were prepared by hydrolysis and condensation of tetraethylorthosilicate (TEOS) and then functionalized by fluorinated alkyl silane (FAS) under an alkaline condition. After purification, the as-obtained silica nanoparticles were dispersed into a SU-8/FAS solution to form the coating solution.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{O} - &\text{Si} - \text{OCH}_2\text{CH}_3 + \text{F}_5\text{C}-\text{(CF}_2\text{)}_5 \text{(CH}_2\text{)}_2 - \text{Si} - \text{OCH}_2\text{CH}_3 \rightarrow \\
&\text{OCH}_2\text{CH}_3 + \text{NH}_4\cdot\text{OH}/\text{ethanol} \rightarrow \text{OCH}_2\text{CH}_3
\end{align*}
\]

Figure 4.1. The reaction route of silica nanoparticles preparation and the chemical structures and coating procedure.

4.2.2 Preparation of hydrophobic silica nanoparticles

In this work, silica nanoparticles were synthesized by a sol-gel process which involved two steps: nucleation and growth. The related chemical reactions processes are as follows:

\[
\text{Si(OR)}_4 + 4\text{H}_2\text{O} \rightarrow \text{Si(OH)}_4 + 4\text{OH} \quad \text{(Hydrolysis process)}
\]
Si(OH)₄ → SiO₂+ 2H₂O  

(Condensation process)

Ammonia used here acts as a catalyst to accelerate the hydrolysis and condensation process of TEOS as the hydrolysis process at neutral condition runs very slowly. After nucleation, particle growth proceeds until the reaction stops due to the equilibrium solubility. Figure 4.2 shows the morphology of the purified silica nanoparticles under scanning electron microscope (SEM).

![SEM image of hydrophobic silica nanoparticles](image)

Figure 4.2. SEM images of hydrophobic silica nanoparticles. Scale bar of the insert image is 1 µm.

### 4.2.3 Coating process

The as-obtained coating solution was dip-coated onto the cotton fabric sample through a three steps coating involving coating solution immersing, UV irradiation and heat curing step.

### 4.2.4 Surface wettability
4.2.4.1 Effect of SU-8 on wettability, air permeability and pore size of the coated fabrics

The effect of different concentration SU-8 on water contact angle (WCA), sliding angle (SA) and air permeability (AP) of the cotton fabric was examined. In this study, a plain weave cotton fabric was mainly used as a model substrate. Figure 4.3 (a, b) shows the WCA, and SA change of the fabrics coated with different concentration SU-8 solutions. Due to the inherent hydrophobicity of SU-8 resin, the WCA increased considerably from 0° to 131° when SU-8 content in the coating solution increased from 0% to 0.4 wt%. Further increasing the SU-8 content led to a small increase in the WCA. Increasing the SU-8 concentration from 0.4% to 1.6% resulted in a small change of SA from 23° to 20°, however, further increasing SU-8 concentration from 1.6% to 2.0% led SA decrease to 15° due to the reduced surface roughness caused by the extra SU-8 resin on the coated fabric.

To estimate the fabric’s breathability after coating, which is an important indicator for wearer’s comfortableness, the air permeability of the fabric was measured. The air-permeability of the coated fabrics was fluctuated at around 25 cm³/cm²/s as shown in Figure 4.3 c. In order to obtain a hydrophobic fabric with higher WCA, small SA, and as well as good AP, 1.4% SU-8 was chosen throughout the further experiments.
Figure 4.3. Effect of SU-8 content in the coating solution (without FAS and nanoparticle) on a) WCA, b) SA and c) AP of coated cotton fabrics.
For fluctuation of air permeability with SU-8 content in the coating solution can be explained by the effect of the SU-8 coating on the pore size of the fabric. At this coating condition, the portion of larger pores (size over 40 µm) increased after coating treatment, while the portion of the smaller pores remained in the same level (Figure 4.4). This increased portion of large pores was attributed to the shrinkage of yarns in the fabric which was induced by the capillary effect during the coating treatment at this condition.

![Figure 4.4. Histogram of pore size distribution for cotton fabric after coating with SU-8 solution of different contents.](image)

4.2.4.2 Effect of SU-8/FAS on WCA, SA, AP and pore size

To improve the water repellent property, FAS was added into the 1.4% SU-8 solution. Figure 4.4 shows the effect of different content FAS in 1.4 wt% SU-8 solution on the wettability and air-permeability of the coated fabric. When the FAS content increased from 0.7 wt% to 7.0 wt%, the WCA increased initially (the FAS content is 2.8 wt%) and then decreased to 140°. The highest WCA (155°) was found at a FAS content of 2.8 wt%. The initial increase in WCA comes from the effect of FAS on surface free energy. FAS is often used to lower surface energy...
for superhydrophobic treatment. The further decrease in the WCA at higher FAS content was attributed to the reduced surface roughness caused by the extra FAS on the coated fabric. In contrast, the presence of FAS in the coating led to decrease in SA as shown in Figure 4.4. When the coating solution contained 2.8 wt% FAS, the coated fabric showed a SA of 15°. The SA value remained almost unchanged with further increasing the FAS content in the coating solution. The addition of FAS to 1.4 wt% SU-8 solution for coating treatment had little effect on the air permeability of the coated fabric.
Figure 4.5. Effect of FAS content in 1.4 wt% SU-8 solution on a) WCA, b) SA and c) AP of coated cotton fabrics.
Figure 4.8 shows the effect of SU-8/FAS on pore side of the coated fabrics. The portion of larger pores (size over 30 µm) decreased after coating treatment, while the medium pores (size over 20 µm) increased after coating. This changes can attribute little effect on the permeability value.

Figure 4.6. Histogram of pore size distribution for cotton fabric treated with SU-8/FAS solution containing 1.4 wt% SU-8 and different concentrations of FAS.

### 4.2.4.3 Effect of SU-8/silica nanoparticles on WCA, SA and AP

Silica nanoparticles were then added into 1.4% SU-8 solution to improve the surface roughness of the coated fabrics. Figure 4.7 shows the effect of different concentration silica particles on WCA, SA and AP of the coated fabric. When SU-8 content was kept at 1.4 wt%, increasing the nanoparticle content from 0% to 1.0 wt%, an increased WCA and a decreased SA can be observed clearly. However, further increasing the nanoparticle content from 1.0 to 2.0 wt% led to very little change in both WCA and SA values. Different to WCA and SA, the AP only showed a monotonic decrease with increasing the nanoparticle content when the nanoparticle content in the coating solution was less than 1.0 wt%. When the nanoparticle
content in the coating solution increased from 1.0 wt% to 2.0 wt%, the AP value was almost unchanged.

Figure 4.7. Effect of silica nanoparticles content in 1.4 wt% SU-8 solution on a) WCA, b) SA and c) AP of coated cotton fabrics.
4.2.4.4 Effect of SU-8/FAS/silica nanoparticles on WCA, SA and AP

Silica nanoparticles were then added into SU-8/FAS solution, Figure 4.8 shows the wettability and AP change with different amount silica nanoparticles content. With increasing the concentration of silica particles, the WCA increased, while SA decreased. The highest WCA and lowest SA can be obtained when the concentration reached 1.0%. AP test showed that increase silica particles concentration to 1.0% did not influence the fabric’s AP.
Figure 4.8. Effect of silica nanoparticle content in FAS/SU-8 solution (SU-8: 1.4 wt%; FAS: 2.8 wt%) on a) WCA, b) SA and c) AP of coated cotton fabrics.
Based on the above results, the WCA of the fabric indicated a maximum increase of 131°, 155°, 153° and 163° after coated with SU-8 alone, SU-8/FAS solution, SU-8/nanoparticles solution and SU-8/FAS/nanoparticles mixture respectively. Accordingly, the SA of the fabric changed to 15°, 10°, 4°, 2°, respectively. SU-8 showed the most significant impact on the WCA due to its inherent hydrophobicity, and the hydrophobic silica nanoparticles affected the SA the most because of the increase in surface roughness.

4.2.5 Surface morphology

Figure 4.9 shows the SEM images of the cotton fibres before and after coating with different materials. In comparison with the uncoated cotton, the fibres after coating with SU-8 or SU-8/FAS showed a similar surface morphology (Figure 4.9 a, b, and c). This suggests that SU-8 and SU-8/FAS have little effect on the fibre morphology, and their increase in the hydrophobicity should come from contribution to lowering the surface free energy. When the fabric was coated with the SU-8/nanoparticles, a particulate morphology can be seen on the fiber surface (Figure 4.9d). In this case, the cotton fibres are considerably increased in the surface roughness. By lowering the surface energy and meanwhile increasing the fiber roughness (Figure 4.9e), the fabric coated with SU-8 containing both FAS and nanoparticles reached the highest WCA (163°) and the smallest SA (2°).
Figure 4.9. SEM image of a) uncoated cotton fabric, and cotton fabric coated with b) SU-8 (1.4 wt%), c) SU-8/FAS (1.4 wt% : 2.8 wt%), d) SU-8/nanoparticle (1.0 wt%) and e) SU-8/FAS/nanoparticles. (Scale bar = 5 µm)

After SU-8/FAS/nanoparticles coating, nanoparticles were uniformly dispersed on the fabric surface, which enhance the surface roughness at the nano-scale to compliment the micro-scale roughness inherent in the fabric weave. The as-obtained hierarchical roughness structures on the nano and micro scales on the treated fabrics are well known to enhance the hydrophobicity. When water (10 µL) was dropped on the fabric, it formed a nearly-sphere droplet, which can stay stably for a long period of time. This is considerably different to the uncoated cotton fabric, in which water drop spread completely into the fabric matrix within a second (Figure 4.10).
Figure 4.10. a) SEM images of the SU-8/FAS/Silica nanoparticles coated cotton fabric, insert image is the magnification of image a), and the photographic images of dyed water droplet (10 µl) on the b) untreated and c) treated cotton fabric (SU-8 1.4 wt%, FAS 2.8 wt%, and Silica nanoparticles 1.0 wt%).

### 4.2.6 Chemical components of the coated surface

#### 4.2.6.1 FTIR spectra results

As shown in Figure 4.11, after coating treatment new peaks appeared at 1500 cm$^{-1}$, which was assigned to the aromatic C=C vibration of SU-8. The peaks at 1240 cm$^{-1}$ and 798 cm$^{-1}$ corresponded to the C-F and Si-O-Si stretching vibrations, respectively. The peaks at 1100 cm$^{-1}$ and 1050 cm$^{-1}$ were assigned to C-O and C-O-C vibrations. These results confirmed that C-F and Si-O-Si bonds were formed on the coated fabric, which could decrease the surface energy.
4.2.6.2 XPS survey spectra results

Figures 4.12 show the XPS survey and high-resolution C1s and Si2p spectra of the cotton fabric before and after coating treatment. The C1s spectra indicated that the uncoated fabric contained C-C bonds (binding energy, 284.8 eV), C-O (286.5 eV) and O-C-O (288.1 eV) bonds. For the coated fabric, three additional broad peaks formed with the binding energy at 291.3 eV, 292 eV and 294 eV, respectively, which are typical characteristics of -C=C-, -CF$_2$ and -CF$_3$ moieties$^{21}$. The Si2p spectra showed a peak with binding energy at 103.3 eV, corresponding to the silica structure. Table 4.1 shows the elemental composition of the cotton fabric before and after coating treatment, these results confirmed that after coating with SU-8/FAS/silica particles, two new elements, i.e. silica and fluorine, were detected on the fabric surface.
Figure 4.12. a) XPS survey spectra and b) XPS high-resolution C1s and c) Si2p spectra of the cotton fabric before and after coating treatment with SU-8/FAS/nanoparticles.

Table 4.1. Elemental composition of the cotton fabric before and after coating treatment

<table>
<thead>
<tr>
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<th>Atomic Content (%)</th>
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<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Pure cotton</td>
<td>60.21</td>
</tr>
<tr>
<td>SU-8/FAS/Silica particles</td>
<td>29.52</td>
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</tbody>
</table>
4.2.7 Coating durability

4.2.7.1 Washing durability

The washing durability of the coated fabrics was evaluated by reference of a standard washing procedure (AATCC Test Method 61-2006 test No. 2A). Figure 4.13a shows the WCA and SA changes of the coated fabrics with laundry cycles. The WCA slightly decreased from 163° to 157°, whereas the SA remained lower than 8°, after 100 washing cycles.

The surface morphologies of the coated fabrics after washing were observed. As shown in Figure 4.13 b ~ f, with increasing the washing cycles, some particles can be removed from the fiber surface, however, after 100 washing cycles, a thin layer of silica particles can be observed clearly, which provide a high surface roughness.
Figure 4.13. a) WCA and SA change with different laundry cycles, and SEM images of the coated fabric after b) 20 cycles, c) 40 cycles, d) 60 cycles, e) 80 cycles and f) 100 cycles of washing (Scale bar = 5 µm).
4.2.7.2 Solvent durability

Solvent resistance was tested by immersing the coated fabrics in various organic solvents respectively. The water contact angle and sliding angle were measured after immersion in different periods of time (up to 96 hours, 4 days). Both WCA and SA showed no change after 96 h of immersion in five organic solvents, i.e. ethanol, dimethylformamide (DMF), acetone, ethyl acetate and 2-butanone, used (Figure 4.14). After 96 hours immersing, the fabric’s WCA and SA still maintained almost no change, which indicated that the coated fabric exhibits excellent stability to many kind solvents.

![Figure 4.14. WCA and SA of the coated cotton fabric after immersion in various organic solvents.](image)

4.2.7.3 Acid/base stability

Chemical stability was tested by immersing the coated fabrics in aqueous solutions of different pH values, respectively. The water contact angle and sliding angle were measured after immersion in different periods of time (up to 96 hours, 4 days). Both WCA and SA showed no change after 96 h of immersion in aqueous solutions of different pH values (Figure 4.15). When the fabric was immersed in aqueous solutions, a thin layer of air was formed.
between the fabric and the water, and the fabric tends to floating. To make the fabric fully contact with the solution, a bulb pipet was used to remove the air layer. After 96 hours of immersion in aqueous solutions with different pH values, both WCA and SA were almost unchanged.

![Graph showing WCA and SA of the coated cotton fabric after immersion in aqueous solutions with different pH values.](image)

Figure 4.15. WCA and SA of the coated cotton fabric after immersion in aqueous solutions with different pH values.

The excellent stability against solvents and acid/base should stem from the chemical stability of the crosslinked SU-8. Upon exposure to UV, SU-8 crosslinks to form a highly crosslinked structure. The silane head of FAS is hydrolysable and can condense to form insoluble macromolecules. These allow the coating highly stable in organic solvents and can withstand chemical damage. The epoxide groups of SU-8 also allows forming chemical bonding with the cotton substrate. It should be indicated that SU-8 in the coating functions as a coating matrix to host FAS and nanoparticles. Because of the chemical reactivity, the SU-8 could also form chemical links with the cotton substrate and nanoparticle (through hydroxyl groups), which enhances the adhesion. Crosslinking of the SU-8 allows the coating have excellent chemical durability and solvent resistance. In comparison with other sticky polymers,
e.g. polyacrylate and polyurethane, SU-8 is easy to form chemical bonding with fabric substrates, which facilitates to enhance the durability, chemical stability and solvent resistance.

### 4.2.7.4 Self-cleaning property

To prove the self-cleaning ability, we placed dusts on the coated fabrics and then cleaned the dust-contaminated surface by rinsing with water. As shown in Figure 4.16 (a ~ c), the dusts are easily taken away by rolling of water droplet, resulting in a completely clean surface. However, the dust on the uncoated cotton fabric was hard to be cleaned in a similar manner (Figure 4.16 a’ ~ c’). This indicates that the treated fabric has a bio-mimicking self-cleaning property similar to lotus leaf.

![Figure 4.16. Still frames taken from videos showing dropping water on the dust contaminated fabrics, a ~ c) superhydrophobic coated fabric, and a’ ~ c’) uncoated cotton fabric.](image)

### 4.2.7.5 Bending modulus

In addition, the bending modulus of the fabric before and after the coating treatment was examined. The fabric rigidity was tested by the cantilever method using a M003B Shirley stiffness tester (BS 3356 BS 9073 part 7 and ASTM D1388). As shown in Figure 4.17, the bending length only increased slightly in both warp and weft directions after the coating
treatment. The bending length is an indication of the fabric handle property. The higher the bending length, the more rigid the fabric is, and the fabric is less comfortable to wearers. The small difference in the bending length indicates that the superhydrophobic coating had a small influence on the fabric handle.

Fig. 4.17. Bending length of the cotton fabric before and after the superhydrophobic coating treatment.

4.2.7.6 Coating treatment on other fabrics

Apart from cotton, we also used other fabrics such as polyester and wool fabrics as substrate. Polyester and wool fabrics were treated by the SU-8/nanoparticle/FAS coating. As expected, both the fabrics turned superhydrophobic after the coating treatment. The treated fabrics had a WCA higher than 167° and SA as small as 2°. (Figure 4.18 a & b), suggesting that the coating system is suitable for treatment of different types of fabrics. SEM images of the coated polyester and wool fabrics clearly show the hierarchical surface roughness (Figure 4.18 c & d).
4.2.8 Discussion

Superhydrophobic surfaces with high water repellency and low contact angle hysteresis (typically < 10°) often have a bio-mimicking self-cleaning property. The majority of self-cleaning, superhydrophobic fabrics are prepared by forming nano-/micro-scaled rough surface and by decreasing the surface free energy.

SU-8 is an epoxy-based photoresist widely used for making optoelectronic devices, micro-electro-mechanical systems (MEMS)\textsuperscript{123-124} platforms and microfluidic devices\textsuperscript{125}, scaffolds for supporting cell growth and tissue repair\textsuperscript{126}, and ultrafine fibres\textsuperscript{76,127}. It is chemically inert, able to produce high-aspect-ratio structures, compatible and easy to integrate with the underlying substrate.
While having a micro-scaled rough surface because of the texture structure, cotton fabric just coated with SU-8 does not show superhydrophobicity. However, when FAS is present in the coating, the coated fabric becomes superhydrophobicity though the fibres have little change in surface morphology. This suggests that lowering the surface free energy contributes to superhydrophobicity.

Superhydrophobicity can also be further improved by just adding nanoparticles to SU-8 coating. In this case, the cotton fibres are considerably increased in the surface roughness. By lowering the surface energy and meanwhile increasing the fibre roughness, the coated fabric reached the highest WCA (163°) but the smallest SA (2°) among all the coated fabric samples. Such a surface causes water to bounce and roll off easily and maintains the surface in a dry state, so that the dirt on these surfaces can be easily removed through the liquid.

It should be indicated that SU-8 in the coating functions as a coating matrix to host FAS and nanoparticles. Because of the chemical reactivity, the SU-8 could also form chemical links with the cotton substrate and nanoparticle (through hydroxyl groups), which enhances the adhesion. Crosslinking of the SU-8 allows the coating have excellent chemical durability and solvent resistance. In comparison with other sticky polymers, e.g. polyacrylate and polyurethane, SU-8 is easy to form chemical bonding with fabric substrates, which facilitates to enhance the durability, chemical stability and solvent resistance. The excellent superhydrophobicity of the fabric should mainly come from the tough SU-8/FAS/silica nanocomposite, independent of the fabric types. SU-8 is a negative photoresist. Its solidification process under UV light would affect the bending property when the underlying substrate is fabrics, however, the superhydrophobic coating only show minimum influence to the handle property of fabrics as only a very small concentration of SU-8 was applied in our case.
4.3 Conclusion

We have prepared a superhydrophobic cotton fabric using a one-pot coating solution comprising commercial photoresist SU-8, a fluorinated alkyl silane and silica nanoparticles. The coated cotton fabrics have high superhydrophobicity with a very low contact angle hysteresis. The coating shows excellent durability against organic solvents, acid and base solutions, as well as repeated washing. This superhydrophobic coating may be useful for developing functional fabrics for various applications in personal protection areas.
Chapter 5

Preparation and Characterisation of Directional Water Transport Fabrics

Directional water transport fabrics were prepared using an electro-spraying method. A hydrophilic fabric after being electro-sprayed with a thin layer of hydrophobic coating on one side showed directional water transport ability. Effect of spraying distance and applied voltage on coating uniformity was examined. The directional water transport property was qualified using moisture management tester (MMT) and the effect of hydrophobic fibrous layer thickness on directional water transport feature was examined. Also, the washing durability of the directional water transport fabric was tested.

5.1 Experimental

5.1.1 Pre-treatment of polyester fabric

The polyester fabric was pre-treated with 10% strong alkali solution at 60 °C for 25 min to break down the polyesters by saponification. And then, the treated fabric was rinsed with DI water, neutralized by 3% acetic acid solution and rinsed with DI water again. The fabric was finally dried at room temperature in air for 24 hours.

5.1.2 Preparation of coating solution

A commercial SU-8 (1.4 g) was dissolved into acetone (100 mL) to get a homogeneous solution, which can be directly used for electro-spraying treatment.
5.1.3 Electro-spraying coating process

The pretreated fabric was coated with SU-8 on one side using a purpose-built electrospraying device which could generate a thin SU-8 coating on fabrics. To prepare fluorescent-labelled samples for confocal microscopy measurement, Rhodamine B (4 wt %) was added to SU-8 coating solution and followed by UV irradiation and heat curing steps.

5.1.4 UV irradiation of electro-sprayed fabrics

The one-side electro-sprayed fabrics were irradiated under a UV light with the intensity of 80 mW/cm² for 10 minutes, and followed by heat curing step.

5.2 Results and Discussion

5.2.1 Pre-treatment of polyester fabric

Polyester fabric was pre-treated by immersing in an aqueous NaOH to hydrolyse the fibre surface. By carefully controlling the treatment conditions such as NaOH concentration, treatment time and temperature to make sure that only fibre surface is hydrolysed, the NaOH treated fabric showed almost no change in fabric surface morphology (as shown in Figure 5.1d). After NaOH treatment, the fabric turned hydrophilic, with a water CA of 0°, while the control polyester fabric showed a CA of 118° (Figure 5.1 e and f).
Figure 5.1. SEM images of polyester before (a & b) and after (c & d) NaOH treatment under low and high resolutions, respectively. And the photographic images of dyed water droplets (10 µL) on the polyester fabrics of: c) before and d) after NaOH treatment, respectively. Scale bar is 10 µm.

As it is well-known, strong alkali can break the ester links in polyester. The hydrolysis reaction leads to change in chemical constitution, converting ester to carboxyl and hydroxyl
groups. Since both carboxyl and hydroxyl groups are hydrophilic, the pre-treatment of polyester fabric with alkaline solution resulted in a hydrophilic surface.

5.2.2 Electro-spraying coating process

Figure 5.2a shows the fabric treatment procedure. SU-8 solution was then deposited on one side of the NaOH pre-treated fabric using an electro-spraying technique. To prove the coating evenness, a red dye was added into the SU-8 solution. As shown in Figure 5.2b, after one side electro-spraying, the fabric is uniformly covered with a layer red substance just on the sprayed surface, whereas the unsprayed side still preserves the original colour.
Figure 5.2. a) Chemical structure of SU-8 and schematic of one-side electro-spraying treatment, b) photos of polyester fabric after NaOH treated (control) and one-side electro-spraying treatment with SU-8 (a red dye was added to SU-8 solution to indicate the coating layer).

5.2.3 Morphologies

5.2.3.1 SEM images

SEM images of the polyester fabric after one-side electro-spraying treatment are shown in Figure 5.3. The un-sprayed side maintained the polyester natural morphology as seen in Figure 5.3a & b. On the electro-sprayed side, however, a thin coating layer can be found on the fibres surfaces (Figure 5.3c & d).
Figure 5.3. SEM images of polyester fabrics: the un-coated side under low a) and high b) resolution, and SU-8 electro-sprayed fabric side under low c) and high d) resolution, respectively. (Scale bar = 10 µm in Figure b and d).

Spraying distance and applied voltage for electro-spraying were optimized to obtain uniform SU-8 coating on the fabric. As shown in Figure 5.4d, a thin conformal coating was formed just on the electro-sprayed fiber surface when the distance is 6 cm and 22 kV voltage was applied.

Figure 5.4. SEM images of polyester fabrics of an un-coated fabric and one-side SU-8 electro-sprayed fabric a) 2 cm, 5 kV, b) 4 cm, 10 kV, c) 5 cm, 15 kV and d) 6 cm, 22 kV.
5.2.3.2 Micro-CT images

X-ray microtomograph (micro-CT) was used to observe the coated fabrics. Figure 5.5 shows the typical cross-sectional micro-CT images of the polyester fabrics before and after one side electro-spraying with SU-8. To increase the image contrast between the hydrophilic and the hydrophobic parts, all the test fabrics were wetted with water during the testing process. Figure 5.4a shows the control hydrophilic polyester fabric. There was no colour difference along the entire cross-section of the wetted fabric. After electro-spraying of SU-8 on one side of the fabric, an obvious image contrast between un-wetted (which is in green) and wetted (which is in blue) areas can be observed as seen (Figure 5.4 b to d). Based on the 2D images, the wetting depth can be measured. Increasing the SU-8 loading resulted in an increased hydrophobic layer thickness, therefore the wetting depth decreased. When the loading was 0.2 g/m², the wetting depth was 388 µm (the coating thickness was 22 µm) as seen in Figure 5.4b, while the wetting depth changed to 351 µm (the coating thickness was 59 µm) when the loading was 0.6 g/m² (Figure 5.4c). Increasing the loading to 2.0 g/m² led to decrease of the wetting depth to 338 µm (the coating thickness was 72 µm) as seen in Figure 5.4d.
Figure 5.5. 2D cross-sectional micro-CT images of the water wetted fabrics before and after one side electro-spraying coating treatment with different loading capacity: a) control fabric; b) 0.2 g/m²; c) 0.6 g/m² and d) 2.0 g/m²; respectively. Scale bar = 250 µm.

The effects of SU-8 concentration on coating thickness was also examined. Figure 5.6 shows the micro-CT images of coating thickness change of the fabrics coated with different concentration of SU-8 solutions under the same loading capacity. It can be seen that the coating thickness decreased constantly when SU-8 content in the coating solution increased from 0.7 wt% to 2.8 wt%. The decrease of coating depth at higher SU-8 concentration mainly comes from the faster solvent evaporation rate. To reach the same SU-8 loading capacity, a slower flow rate is applied for the higher SU-8 concentration solution. Thus, a faster evaporation would be developed as acetone is a highly volatile solvent, which eventually cause a decreased penetration depth of SU-8 resin on the fabric.
Figure 5.6. 2D cross-sectional micro-CT images of the water wetted fabrics before and after one side electro-spraying coating treatment with different SU-8 concentration under the same loading: a) 0 wt%; b) 0.7 wt%; c) 1.4 wt% and d) 2.8 wt%; respectively. Scale bar = 250 µm.

5.2.3.3 Confocal microscopy images

Apart from micro-CT, laser scanning confocal microscopy (LSCM) imaging was also employed to observe the one side SU-8 sprayed fabrics and verified the coating thickness (Figure 5.7). To distinguish the SU-8 coating layer from the uncoated area, a fluorescence indicator (Rhodamine B) was added into SU-8 coating solution. The light blue area clearly indicated that a thin SU-8 coating was formed on one side of the fabric. The coating thicknesses were 14 µm, 45.6 µm, and 67.7 µm, respectively, when the loadings were 0.2 g/m², 0.6 g/m², and 2.0 g/m². This result confirmed that with increasing SU-8 loading, the hydrophobic thickness increased.
Figure 5.7. LSCM images of the fabrics before and after one side electrospray coating with SU-8 with different loading capacity, a) 0 g/m$^2$; b) 0.2 g/m$^2$; c) 0.6 g/m$^2$ and d) 2.0 g/m$^2$; respectively. The light blue profile can be converted as coated area.

### 5.2.3.4 Optical microscopy images

In addition, optical microscopy was used to observe the SU-8 coating layer when a red dye was added into the SU-8 solution. Photographic imaging also revealed that fabric after one-side electro-spraying treatment had a thin layer of coating on just the sprayed side. (Figure 5.8)
5.2.3.5 Optical images

Upon electro-spraying with a hydrophobic resin (SU-8) on just one-side, the treated fabric showed a different wettability on two sides. Depending on the SU-8 loadings, the sprayed fabrics showed different water transport feature to water. As shown in Figure 5.9, the water can transfer through the fabric thickness from both sides when the SU-8 loading is 0.2 g/m², and, fabric with 0.6 g/m² SU-8 loadings shown a directional water transport property. When the SU-8 loading reached to 2.0 g/m², the dyed water will be blocked from both sides of the fabric.
Figure 5.9. Photographic images of dyed water droplets on the coated side and uncoated side of NaOH pre-treated polyester fabric with (a) 0.2 g/m², (b) 0.6 g/m², and (c) 2.0 g/m² SU-8 loadings. (10µL for the measurement, the small amount of dyes used here have no influence on the CA values).

5.2.4 Surface wettability

5.2.4.1 Optical images

a) Water drops on uncoated fabric
Figure 5.10 shows the CA change with time on the two sides of uncoated polyester fabric. The CA change from 114° to 0° within 10 seconds on both sides, indicating the gradient wettability of the uncoated fabric.

**Figure 5.10.** Still frames from digital videos to show dropping blue-dyed water on the uncoated polyester fabric on a) the top surface and b) on the bottom surface.

**b) Water drops on NaOH pre-treated fabric**

Figure 5.11 shows the CA change with time on the two sides of NaOH pre-treated fabric. After treatment, the CA of the fabric is unable to measure as the testing water would penetrate into the fabric matrix very fast (within half second).

**Figure 5.11.** Still frames from digital videos to show dropping blue-dyed water on the NaOH pre-treated polyester fabric on the top surface (top) and on the bottom surface (bottom).
c) Water drops on one-side sprayed fabric

Figure 5.12 shows dropping water on the sprayed fabric (SU-8 loading, 0.6 g/m²). On the SU-8 coated surface, water drops rapidly penetrated through the fabric and spread into the opposite side which was not coated with SU-8 (Figure 5.12a). However, when dropping water on the uncoated side, it just spread in the uncoated fabric layer without penetrating to other side. These indicate that the SU-8 coated fabric with specific coating thickness after UV irradiation shows directional water transport feature.

![Figure 5.12](image)

Figure 5.12. Still frames from digital videos to show dropping blue-dyed water on electro-sprayed polyester fabric (a) on the SU-8 sprayed surface and (b) on the unsprayed back surface.

c) Hot water drops on one-side sprayed fabric

The directional water transport ability of the sprayed fabric (SU-8 loading, 0.6 g/m²) was observed horizontally using a digital camera. Figure 5.13 a ~ b show dropping red-colored warm water (temperature 37 °C) on the sprayed side of fabric (SU-8 loading, 0.6 g/m²). On the SU-8 coated hydrophobic surface (Figure 5.13a), red-colored cold water drop spherically stand on the surface at first and then rapidly penetrated the coating and wicked into the uncoated fabric matrix, which was not coated with SU-8. However, when dropping water on the uncoated
hydrophilic side, it just directly spread into the uncoated fibrous matrix layer without penetrating to other side.

Figure 5.13. Still frames from digital videos to show dropping red-colored cold water on a) the SU-8 sprayed surface and b) the unsprayed back surface of one-side electro-sprayed polyester fabric.

For comparison, when the directional transport ability for hot water on the SU-8 sprayed fabric samples was observed vertically as shown in Figure 5.14, it showed different water penetration process. As expected, when hot water was dropped on the SU-8 coated hydrophobic surface (Figure 5.14a), it moved through and spread on the uncoated hydrophilic side immediately. However, when dropping water on the uncoated hydrophilic side (Figure 5.14b), it only spread on the fabric surface, without penetrate to the fabric. The results indicate that the SU-8 one side electro-sprayed polyester fabrics shows a directional water transport effect to both cold and hot water.
5.2.4.2 Contact angle changes

a) Horizontal contact angle

Figure 5.15 shows water contact angle (CA) change during dropping water (5µL) on the horizontally-laid fabric samples. For the electro-sprayed fabric, the CA on the sprayed side of all samples increased to 138°, however, the CA changed from 138° to 0° within a few seconds when the loading was lower than 0.8 g/m² (2 seconds for 0.2 g/m² and 0.4 g/m², 3 seconds for 0.6 g/m² and 7 seconds for 0.8 g/m², respectively). When the loading was higher than 0.8 g/m² g, however, the CA was maintained at 138° (Figure 5.15a) without further change with time. While the CA of the unsprayed surface showed difference in the initial contact angle (0° for 0.2 g/m², 38° for 0.4 g/m², 64° for 0.6 g/m², 100° for 0.8 g/m², 1.0 g/m² and 1.5 g/m², and 120° for 2.0 g/m², respectively), and all non-zero contact angle reduced to 0° rapidly (within a second for 0.2 g/m² and 0.4 g/m², 7 seconds for 0.6 g/m², 10 seconds for 0.8 g/m², 15 seconds for 1.0 g/m², 28 seconds for 1.5 g/m² and 57 seconds for 2.0 g/m², respectively) (Figure 5.15b).
Although CA on both sides showed a reduced trend, they came from different water transport features. On the SU-8 sprayed surface, water penetrated the coating and wicked into the uncoated fabric matrix when the loading was lower than 0.8 g/m², whereas water on the SU-8 un-sprayed side spread directly into the fibrous matrix because of the hydrophilic nature of the pre-treated fabric.

Figure 5.15. Water contact angle changes from (a) SU-8 coated side and (b) uncoated side of fabrics with different SU-8 loadings.
b) Vertical contact angle

After electro-spraying of SU-8 coating solution on one-side of the fabrics, the fabric showed different wettability on both sides. When the SU-8 sprayed fabric samples were vertically dipped in water, they showed different water contact profiles, depending on the loading weight of SU-8. As shown in Figure 5.16, asymmetric cross-sectional wetting profile results for the SU-coated fabric at a low SU-8 loading weight (0.2 g/m²). On the un-sprayed side, the apparent water-fabric contact (also referred to as “vertical contact angle”, in this study) was around 32°, while the SU-8 coated side shows a slightly increased vertical contact angle (VCA), being around 42°. With increasing SU-8 loading weight to 0.6 g/m² and 2.0 g/m², the VCA on the SU-8 coated side increased to 70° and 137°, respectively. However, the uncoated side still maintained a low VCA value. For comparison, we also tested the vertical wetting profile of the control fabric (i.e. NaOH pre-treated polyester). As shown in Figures 5.16a and e, both fabrics showed almost symmetric VCA, and they had different VCA values, 30° and 131° for the control and the SU-8 dip-coated fabric, respectively.

![Figure 5.16](image-url) Cross-sectional view and corresponding wetting profile of vertically laid fabric with different SU-8 loadings in water, a) 0 g/m², b) 0.2 g/m², c) 0.6 g/m², d) 2.0 g/m², and e) dip-coated fabrics respectively.
5.2.5 Directional water transport ability

Table 5.1 lists water transport feature of SU-8 spraying coated fabrics with different SU-8 loadings. It was interesting to note that directional water transport effect happened when the SU-8 loading on one side of the fabric was in the range of 0.4-1.0 g/m². When the loading lower than 0.4 g/m², the fabric showed two way water transport feature. In this case, water can penetrate from either side of the fabric. However, when the loading was larger than the upper limit, water cannot penetrate through the fabric matrix from both sides. Based on the time required when the water transfer through the fabric and the wettability difference from both sides, the fabric with a SU-8 loading of 0.6 g/m² showed the optimized directional water transport effect.

Table 5.1. Effect of SU-8 loading weight on water transport feature VCA and coating depth.

<table>
<thead>
<tr>
<th>SU-8 loading (g/m²)</th>
<th>Water transport ability</th>
<th>VCA (°)</th>
<th>SU-8 coating depth (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Sprayed side</td>
<td>Unsprayed side</td>
</tr>
<tr>
<td>NaOH treated</td>
<td>Two way transport</td>
<td>30.7±4.3°</td>
<td>30.6°±3.1°</td>
</tr>
<tr>
<td>0.2</td>
<td>Two way transport</td>
<td>42.0±1.2°</td>
<td>32.0±1.7°</td>
</tr>
<tr>
<td>0.6</td>
<td>Directional transport</td>
<td>70.0±2.2°</td>
<td>36.0±1.8°</td>
</tr>
<tr>
<td>2.0</td>
<td>None transport</td>
<td>137.0±1.2°</td>
<td>41.0±2.5°</td>
</tr>
<tr>
<td>SU-8 dip-coated</td>
<td>None transport</td>
<td>132.3±3.1°</td>
<td>131.4±3.2°</td>
</tr>
</tbody>
</table>
5.2.6 Moisture management test (MMT)

A moisture management tester (MMT) was employed to characterize water transport profile on polyester fabrics. Figure 5.17 shows the basic principle of MMT. A fabric sample was placed horizontally between two arrays of moisture sensors. During testing, a small volume (0.167 g) of saline water (0.9% NaCl in DI water) was dropped from top to the centre of the sample. The areas where were wetted by the saline water increased the local conductivity considerably. Through measuring the conductivity change on the two fabric sides, the relative water content (unit %) based on the dry state was obtained, which be reported directly by the MMT (see measurement details in 129-130).

Figure 5.17. Basic testing principle of MMT.
5.2.6.1 MMT results on one-side electro-sprayed fabric

Figure 5.18 (a, b) shows the relative water content on the two sides of the electro-sprayed fabric with SU-8 loading of 0.6 g/m². When water was dropped on the SU-8 sprayed surface as seen in Figure 5.18a, the relative water content on the dropping surface which had SU-8 remained 0 until 56 seconds. After that the content value increased slowly to 30% at 120 seconds. However, the relative water content on the lower surface without SU-8 increased rapidly as seen in Figure 5.18b. In 7 seconds, the water content increased to 500%. After a small decrease at 20 seconds, it increased slowly to 623% at 120 seconds. This indicates that water on the SU-8 coated surface rapidly penetrates through the fabric and spread into the uncoated fabric matrix.
Figure 5.18. Typical MMT water content curves from the two sides of a one-side electro-sprayed treated fabric: a) Side A means SU-8 coated side is face up, b) Side B means SU-8 coated side is faced down.

5.2.6.2 One-way transport index (R value)

The MMT also reported wetting time, maximum wet radius, spreading speed, one-way transport index (also referred to as R value). R value has no unit. In the MMT, the R value is calculated by the equation: 
\[ R = \frac{\int (U_b - U_t)}{T} \]  
where \( U_b \) and \( U_t \) are the water content (%) of bottom layer and top layer respectively and \( T \) is the total testing time (s).

The one-side electro-sprayed fabric had an R value over 850 from sprayed side and -157 from unsprayed side (Table 5.2) when the loading was 0.6 g/m\(^2\). The R value is an indication of moisture management capacity in terms of textile applications. According to the standard \(^8\), R value between 200 and 300 represents very good water transport ability, and the value over 300 indicates excellent directional water transport ability. The R value difference from the two sides of fabrics can be a new indication of directional water transport feature. Since moisture transport is a critical property deciding the thermo-physiological characteristic of garment, one way water transport allows rapid removal of sweat from skin side to external garment surface. Fabrics with a high R value will improve perspiration when peoples are excessively sweating such as in tropical climes or during heavy physical work and hence regulate body surface temperature. This could enhance peoples’ endurance against high temperature and nervous perspiration, maintain the wearers in high competitive state, and reduce the chances to get heat stress. We also compared our fabrics with those which were reported to have a directional water transport feature prepared by other techniques\(^46, 48-54\). Most of the fabrics showed an R value far below 600, and they have no directional water transport either. High R value directional
water transport fabrics will be very useful for making high performance summer clothing, sportswear, special workwear and soldier uniform.

Table 5.2. MMT results in value of sample fabrics

<table>
<thead>
<tr>
<th>SU-8 loading (g/m²)</th>
<th>Wetting time (sec)</th>
<th>Max wetted radius (mm)</th>
<th>Spreading speed (mm/sec)</th>
<th>One-way transport index (R*)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Top</td>
<td>Bottom</td>
<td>Top</td>
<td>Bottom</td>
</tr>
<tr>
<td>NaOH treated</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
<td>25.0</td>
<td>25.0</td>
</tr>
<tr>
<td>0.2</td>
<td>2.7</td>
<td>2.2</td>
<td>20.0</td>
<td>30.0</td>
</tr>
<tr>
<td>0.6</td>
<td>65.5</td>
<td>6.4</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>2.0</td>
<td>7.2</td>
<td>120.0</td>
<td>5.0</td>
<td>0.0</td>
</tr>
<tr>
<td>SU-8 dip-coated</td>
<td>6.5</td>
<td>120.0</td>
<td>5.0</td>
<td>0.0</td>
</tr>
<tr>
<td>0.6 after 50 washing cycles</td>
<td>99.5</td>
<td>7.3</td>
<td>5.0</td>
<td>5.0</td>
</tr>
</tbody>
</table>

* R value was calculated using the equation \( R = \frac{\int (U_b - U_t)}{T} \), where \( U_b \) and \( U_t \) are the water content of bottom layer and top layer respectively and \( T \) is the total testing time (s)

5.2.6.3 MMT results on dip-coated fabric

Figure 5.19 shows the relative water content of saline water on the fabric with SU-8 dip coated in the MMT. Once water was dropped on the fabric, the water content on the top surface started increased, reaching 700% in 20 seconds. When water supply stopped, water content on the top surface decreased gradually until 30 seconds, after which the content stabilized at around 600%. In comparison, the bottom surface remained non-wetted during the test, and the water content kept 0% for 120 seconds.

It was expected that the water content measured on the SU-8 dip coated fabric should be very low because of the high hydrophobicity. This unexpectedly high water content on the top
surfaces were attributed to the non-transport property of the tested fabric. Due to the sensor tips were closed to each other, the pumped water would gather together on the top surface because of the high hydrophobicity of the fabrics and be measured by the adjacent sensor tips.

Figure 5.19. Typical MMT water content curves on SU-8 dip-coated fabric when the water was dropped on different sides.

5.2.6.4 MMT results on uncoated and NaOH pre-treated fabrics

To gain better understanding of the MMT result, we also tested uncoated and NaOH pre-treated polyester fabrics. Both fabrics showed similar water content profile between the two sides, although the water content on the two fabrics changed in different trends with time (Figure 5.20a). This can be explained by the different wettability of the fabrics. In addition, we
also tested water content on SU-8 dip-coated fabric, which showed similar water content profile on the two sides as well (Figure 5.20b).

The MMT results indicated that water wicked into the hydrophilic zone of the SU-8 electro-sprayed fabric, no matter on which side the water was fed. Such a directional water transport feature comes from a combination of hydrophobic and hydrophilic surfaces along fabric thickness.

![Side A](image1)

![Side B](image2)

Figure 5.20. Typical MMT water content curves from the two sides of a) uncoated polyester fabric, and b) NaOH pre-treated fabric.
5.2.7 Breakthrough pressure

To further understand the effect of SU-8 coating depth on the fabrics, we measured the water breakthrough pressure which is defined as the initial pressure required for water to breakthrough the fabric. For the fabric with a directional water transport ability, the breakthrough pressure on the hydrophobic side was often lower than that on the hydrophilic side.\textsuperscript{114,117} For the fabric with SU-8 coating depth around 58 µm, the breakthrough pressure on the SU-8 coated and uncoated sides was 3.17 ± 0.29 cmH\textsubscript{2}O and 13.67 ± 1.61 cmH\textsubscript{2}O (Figure 5.21a) respectively. This result is in good accordance with our previous reports.\textsuperscript{118} When the loading was higher than 1.0 g/m\textsuperscript{2}, (i.e. coating depth 62 µm), the breakthrough pressure on the uncoated side was larger than that on the SU-8 coated side, indicating no directional water transport took place when the SU-8 depth was larger than 62 µm. Figure 5.21 b shows the details of the values difference of the breakthrough pressure between the uncoated side and the coated side on all tested samples.
Figure 5.21. a) Water breakthrough pressure changes on fabrics with different SU-8 loadings and b) the values difference of the breakthrough pressure between the uncoated side and the coated side on all tested samples.

5.2.8 ATR-FTIR spectra

As shown in Figure 5.22, after one-side electro-spraying treatment, new peaks appeared at 1608 cm\(^{-1}\) and 1504 cm\(^{-1}\), which were assigned to the aromatic C=C stretch and aromatic ring vibrations of SU-8, respectively. These results confirmed that SU-8 was successfully formed on the coated fabric.
Figure 5.22. ATR-FTIR spectra of the polyester fabric before (black) and after (red) NaOH pre-treated and after coating treatment with SU-8 resin (blue), respectively.

5.2.9 Theoretical model

5.2.9.1 Force equilibrium model

A schematic of the coating process and mechanism have been proposed in Figure 5.23 to explain the directional water transport process. The fabric was coated on just one side through an electro-spraying coating technique (Figure 5.23a). If the water is dropped on the coated hydrophobic surface, two forces (hydrostatic pressure (HP) and hydrophobic force (HF)) appear on it respectively. HP tends to facilitate the water pass through the fabric matrix while HF resists the transport of water (Figure 5.20b top). As HF is constant for a specific material, water goes deeper under a larger HP by accumulating the water volume. Once it reaches the hydrophilic part of yarn, HF becomes smaller but capillary force (CF) provided by the hydrophilic yarn from the reverse direction would be increased, this increased CF together with HP accelerate the water transport process (Figure 5.23b bottom). Thus, the water could transport from hydrophobic side to hydrophilic side of fabric. On the contrary, when water is
dropped on the uncoated hydrophilic side, a force combined with CF and HP makes water spread to 3D directions on the fabric matrix (Figure 5.23c top). When the water reaches the hydrophobic yarn, HF will resists the further penetration of water (Figure 5.23c bottom). Unlike the hydrophobic side of fabric could generate a larger HP through accumulating the water volume, the increasing of water volume on the hydrophilic side mainly spread into XY direction instead of elevating the water height. Therefore, water cannot transport from hydrophilic side to hydrophobic side of fabric.

Figure 5.23. a) Schematic illustrating the coating process on yarn of polyester fabric, (b, c) mechanism of unidirectional water transport on a single-side coated polyester fabric: b) Water is dropped on the hydrophobic side. The water suffers two opposite but different forces at the
beginning: HP and HF respectively. Water goes deeper with increasing HP while the HF is constant. Once the penetration depth reaches the hydrophilic side, the CF together with HP facilitate the water transport process continuous. c) Water is dropped on the hydrophilic side. Water spreads to the fabric matrix under capillarity together with HP. When water reaches the hydrophobic side, the increasing force as HF tends to resists water’s further penetration.

5.2.9.2 Mathematic calculation

It is known that the directional fluid transport property has a closer relationship with the thickness of hydrophobic layer of a hydrophobic substrate, however, critical layer thickness offer a single layer fabric to have a directional water transport property has not been reported. To explain the effect of hydrophobic coating layer thickness on water transport behaviour, we develop a model by simplifying the fabric into a mono filament fabric structure. Figure 5.24 schematically illustrates the cross-sectional structure of the simplified structure with two in-parallel adjacent filaments in the model.
Figure 5.24. Schematic illustration of water on the simplified fabric model. Water on (a) hydrophobic (SU-8 sprayed) side and (b) hydrophilic (unsprayed) side.

When water is dropped on fabric, it will either spread into fabric matrix or suspend on fabric surface depending on the wettability of the fabric. A gas-solid-liquid three phase equilibrium reaches eventually. According to the Akshaya’s equation\textsuperscript{131}, the pressure difference (\(\Delta P\)) that is the exerted on a liquid-air interface (also called “extrusion pressure”) is equal to the tolerable pressure difference of the liquid-air interface.

\[
\Delta P = \frac{4y \cos \theta}{d_0} \tag{1}
\]
where $\gamma$ is water surface tension and $\theta$ is the Young’s contact angle \(^{132}\), $d_0$ is the pore diameter (for long rectangular pore, $d_0$ is the inter-fiber distance). The distance ($d$) between the water contact lines of the adjacent filaments can be calculated as \(^{121}\):

$$
\begin{align*}
  d &= d_0 + D(1 - \sin \psi) \\
\end{align*}
$$

Here $D$ is the filament diameter, $\psi$ is the local geometrical contact angle (the intersection angle between the tangent plane along the cylinder and horizontal plane). Therefore,

$$
\Delta P = \frac{4\gamma \cos \theta}{(d - D(1 - \sin \psi))}
$$

A critical contact angle ($\alpha$) was proposed to measure the propagation of the liquid between the filaments \(^{133}\) (Figure 5.20). For cylindrical filaments, $\alpha$ can be calculated by,

$$
\tan \alpha = \frac{T}{L}
$$

Where $T$ is the wetting depth, i.e. the vertical distance between the wetting line on filament surface and filament top. $L$ is the horizontal distance between the wetting line and the vertical center line of the adjacent filament. Therefore, $L = d + \frac{D \sin \psi}{2}$. Here, $\psi$ is the local geometrical contact angle. Then equation (4) can be rewritten as:

$$
\begin{align*}
  d &= \frac{T}{\tan \alpha} - \frac{D \sin \psi}{2} \\
\end{align*}
$$

Substituting these expressions into equation (2), the extrusion pressure difference $\Delta P$ can be expressed as:

$$
\Delta P = \frac{4\gamma \cos \theta}{\frac{T}{\tan \alpha} + \frac{D \sin \psi}{2}}
$$

When water is dropped on the hydrophobic side and the hydrophobic layer (vertical depth $T^*$, $T^* > 0$) is fully wetted ($T = T^*$), water penetrates through the fabric if $\Delta P_1 > 0$, whereas water is blocked when $\Delta P_1 < 0$. Since $\theta_1$ is higher than $90^\circ$, $\cos \theta_1 < 0$, thus $\frac{T}{\tan \alpha_1} - D + \frac{D \sin \psi_1}{2} < 0$. The relationship between $T^*$ and $\psi_1$ is:

$$
T = T^* < \frac{2D - D \sin \psi_1}{2\tan \alpha_1}
$$

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In comparison, when water is dropped on the unspayed hydrophilic side, \( T = D - T^* \) and the intrinsic contact angle \( \theta_2 \) is smaller than 90° (as shown in Fig. 5b), thus \( \cos \theta_2 > 0 \). If the treated fabric has a directional water transport ability, the extrusion pressure \( \Delta P_2 < 0 \). As the value of \( \cos \theta_2 \) is positive, the value of \( \frac{T}{\tan \alpha_2} - D + \frac{D \sin \psi_2}{2} \) should be less than 0. Therefore, the relationship between \( T^* \) and \( \psi_2 \) is:

\[
T = D - T^* < \left( D - \frac{D \sin \psi_2}{2} \right) \times \tan \alpha_2
\]  

(8)

For a fabric with directional water transport ability, the hydrophobic layer thickness \( T^* \) satisfies the following condition:

\[
D - \left( D - \frac{D \sin \psi_2}{2} \right) \times \tan \alpha_2 < T^* < \frac{2D - D \sin \psi_1}{2 \tan \alpha_1}
\]

(9)

The filament diameter obtained from the idealized plain woven polyester fabric was 420 µm. The thickness of the fabric was 420 µm, and the average pore size \( (d_0) \) calculated based on the inter-yarn space was 85 µm. \( T_1 = D - \left( D - \frac{D \sin \psi_2}{2} \right) \sim \psi_2 \) and \( T_2 = \frac{2D - D \sin \psi_1}{2 \tan \alpha_1} \sim \psi_1 \) relationships for \( \alpha \) in the range of 0-45°, \( \psi_1 \) in the range of 90-180°, and \( \psi_2 \) in the range of 0-90° were calculated, as shown in Figure 5.25.
Figure 5.25. Estimated (a) $T_1 \sim \psi_2$ and (b) $T_2 \sim \psi_1$ relationships.

The critical contact angle $\alpha$ on the two proposed situation ($\alpha_1$ and $\alpha_2$) can be estimated based on the fact that the hydrophobic layer was thinner than the half of the fabric as show in Figure 5.26. In here, three different situations were discussed to estimate the value of $\alpha$, there are when the wetting line ($T$) is equal to (1) the whole fibre diameter, (2) half of the fibre diameter, (3) a quarter of the fibre diameter. When water is dropped on the hydrophobic side (a), $\tan \alpha = \frac{T}{L}$, $T = T_2$, $L = L_2 = L_1 + d$, $L_3 = L_2 + L_1$. Where $D$ is the fibre diameter, $T_2$ is the wetting
depth, $L_1, L_2, L_3$ are the horizontal distance between the vertical centre of the filament and the wetting line, the adjacent filament wetting line and the vertical centre of the adjacent filament, respectively. Based on the three situations, (1) $\tan \alpha_1 = \frac{T_2}{L_3} = \frac{D}{D+d_0}$, (2) $\tan \alpha_1 = \frac{T_2}{L_2} = \frac{D}{D+d_0}$, (3) $\tan \alpha_1 = \frac{T_2}{L_2} = \frac{D}{D+d_0}$. As $D = 420 \, \mu m$, $d_0 = 85 \, \mu m$, so (1) $\tan \alpha_1 = \frac{420}{420+85} \approx 0.83$, $35^\circ < \alpha_1 < 45^\circ$, (2) $\tan \alpha_1 = \frac{210}{210+85} \approx 0.71$, $30^\circ < \alpha_1 < 40^\circ$ and (3) $\tan \alpha_1 = \frac{105}{420-105\sqrt{3}+85} \approx 0.32$, $0^\circ < \alpha_1 < 20^\circ$. As the fact during our experiments, the exact coating thickness is lower than 62 $\mu m$, thinner than a quarter of the fiber diameter, so $0^\circ < \alpha_1 < 20^\circ$. When water is dropped on hydrophilic side (b), $\tan \alpha = \frac{T}{L}$, $T=T_1$, $L=L_2=L_1+d$, $L_3=L_2+L_1$. Based on the three situations, (1) $\tan \alpha_2 = \frac{T_1}{L_3} = \frac{D}{D+d_0}$, (2) $\tan \alpha_2 = \frac{T_1}{L_2} = \frac{D}{D+d_0}$, (3) $\tan \alpha_2 = \frac{T_1}{L_2} = \frac{3D}{D-\sqrt{3}D+d_0}$. As $D = 420 \, \mu m$, $d_0 = 85 \, \mu m$, so (1) $\tan \alpha_2 = \frac{420}{420+85} \approx 0.83$, $35^\circ < \alpha_2 < 45^\circ$, (2) $\tan \alpha_2 = \frac{210}{210+85} \approx 0.71$, $30^\circ < \alpha_2 < 40^\circ$ and (3) $\tan \alpha_2 = \frac{315}{420-105\sqrt{3}+85} \approx 0.98$, $35^\circ < \alpha_2 < 45^\circ$. As the fact during our experiments, the exact coating thickness is lower than 62 $\mu m$, thinner than a quarter of the fiber diameter, so $35^\circ < \alpha_2 < 45^\circ$. 


Figure 5.26. Schematic illustration of $\alpha_1 \sim \alpha_2$ on the simplified fabric model. Water is dropped on (a) hydrophobic (SU-8 sprayed) side and (b) hydrophilic (unsprayed) side.

For SU-8 coating, the Young’s CA is $98^\circ$. Here we supposed the $\psi_1 \approx \theta$ and $\psi_2 \approx 180^\circ - \theta$. As the sagging angle was very small, we estimated the hydrophobic layer thickness in sagging angle of $\pm 5^\circ$ range. The $T_1$ and $T_2$ at the $\psi_1 \pm 5^\circ$ ($\psi_1 = 98^\circ$) and $\psi_2 \pm 5^\circ$ ($\psi_2 \approx 180^\circ - \theta$) are highlighted in Figure 5.25. When $0^\circ < \alpha_1 < 20^\circ$ and $35^\circ < \alpha_2 < 45^\circ$, $T_1$ and $T_2$ are 18 $\mu$m and 88 $\mu$m, respectively. The estimated results were close to the experiment data (22 $\mu$m to 62 $\mu$m).
5.2.10 Coating durability

In addition, washing durability of the coated fabrics was tested according to the washing standard AATCC Test Method 61-2006 test No. 2A. Figure 5.27 (a, b) show the SEM images of both coated and the un-coated side of the electro-sprayed fabric with SU-8 loading of 0.6 g/m², after 50 washing cycle test. After 50 cycles of repeated washing, the coating morphology can be observed clearly on the coated fabric side as shown in Figure 5.27a.

Figure 5.27. SEM images of (a) coated side and (b) uncoated side of the treated fabric after 50 cycles of repeated washing (scale bar= 20 µm).

Figure 5.28 are still frames taken from video showing dropping water on electro-sprayed and the un-sprayed side of the fabric with SU-8 loading of 0.6 g/m² after 50 cycles of repeated washing test. A clear directional water transport effect can be observed, that is, the water can penetrate from the hydrophobic side to the hydrophilic side (Figure 5.28a), and being blocked when dropping from the hydrophilic side (Figure 5.28b).
Figure 5.28. Still frames from digital videos to show dropping blue-dyed water on electro-sprayed polyester fabric after 50 cycles of washing cycles (a) on the SU-8 sprayed surface and (b) on the unsprayed back surface.

After 50 washing cycles, the fabric still showed a high R value (516) from the coated side and low value from the uncoated side (-98) as shown in table 5.2. Figure 5.29 shows the relative water content of saline water on the fabric with SU-8 dip coated in the MMT. When water was dropped on the SU-8 sprayed side of fabric, the relative water content on the top surface without SU-8 started increasing, and the content reached near 600% within 8 seconds. When water supply stopped, the relative water content on the top surface was stabilized at around 600% at 120 seconds. In comparison, the bottom surface which has SU-8 remained non-wetted until 100 seconds, after that the water content value increased slowly to 30% at 120 seconds. This indicates that the directional water transport fabric prepared by one-side electro-spraying of SU-8 has reasonable durability against washing. This good durability should come from the excellent durability of SU-8 coating on fabrics.\textsuperscript{134}
Figure 5.29. Typical MMT water content curves on the one-side SU-8 coated fabric (loading 0.6g/m²) after 50 cycles.

5.3 Conclusions

A novel method to prepare directional water transport fabric has been developed. Electro-spraying allows controlling coating depth on the fabric substrate. This offers an opportunity to understand the effect of the hydrophobic layer thickness on water transport through the fabric. Apart from the preparation technique, theoretical understanding of directional water transport
through fabrics have been performed. Some parameters such as wettability, loading capacity and coating thickness on directional water transport ability and breakthrough pressure have been analysed. A theoretical model is proposed to explain the mechanism of this directional water propagation phenomenon. It is known that the directional water transport property has a close relationship with the thickness of hydrophobic layer of a hydrophobic substrate. The critical thickness for the SU-8 layer reveals the role of the SU-8 hydrophobic layer on directional fluid transport property. Since the coating showed excellent durability on the fabric, the coating on the fabric create a lasting directional water transport effect, which is suitable for development of functional fabrics for various applications.
Chapter 6

Heat Transfer within directional water transport Fabrics

Two different setups were used to examine the heat transfer behaviour of directional water transport fabrics. The thermal conductivity measurement showed a 12.27% enhancement in the thermal conductivity. Heat transfer property of directional water transport fabric containing a small amount of water was demonstrated.

6.1 Experimental

To evaluate the thermal properties of fabric, a purpose-built device (as shown in Figure 6.1) was used to record temperature change on the one-side SU-8 electro-sprayed polyester fabric and NaOH pre-treated polyester fabric. All measurements were tested in the conditioned lab (25 °C, 65% RH). All samples were conditioned in the lab for at least 24 hours prior to measuring.
Figure 6.1. Schematic of the purpose-built setup for measuring the heat transfer property of fabrics.

A WL 372 heat conduction unit (Figure 6.2) was used to measure the thermal conductivity and heat transfer property of the fabrics.

Figure 6.2. Experimental setup for measuring thermal conductivity in WL 372 heat conduction unit. 1--heater, 2--measuring object, 3--cooling element; x1-x3, x4-x6 and x7-x9--measuring points.

6.2 Results and Discussion

6.2.1 Thermal conductivity
The thermal conductivity of the different fabrics were measured based on the Newton’s law of cooling. As listed in Table 6.1, the thermal conductivity increased from 54.6±1.4 mW/mK to 61.3±1.5 mW/mK after one-side electro-spraying treatment, 12.27% enhancement in the thermal conductivity was attained. When the fabrics were wetted with 100 µL water, an increase in thermal conductivity for the NaOH pre-treated fabric (436.21±5.61 mW/mK) and directional water transport fabric (316.3±3.2 mW/mK) resulted. Therefore increased maximum temperature comes from the effect of SU-8 coating and wetting on the thermal conductivity of the fabric. Water contact angle (WCA) was measured to understand the wettability of the fabrics. The WCA of the polyester fabric decreased from 118° to 0° after NaOH treatment due to the hydrolysis of polyester on polyester fibre surface. Once water was dropped onto the NaOH treated fabric, it spread rapidly into the entire fabric layer. The NaOH treated fabric showed a slightly lower thermal conductivity than the control fabric. For the directional water transport fabric, the initial contact angle on the SU-8 coated side was 131°, while the uncoated side still remained the WCA 0°. It had slightly higher thermal conductivity compared to the control fabric and NaOH treated fabric, because of the SU-8 coating which has a high thermal conductivity. For the polyester fabric entirely coated with SU-8, it showed a WCA of 131° on both fabric sides. As expected, there was no directional water transport feature on the SU-8 dip coated fabric. The thermal conductivity of the SU-8 dip coated fabric was higher than the directional water transport fabric. Table 6.1 summarizes the heat transfer results, water contact angle (CA), fluid transport ability and thermal conductivity of the four fabrics.

**Table 6.1.** The comparison among the control fabric, NaOH pre-treated fabric, directional water transport fabric and SU-8 dip-coating fabrics.

<table>
<thead>
<tr>
<th>Fabric type</th>
<th>Method</th>
<th>WCA (°)</th>
<th>Water transport</th>
<th>Thermal conductivity (mW/mK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>—</td>
<td>118</td>
<td>Bidirectional</td>
<td>59.7±1.0 (dry) 405.4±4.2 (wetted)</td>
</tr>
<tr>
<td>NaOH treated</td>
<td>Immersing in NaOH solution</td>
<td>0</td>
<td>Bidirectional</td>
<td>54.6±1.4 (dry) 436.2±5.6 (wetted)</td>
</tr>
<tr>
<td>Directional water transport</td>
<td>SU-8 single-side electrospraying</td>
<td>131* on the coated side, and 0 on uncoated side</td>
<td>Unidirectional (from the coating to uncoated)</td>
<td>61.3±1.5 (dry) 316.3±3.2 (wetted)</td>
</tr>
<tr>
<td>SU-8 dip-coated</td>
<td>SU-8 dip coating</td>
<td>131 on both sides</td>
<td>No transport</td>
<td>62.5±1.0 (dry)</td>
</tr>
</tbody>
</table>

*Initial contact angle
6.2.2 Transport behaviour of warm water

An IR camera was used to record the temperature change when warm water (37 °C) was dropped on polyester fabrics. Figure 6.3 shows temperature change on a SU-8 treated directional water transport fabric (SU-8 loading on one side, 0.6 g/m²). On the coated side, the surface temperature increased rapidly and spread into a larger area (Figure 6.3a). The initial small spot with relatively higher temperature indicated that the water had a small contact with fabric surface. However, when dropping water on the uncoated hydrophilic side (Figure 6.3b), the temperature increase spread to a larger area compared with the SU-coated surface. This asymmetric heat transfer profile on the two sides of the directional water transport fabric stems from the different wettability. As indicated in the previous chapter, SU-8 is hydrophobic, and water droplet on the SU-8 coated side has a small contact area with fabric, which slows down the heat transfer to the fabric substrate. Since water transferred from the hydrophobic side to the hydrophilic side, the temperature increase mainly occurred on the hydrophilic side. When dropping water on the hydrophilic side, the heat transport comes with water spreading, which spread mainly on the hydrophilic matrix.

Figure 6.3. IR thermography images to show temperature change when dropping 37 °C water on a directional water transport fabric, (a) on the SU-8 sprayed surface and (b) on the unsprayed back surface. (SU-8 loading, ambient temperature 25 °C)
For comparison, the temperature change on fabrics with a homogeneous wettability was measured. Here, a SU-8 dip-coated fabric and a NaOH treated fabric were chosen. When warm water was dropped on the SU-8 dip-coated fabric (Figure 6.4), the temperature change profile was similar between the two fabric surfaces. Because the dip coated fabric is hydrophobic on both sides, water drop sat on the fabric with a small contact area.

Figure 6.4. IR thermography images to show temperature change during dropping 37 °C water on the two sides of a SU-8 dip-coated polyester fabric.

When water was dropped on the NaOH treated fabric, which has a hydrophilic surface on both sides (Figure 6.5), the temperature change spread along the fabric surface immediately.
Infrared (IR) thermography is a non-contact and non-intrusive technique, which is based on the principle that all objects above have absolute zero emit IR radiant heat in an amount that is directly related to the object temperature. In comparison with some conventional temperature measurement techniques such as thermocouples and thermometers, IR thermography offers many advantages including easy operation, large measurement area, and ability to visualize temperature change and distribution profile. It is especially suitable for studying the heating/cooling performance of fabrics where only the surface temperature needs to be monitored.

6.2.3 Heat transfer behaviour

Figure 6.6a shows the setup for measuring the temperature change on fabric when it contacts with a hot plate of which the surface temperature was controlled at 37 °C. The accuracy of the thermocouple in the setup was checked by measuring boiling water and ice-water mixture at ambient pressure. As shown in Figure 6.6b, at ambient pressure, the boiling water and ice-water mixture were measured to have the temperature of 99.67 °C and 0.11 °C, respectively, indicating the reasonable accuracy (< 0.33 °C). However, a larger experimental error could result when measuring a thin porous fabric uses a thermal couple due to incomplete contact of thermal couple bead with porous texture of fabric. Normally, 1° of experimental error is expected for this measurement. Figure 6.6c and 6.6d shows the measurement result on the temperature change of the fabric samples upon attaching the hot plate. The fabric temperature increased initially and then reached an equilibrium value. In dry state, the NaOH pre-treated fabric and the directional water transport fabric had a similar equilibrium temperature, being 36.1 °C and 36.2 °C, respectively. For comparison, we also coated the entire fabric with SU-8 using a dip-coating technique and measured the temperature change on the hot plate, which also reached a similar equilibrium temperature of 36.2 °C. In addition, the control fabric
without NaOH treatment was evaluated at the same condition, which showed a similar temperature profile and equilibrium temperature to the NaOH pre-treated one.

When the fabrics were brought to contact with the hot plate and then pre-wetted with water, they showed different equilibrium temperature to the dry state. A large difference was observed on the control, the pre-treated and the directional water transport fabric due to the different wettability to water. When 100 µL water was dropped on the control fabric, it took more than 10 seconds to spread into the matrix. However, when dropping the same amount of water on the NaOH treated fabric, water spread into the fabrics in 1-2 seconds. This is because NaOH treatment makes polyester fabric have a hydrophilic surface. Water can also move rapidly into the directional water transport fabric when it was dropped on the sprayed side because of the one way transport effect, however it just spread in the hydrophilic layer. The four fabric samples showed a similar equilibrium temperature, suggesting that they were eventually heated up to a similar temperature level. The major difference in temperature among those fabric samples was found in the inflection point. Time to reach the inflection point varied among those fabrics. As shown in Figure 3d, the control fabric, NaOH pre-treated fabric and directional water transport fabric showed 586 seconds, 599 seconds and 661 seconds to reach the inflection point respectively. The different inflection point can be explained by the difference in thermal conductivity and the effect of liquid water on thermal transfer in fabric. For directional water transport fabric, water is filled just on the surface layer of the SU-8 non-spray matrix, leaving the SU-8 sprayed layer at a dry state. However, water penetrated into the entire fabric matrix with different speed on the control fabric (more than 10 seconds) and NaOH pre-treated fabric (within 1 seconds).

For practical applications where skin is covered with directional water transport fabric, sweat penetrates the inner hydrophobic layer and wick into the external hydrophilic layer. The noon-wetting feature of the hydrophobic surface allows the fabric would not stick on the skin surface, leaving a dry and comfortable micro-environment to the wearer. Moving sweat on the external surface assist in water evaporation. Here, the temperature-time curve for the SU-8 dip-coated fabric in wet state was unavailable due to the hydrophobicity property of the fabric.
Figure 6.6. a) Schematic of the purpose-built setup for measuring the heat transfer property of fabrics, and b) temperature of boiling water and ice-water mixture measured by thermocouple, c)~d) temperature ~ time curves of the NaOH pre-treated fabric, directional water transport fabric and SU-8 dip-coated fabric in both c) dry and d) wetted states.

The temperature change during heating and then cooling a wet fabric was also measured. During the test, all fabric samples were heated to 50 °C by manually adjusting the heat power to 15 W, and then turned off to cool naturally in a standard ambient condition. To accurately investigate the temperature change, WL 372 was used, and the temperature data on sensor 1 and sensor 4 were collected and demonstrated in Figure 6.7. It presented the temperature change of 50 µL and 100 µL of pre-loaded water on different SU-8 loading fabrics. Figure 6.7a shows that all of the tested fabrics reach the maximum temperature at the same time, indicating the heat gained from the heat source and the heat lost through evaporation on all fabric samples were become equilibrium. When 100 µL was added, without increase the heat gained from the
heat source, it only increased the heat loss through evaporation. So more heat should be supplied from the heat source to reach the maximum temperature (Figure 6.7c), in other words, the heat flux of the fabrics decrease with the SU-8 loading. The temperature-time curve in Figure 6.7b showed that the surface temperature increased with SU-8 loading when heating the coated side of fabrics. It was further increased when increasing the pre-loaded water content from 50 µL to 100 µL, shown in Figure 6.7d. This behaviour can be explained by the increase in water content since the thermal conductivity increases with water content.

Figure 6.7. Temperature change during a heating and cooling process for the fabrics with different SU-8 loadings containing a) ~b) 50 µL and c) ~d) 100 µL of pre-loaded water.

Figure 6.8 shows thermal imaging results of a fabric covering on a naked skin and the naked skin without fabric. The skin in the selected area had a uniform distribution in surface
temperature (Figure 6.8a). Two pieces of the same fabric sample were placed on arm, with one contacting the skin on the SU-8 coated side while the other in reverse (Figure 6.8b). No external force was applied on the fabrics. The image color of indicated the temperature. Once the fabrics contacted the skin, they were warmed up by the skin and the surface temperature increased. The fabric surface having a temperature closer to the skin surface temperature suggests a better heat transfer of the fabric. Smaller temperature difference was attained on the directional water transport fabric when compared to the control fabric (Figure 6.8c) and the NaOH treated fabric (Figure 6.8d), which indicates a better heat transfer performance.

Figure 6.8. IR thermography images of a) naked dry skin, b) naked dry skin partially covered with b) directional water transport polyester fabric, c) control fabric and d) NaOH pre-treated fabric. The top right number indicates the time of the frame. The middle line numbers are the surface temperature on fabrics and skin. The bottom line numbers are the temperature difference between the fabrics and skin. The dot squares demonstrate the fabric covered area, the rest indicates the naked skin. Scale bar is 1 cm.
6.3 Conclusion

Heat transfer in a SU-8 treated directional water transport fabric was studied. In comparison to untreated control fabric and NaOH pre-treated fabric, directional water transport fabric showed different heat transfer performance. In comparison to the control fabric and NaOH pre-treated fabric, the directional water transport fabric at dry state showed higher equilibrium temperature, while the equilibrium temperature was lower at a wetted state. The fabric treatment method and wet state affect heat transport profile. Thicker SU-8 coating improves thermal transfer within the fabric, hence having higher temperature on the fabric surface. In wet state, a dramatically enhanced thermal conductivity can be noticed on the fabric due to the effect of water, hence accelerating moisture evaporation and meanwhile cooling down the fabric surface temperature. This study may be useful for development of “smart” textiles for various applications such as sports garments and other active wears.
Chapter 7
Conclusions and suggestions for future work

7.1 Summary

This PhD study has resulted in the main conclusions below:

In this work, a simple method has been developed to fabricate self-cleaning superhydrophobic fabrics using a photoresist resin (SU-8), fluoroalkyl silane and silica nanoparticles as coating materials. The treated cotton fabrics show excellent superhydrophobicity with a water contact angle of $163 \pm 3^\circ$ and sliding angle as small as $2^\circ$. The coating slightly reduces the fabric air-permeability (from 30 cm$^3$/cm$^2$/s to 25 cm$^3$/cm$^2$/s), but shows excellent solvent resistance. It coating can withstand over 100 cycles of repeated washing, and long-time immersing in acid and base solutions.

For the first time, electro-spraying technique was used to prepare one way water transport fabric. By one side electro-spraying a SU-8 solution on a hydrophilic fabric, the fabric shows a directional water transport property. Moisture management tester (MMT) was employed to qualitatively characterize the directional water transport property and the effect of SU-8 coating layer thickness on directional water transport feature was examined. It was interesting to note that SU-8 coating layer thickness played a critical role in deciding the transport ability. The treated fabric showed directional water transport ability when the SU-8 coating depth was in the range of 22 - 64 µm. A one way transport index as high as 861 can be attained with the reverse one way transport index of -157. The directional water transport fabric was durable against repeated washing.
A theoretical model was developed to explain the effect of hydrophobic layer thickness on directional water transport property. The relationship between the thickness of hydrophobic layer and the directional water transport property was obtained, which can be used to explain the critical thickness.

The heat conduction and radiation through the treated fabrics under dry and wet status were also studied. The heat transfer rate of directional water transport fabrics at dry state was faster than the untreated fabric. In wet state, directional water transport showed a significant effect on heat transfer properties.

7.2 Suggestions for future work

This PhD study focused on preparation method and basic properties of directional water transport fabrics. From the fundamental and theoretical point of view, other hydrophilic fibrous media or membranes after treated with this techniques should have the same directional water transport ability, which could increase the applications on high value added area such as water or protein purification, functional biomedical membranes and so on. Other techniques that can achieve a controllable hydrophobic layer thickness across the hydrophilic fabrics thickness, other than one-side electro-spraying coating, could help to enhance the understanding of the hydrophobic layer thickness in deciding the one-way transport ability. Future work on systematic study of the directional water transport fabrics and their applications as functional textiles in daily life, industry and biomedicine are suggested.
References:


[81] Huang, Z.-M.; Zhang, Y. Z.; Kotaki, M.; Ramakrishna, S., A review on polymer nanofibers by electrospinning and their applications in nanocomposites. Composites Science and Technology 2003, 63(15), 2223-2253.


