ABSTRACT

LI, GUOQING. Design and Development of Superhydrophobic and Superoleophobic Surfaces (Under the direction of Dr. Stephen Michielsen).

Inspired by biomaterials exhibiting special wettability in nature, design of superhydrophobic (SH) and superoleophobic (SO) surfaces has rapidly emerged at the forefront of materials research. These materials display high contact angle (>150˚) and small sliding angles for water and oil respectively. Through the understanding of the complementary roles of surface energy and roughness on the wettability of the solid surfaces, a number of SH surfaces have been fabricated. However, SO surfaces are still very rare and difficult to create because of the low surface tension of oils.

Two main characteristics of superhydrophobic and superoleophobic surfaces are a large contact angle and a low contact angle hysteresis. Young was the first to describe the equilibrium contact angle of a liquid droplet on an ideally flat surface. However the wetting properties of solid surfaces are dramatically affected by surface roughness. Meanwhile, most surfaces in the real world are not ideally flat surfaces. To describe the wetting behavior of liquid droplets on rough surfaces, the Wenzel and Cassie-Baxter models were developed and are now commonly used. According to these two models, there are two regimes of wetting on a rough surface including a homogeneous regime with a solid-liquid interface and a composite regime with a solid-liquid-vapor interface where vapor is interspersed with the solid surface in contact with liquid droplets. However, neither the Wenzel nor the Cassie-Baxter models can explain the complexity of wetting behaviors of rough surfaces. A transition from these two states may occur as the equilibrium contact angle increases. Thermodynamic considerations
can be used to determine whether a surface will exist in the Wenzel, Cassie-Baxter or a metastable state.

After understanding the role of surface chemistry and morphology, many fabrication methods for SH and SO surfaces have been developed based on the idea of forming an air-solid composite surface to make the liquid droplets reside in a metastable state. According to this idea, SH and SO surfaces with overhanging or re-entrant structures were fabricated and found to be able to prevent liquids from penetrating the texture due to capillary force. In addition to the topography of the surface, surface free energy is another governing factor of the wettability of solid substrates. In order to achieve superoleophobicity, the surface energy of the solid surface should be sufficiently low.

Although much work has been done, to be commercially successful (1) the fabrication method should be facile, inexpensive and applicable for large area production; (2) the coating should not impact the properties of textile fabrics, such as air permeability; (3) the produced surfaces should be able to repel liquids with extremely low surface tension, such as hexane (18.0 mN/m); (4) and the coating should be able to endure mechanical friction.
Design and Development of Superhydrophobic and Superoleophobic Surfaces

by
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CHAPTER I INTRODUCTION

Wetting behavior of a solid surface is a complex but important problem in surface chemistry. The “lotus effect” and the emergence of materials with controllable surface structure inspired the design of materials with special wetting behavior, such as superhydrophobic or superoleophobic materials. Young introduced the definition of contact angle (CA) to describe the wetting behaviors of liquid droplets on solid surfaces.\(^1\) When the CA is smaller than 90°, the surface is usually called philic (hydrophilic or oleophilic), whereas a surface with CA smaller than 180° but higher than 90° is usually called phobic (hydrophobic or oleophobic). A superhydrophobic (SH) or superoleophobic (SO) surface shows an apparent contact angle greater than 150° and a roll-off angle smaller than 5° for water and oil respectively.\(^2\)

Superhydrophobic surfaces exist broadly in nature, such as various plant leaves\(^3\), legs of water striders\(^4\) and geckos’ feet \(^5\). On such surfaces, water droplets can easily roll off taking away dirt, which is defined as self-cleaning property.\(^6\) Inspired by the surface structures of these biomaterials with superhydrophobicity, a number of artificial SH surfaces have been designed. Recently many researchers have devoted themselves into extending the SH materials to SO materials. However, compared with the SH surfaces, SO surfaces are much rarer in nature and are harder to fabricate because of the low surface tension values of oils (see Table 1).\(^7\) However, design of SO surfaces is not only important in fundamental research but also for various important real applications, such as self-cleaning materials, corrosion resistance, anti-fogging, anti-bacteria, smart coatings, and other fields.\(^8\)
Table 1.1 The surface tension of various liquids.\textsuperscript{9,10,11,12}

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Surface tension (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vertrel XF</td>
<td>14.2</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>18.4</td>
</tr>
<tr>
<td>n-Heptane</td>
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<tr>
<td>Dodecanol</td>
<td>29.4</td>
</tr>
<tr>
<td>Water</td>
<td>72.3</td>
</tr>
</tbody>
</table>

Understanding the wetting behavior of liquid droplets on smooth and rough surfaces is also necessary for designing superhydrophobic and superoleophobic surfaces. Young’s equation describes the wetting behavior of a liquid droplet on an ideally flat homogeneous surface.\textsuperscript{1} However, few solid surfaces in the real world are ideally flat. After decades of study, surface roughness was realized to be a critical factor in determining the wettability of solid surfaces. Generally, a liquid droplet can take one of two states on a rough surface. The first one is where a liquid fills every crevice to form a perfect liquid-solid contact area, which is called the Wenzel state\textsuperscript{13}; the other one is liquid resting only on peaks of roughness, leaving air pockets in the crevices beneath, which is called the Cassie-Baxter state.\textsuperscript{14} Both Wenzel and Cassie-Baxter models described the relationship between contact angle and surface roughness successfully, but neither of them is perfect in describing real cases. Recently, the coexistence and transition between Wenzel and Cassie-Baxter states have been investigated and many new models providing guidance for the design and prediction of functional surfaces with special wettability have been proposed based on experiments and simulations.\textsuperscript{15,16,17}
The wettability of a solid substrate is usually controlled by the surface free energy and surface structures. Researchers discovered that SO and SH surfaces could be obtained by an optimal combination of surface roughness, surface chemistry and re-entrant structures. According to this principle, researchers have recently developed many fabrication methods, such as dip-coating, electro-spinning, spray coating, templating, plasma treatment, photolithography, nanoparticle coating and so on, to create SH and SO surfaces. However, one of the greatest issues hindering the widespread application of SH/SO surfaces is generally their low mechanical durability. Even mild abrasion, in some cases, may damage the delicate structures that is necessary for maintaining superhydrophobicity/superoleophobicity.

In this work, I aimed to develop a treatment process that can superhydrophobic/superoleophobic surfaces, especially textile surfaces, that can repel water and oils with low surface tension energies with strong abrasion resistance. The fabricated surfaces should be able to repel solvents with a surface tension down to 20 mN/m. Additionally, the fabricated SH/SO surfaces should endure 5000 cycles abrasion under 12 kPa, which is the minimum requirement to possess potential daily applications.
CHAPTER 2 LITERATURE REVIEW

2.1. Theoretical background of anti-liquid surfaces

The fundamental knowledge of surface wetting behavior, such as surface tension, Laplace pressure, contact angle and roll-off angles, will be discussed in the following chapter. Also, the different wetting behavior of liquid drops on flat surfaces and rough surfaces will be compared. The Cassie-Baxter and Wenzel models used to describe liquid drops placed onto rough solid surfaces will also be covered. Moreover, the three parameters influencing the superhydrophobic and superoleophobic properties, including the chemical composition, surface roughness and re-entry structure, will be reviewed.

2.1.1 Surface tension and Laplace pressure

Surface energy, also referred to as surface tension, is a basic physical property of surface chemistry. Surface tension is defined as a tendency of liquid surfaces to resist an external force and to keep its original shape. It is a measurement of the cohesive energy present at an interface.\(^\text{18}\) In the bulk liquid, the interactions of a molecule are balanced by a pair of equal forces in any two opposite directions. While on the surface of a liquid, molecules are under imbalanced forces, as shown in Figure 2-1. Surface energy results from the fact that the molecules on the surfaces have more energy than molecules in the bulk.\(^\text{19}\) Sometimes, surface tension and surface energy are used interchangeably. They are affected by the properties of the material, such as the polarity,\(^\text{20}\) viscosity\(^\text{21}\) and so on. Water has a high surface tension due to the high polarity of water molecules. Organic oils, such as heptane, have low surface tension values because of the low intermolecular forces.
Figure 2.1. Attractive forces of a liquid molecule in the liquid bulk and at the interface.

Figure 2.1 shows that the molecules at the liquid-vapor interface experience unbalanced forces. This force imbalance generates higher free energy and the excess free energy per unit area is defined as surface energy expressed by Equation (2.1).

$$\gamma_{LV} = \frac{\partial G}{\partial A}$$

(2.1)

Where $\frac{\partial G}{\partial A}$ is the change of the Gibbs free energy with respect of the change in the interfacial area, and $\gamma_{LV}$ is the liquid-vapor surface energy. This equation is true at constant temperature, volume and number of molecules.

Laplace pressure, for a spherical shape droplet, is the pressure difference between the outside and inside of the spherical surface caused by surface tension. The surface tension tries to contract the droplet but is stopped by an extra positive pressure $p$ inside the liquid. In equilibrium state, the contraction forces must equal the pressure forces. The Laplace pressure of a droplet on a flat surface can be written in equation 2-2.

$$\Delta p = \frac{2\gamma}{R}$$

(2.2)

Where $\gamma$ is the surface tension of liquid and vapor interface and $R$ is the radius of the sphere cap.

In the more general case of a curved surface, consider a small rectangle with sides $dl_1$ and $dl_2$ in principal directions for a given point on the surface and the principle radii of curvature are $R_1$ and $R_2$. According to the Laplace Law,
\[ \Delta p = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \] (2.3)

\( \Delta p \) is the Laplace pressure which is the pressure difference across an interface. \( R_1 \) and \( R_2 \) are the principal radii of curvature of the interface at the point considered.\textsuperscript{12}

Figure 2.2. The rectangular portion of the surface with sides \( dl_1 \) and \( dl_2 \) is subject to two tension forces resulting in a normal force pointing away from the center of curvature. \( R_1 \) and \( R_2 \) are the principal radii of curvature.\textsuperscript{19}

2.1.2 Contact angle, contact angle hysteresis and wetting behavior

Contact angle on flat surface

The contact angle is commonly used to measure the wettability of a liquid on a solid surface. For homogeneous surfaces, the contact angle is defined as the included angle between liquid-vapor line and solid-liquid interfaces of a solid-liquid-vapor system, as shown in Figure (2.3).\textsuperscript{23,24,25} The relationship between the surface tension and contact angle on an ideal flat surface was derived by Young:\textsuperscript{1}

\[ \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} = \cos \theta_c \] (2.4)
Where $\gamma$ is the surface tension; and $S_V$, $S_L$ and $L_V$ stand for the solid-vapor, solid-liquid and liquid-vapor interfaces respectively, as shown in Figure 2.3. Young’s equation only applies to flat surfaces in the equilibrium state. Since it is hard to measure the surface tension of solid surfaces directly, contact angles between liquid droplets with known surface tensions and the solid surface to be evaluated are measured to describe the surface tension and wettability of a surface. According to Willard,26 when $\theta_e$ is larger than 20°, $\gamma_{SV} = \gamma_S$ and $\gamma_{LV} = \gamma_L$ can be assumed to simplify equation 2.4 as:

$$\frac{\gamma_S - \gamma_{SL}}{\gamma_L} = \cos \theta_e$$  \hspace{1cm} (2.5)

Figure 2.3. A liquid droplet on a flat surface.

According to the Dupre equation, the reversible work of adhesion for solid-liquid interaction is equal to the negative of the free energy of adhesion.

$$W_{SL} = \gamma_S + \gamma_L - \gamma_{SL}$$  \hspace{1cm} (2.5)

So if we combine the Young’s and Dupre equations, the Young-Dupre equation can be derived.

$$W_{SL} = \gamma_L (1 + \cos \theta_e)$$  \hspace{1cm} (2.6)

$\theta_e$ can be measured, $\gamma_{SL}$ can be evaluated by $\gamma_S$ and $\gamma_L$ as described below. Then

$$\gamma_{SL} = \gamma_L + \gamma_S - 2\sqrt{\gamma_L \gamma_S} e^{-\beta(\gamma_L - \gamma_S)^2}$$  \hspace{1cm} (2.7)

Where $\beta$ is a constant.

Alternatively, according to Fowkes, the solid-liquid interfacial energy can be given as:
\[
\gamma_{SL} = (\sqrt{\gamma_S} - \sqrt{\gamma_L})^2
\]  

(2.8)

Young’s model has some drawbacks. Firstly, equations (2.4) and (2.5) suggest that the contact angle is not dependent on the droplet size and shape, which is not true for a system in static equilibrium. Another issue is that the equations did not consider the line tension, deformability of the solid surface, or the effective interfacial energies in the presence of surface films.\(^\text{27}\)

Contact Angle on Heterogeneous Surfaces

Wetting on heterogeneous surfaces is more common in nature due to the spatial variations in chemistry or surface roughness for every natural solid surface. Since Young’s equation is only applicable for a flat surface with homogeneous surface chemistry under equilibrium conditions, researchers proposed other approaches to express the relationship between contact angles of liquid droplets with the rough surfaces. Among them, two distinct models developed by Wenzel\(^\text{13}\) and Cassie-Baxter\(^\text{14}\) (Figure 2.4) are commonly used to explain the effect of roughness on the apparent contact angle of liquid droplets on rough surfaces. Recently, the transitions between Wenzel and Cassie-Baxter states have been widely considered in designing stable SH and SO surfaces.

Figure 2.4. Three typical wetting behavior of liquids on solid surface. (a) Young’s model on flat surface, (b) Wenzel’s and, (c) Cassie-Baxter’s models on rough surfaces.
The Wenzel model states that the contact angle of a liquid droplet on a rough surface is modified due to more available surface area caused by roughness, which is defined as the ratio of the real liquid-solid contact area to the projected area. The basic assumption in Wenzel’s model is that the liquid droplet completely fills the grooves and wets entire the rough surface. Wenzel derived the apparent contact angle $\theta^*$ on a rough surface to be given by:

$$\cos \theta^* = r \cos \theta_e$$

(2.9)

where $r$ is the surface roughness defined as the ratio of the total true wetted area to the projected area of a plane beneath the drop (the ratio of actual surface to geometric surface), and $\theta_e$ is the equilibrium Young’s contact angle on the same material. In this equation, $r$ is always greater than or equal to 1. Therefore, the Wenzel model can describe two different behaviors, enhancing both wetting and anti-wetting, based on the value of $\theta_e$. When $\theta_e$ is smaller than 90˚, $\theta^*$ is smaller than $\theta_e$ and goes to 0 for a rough surface, which means the liquid will wet the surface and the surface becomes more philic. While if $\theta_e$ is larger than 90˚, $\theta^*$ is becoming larger on a rough surface and approaches 180˚, which means the surface becomes more phobic.

The Cassie-Baxter model suggests that superhydrophobicity and superoleophobicity of rough surface is because of a composite interface formed by microscopic pockets of air between liquid droplets and solid surfaces (Figure 2.4c). In this composite state, air is considered to be non-wetting. The model can be expressed as:

$$\cos \theta^* = f_1 \cos \theta_e - f_2$$

(2.10)

where $f_1$ is the ratio of solid surface area in contact with liquid to the projected area, and $f_2$ is the ratio of solid surface area in contact with air to the projected area. When there is no air between the drop and the surface, $f_2$ is 0 and $f_1$ is the same as $r$ in the Wenzel model.
Equation 2.11 can also be rewritten as in equation 2.12 based on He, Patankar, and Lee\textsuperscript{28} and Quere’s\textsuperscript{29} studies.

\begin{equation}
\cos \theta^* = -1 + \phi_s (1 + \cos \theta_e) \tag{2.11}
\end{equation}

where $\phi_s$ is the fraction of the solid supporting the liquid droplets. Since $\phi_s$ cannot be larger than 1, $\theta^*$ is always larger than or equal to $\theta_e$.

Cassie-Baxter to Wenzel transition

Both Wenzel and Cassie-Baxter models were successful in describing the relationship between contact angle and surface roughness for their own aim. However, neither of them can fully describe the complexity of the droplet’s wetting behavior on rough surfaces. Recently, the investigation of the coexistence and transition between the Wenzel and Cassie-Baxter states have been studied.

The relationship between apparent contact angle and Young’s contact angle for the two states can be plotted as in Figure 2.5 following equations 2.10 and 2.11. In Figure 2.5, the two lines associated with the two states intersect at a critical angle $\theta_c$.

\begin{equation}
\theta_c = \cos^{-1} \frac{\phi_s - 1}{r - \phi_s} \tag{2.12}
\end{equation}

where $\theta_c$ is the critical angle at which the transition between Wenzel and Cassie-Baxter states occurs. In this equation, $\phi_s$ is the ratio of the rough surface area in contact with liquid to the total projected area covered by liquid.

When Young’s contact angle for a liquid is smaller than the critical angle, the Wenzel state is preferred since it has the lowest surface free energy. However, droplets in the Cassie-Baxter state also have been observed on such surfaces, which is referred to as the metastable state.
Relationship between Contact Angle and Wettability

According to the contact angles of solid surfaces for a specific liquid droplet, the surfaces can be classified as wetting, equilibrium or anti-wetting surfaces, see Fig 2.6. When the contact angle of a liquid droplet is lower than 90°, the surface is easily wetted by this liquid. When the contact angle equals 0°, the surface can be completely wetted. When the contact angle is larger than 90°, the surface is an anti-wetting surface for the liquid. When the contact angle is 180°, the surface cannot be wetted at all.30
Whether liquid wets a surface or not is determined by the spreading coefficient $S$, which is expressed as:

$$S = \gamma_{SV} - \gamma_{SL} - \gamma_{LV}$$  \hspace{1cm} (2.13)

When a finite liquid droplet is placed on a flat surface, the relationship between free energy, surface tension and interfacial surface area can be expressed as:

$$G_1 = \gamma_{LV}A_{LV} + \gamma_{SL}A_{SL} + \gamma_{SV}(A_s - A_{SL})$$  \hspace{1cm} (2.14)

$$G_2 = \gamma_{LV}A_s + \gamma_{SL}A_s$$  \hspace{1cm} (2.15)

Where $G_1$ and $G_2$ are the free energies of spherical cap and the flat uniform film forms respectively. $A_{LV}$ and $A_{SL}$ are interfacial surface areas between the liquid and the vapor and the solid and the liquid, respectively. The difference between the energies before spreading and after spreading of the liquids can be expressed as:

$$\Delta G = G_2 - G_1 = \gamma_{LV}(A_s - A_{LV}) + (\gamma_{SL} - \gamma_{SV})(A_s - A_{SL})$$  \hspace{1cm} (2.16)

Because $A_{SL} = -A_{LV}$, Equation 2.17 can be simplified to:

$$\Delta G = (\gamma_{LV} + \gamma_{SL} - \gamma_{SL})A_s = -SA_s$$  \hspace{1cm} (2.17)

According to the relationship between the energy change and spreading coefficient $S$, liquid cannot spread on the solid surface when $S$ is negative, while when $S$ is larger than 0, liquid droplet will spread on the solid surface.

According to Li and Amirfazli,$^{31}$ SH and SO surfaces mean the surfaces with a strong “fear” of water and oil solutions respectively. Some researchers pointed out that SH and SO surfaces should not only show large contact angles for the test liquids, but also have low contact angle hysteresis, which means the liquid droplets can easily roll off the surfaces with small tilt angles.$^{32}$ Some non-wetting surfaces with very large contact angles for test liquids are not really super-repellent.
surfaces but rather they are sticky non-wetting surfaces. Therefore, it is necessary and important to consider the contact angle hysteresis when evaluating the super-repellent properties of fabricated surfaces.\textsuperscript{33,34,35,32,36,37,38,39,40.}

Contact angle hysteresis and roll-off angle

For some non-wetting surfaces, liquid droplets can easily roll off, corresponding to the slippery superhydrophobic or superoleophobic surfaces, while for others, the drop clings to the surface even under high tilting angles, which can be called sticky super-hydrophobic or superoleophobic surfaces. The ability of a drop to move on solid surfaces is determined by the values of contact angle hysteresis.\textsuperscript{41,42,43,44} In order for a droplet to move on a heterogeneous surface, the droplet must both advance (on the downhill side) and recede (on the uphill side), as shown in Figure 2.7. The difference between advancing and receding contact angles is defined as hysteresis.\textsuperscript{45} Contact angle hysteresis is an important aspect to be considered and studied in making self-cleaning surfaces. Predicting contact angle hysteresis is complex.\textsuperscript{46,47,48,49,50,51} According to Nosonovsky and Bhushan, the contact angle hysteresis is equal to the adhesion hysteresis term and the term related to the pinning effect of roughness, which is given by equation (2.19).\textsuperscript{52,53,54,55}

\[
\cos \theta_{\text{adv}} - \cos \theta_{\text{rec}} = R_f (1 - f_{\text{LA}}) (\cos \theta_{\text{adv}0} - \cos \theta_{\text{rec}0}) + H_r
\]  

(2.18)

\(f_{\text{LA}}\) is the fraction of air-liquid contact area. While the first term on the right hand side is the inherent contact angle hysteresis of a smooth surface. The second term \(H_r\) is the effect of the surface roughness. \(\theta_{\text{adv}0}\) and \(\theta_{\text{rec}0}\) can be related to the advancing and receding contact angles for a flat surface and equation 2.19 can be changed to

\[
\theta_{\text{adv}} - \theta_{\text{rec}} = (1 - f_{\text{LA}}) R_f \frac{\cos \theta_{\text{adv}0} - \cos \theta_{\text{rec}0}}{-\sin \theta_e}
\]  

(2.19)
For a homogeneous interface, increasing roughness will enlarge the contact angle hysteresis. While for a composite interface, increasing the fraction of air-liquid contact area provides both high contact angle and small contact angle hysteresis.

Figure 2.7. A schematic of a droplet showing advancing (\(\theta_{\text{adv}}\)) and receding (\(\theta_{\text{rec}}\)) contact angles. The difference between these angles is the contact angle hysteresis.

The roll-off angle, refers to the minimum angle that a surface must be tilted to make a liquid droplet roll off due to its own weight under the force of gravity. It has also been used to illustrate the wettability of a solid substrate. According to the definition and experiments, roll-off angle is directly related to the volume of liquid droplet in addition to the surface tension and polarity of the liquid, the surface energy of the solid surface and the rate of tilting the surface. Under the same conditions, a large volume leads to lower roll-off angle and a smaller volume results in larger roll-off angle. As shown in Figure 2.8, \(\alpha\) is the roll-off angle; \(l\) is the length of the drop on a tilting surface and is equal to the width of the drop if the liquid can be considered to be circular in plane.

Figure 2.8. Tilting plate method. \(\theta_A\) is the advancing CA, while \(\theta_R\) is the receding CA. \(\alpha\) is the roll-off angle.
The relationship between roll-off angle and advancing and receding contact angles can be expressed as:

\[
\frac{mg \sin \alpha}{l} = \gamma_{LV} (\cos \theta_R - \cos \theta_A)
\]  

(2.20)

where \( m \) is the mass of the drop, \( g \) is gravitational acceleration, \( \alpha \) is the roll-off angle, \( l \) is the length of the drop on a tilting surface, \( \gamma_{LV} \) is liquid-vapor interfacial energy, \( \theta_R \) is receding CA and \( \theta_A \) is advancing CA.

When attempting to determine the wetting behavior of coated fabrics, contact angle, contact angle hysteresis and roll-angle measurements are not suited for the macroscopically rough, pliant and non-reflective textile surfaces because a reliable determination of the substrates baseline is impossible and single textile fibers may stick out of the fabric surface. Zimmermann developed a new technique to evaluate the liquid repellent properties of superhydrophobic and superoleophobic surfaces, which was called liquid shedding angle.\textsuperscript{57,58} In brief, a drop of liquid is released onto the inclined surface from a defined height and the minimum angle of inclination at which the drop can completely roll off the surface is defined as the liquid shedding angle.

2.1.3 Wetting behavior of small liquid drop and textile structures

Fiber structure

The influence of the geometry of a surface on its wettability is not restricted to the flat and rough surfaces reviewed above. The coating and wetting of liquid droplets on fibers is also important experimentally and industrially.\textsuperscript{59,60,61} Due to the geometry of the fiber shape, the wetting behavior
of liquid droplets is quite different from that of the same liquid on a flat surface. A small droplet placed on a cylindrical fiber can take two conformations, an axisymmetric barrel shape and a non-axisymmetric clam-shell shape. For larger size droplets with smaller contact angles, a barrel shape is preferred over the clam-shell shape. While reducing the size of a barrel shape liquid droplet can lead to a transition to clam-shell shape, which is known as the roll-up process. The bell-shape of liquid on a cylindrical fiber has been investigated with elliptic integrals under the condition that the pressure through the entire liquid-vapor interface is the same.

![Diagram of two preferred conformations on a fiber](image)

Figure 2.9. The two preferred conformations on a fiber are (a) the barrel shape, and (b) the clam-shell (pearl) shape.

Yarn structure

Yarns can be classified into filament yarn and spun yarn, or twisted staple yarns and untwisted parallel multi-filaments. Due to the complex structures, the wetting behavior of twisted staple yarns has not been studied thoroughly. However, filament yarn has a relatively simple structure and it can be modified by texturing, crimping or twisting. The wetting behavior of liquid droplets on filament yarns has been studied.
In Figure 2.10, a liquid sits on parallel monofilaments while the sagging is simplified. Here \( d \) is the distance between two monofilaments and \( r \) is the radius of the filaments. When the liquid is in Wenzel and Cassie-Baxter states, the contact angle can be predicted. In Figure 2.11, the wetting
behavior of three cylinders is shown. There is a critical separation distance, \( d/r = 0.079 \) for which a hole forms when the separation is decreased to less than this distance, while a higher encompassing angle needs to be reached to eliminate the hole. These properties provide evidence to design yarns with the desired wetting behaviors. 64

Fabric structure

Structure can have great effects on the wetting behavior of fabrics with the same materials and different fabrics with the same materials but different weave structures can lead to surfaces showing different wettability after the same treatment. Woven fabrics made from monofilament yarns and multifilament yarns have been used to make superoleophobic and superhydrophobic surfaces, such as shown in Figure 2.12 and Figure 2.13.

![Figure 2.12](image)  
(a) Cross-section views of a plain woven fabric at (a) the warp yarn direction and (b) the weft yarn direction. 65
According to Lee and Michilsen\textsuperscript{65}, the predicted apparent contact angle can be expressed as:

$$\cos \theta^* = \frac{b + R(\pi - \theta_e)}{b + R + 0.5D} \cos \theta_e + \frac{b + R \sin(\pi - \theta_e)}{b + R + 0.5D} - 1$$ (2.22)

Parameters b, R and d can be measured from SEM images of rough surfaces. According to the equation, larger distances between adjacent fibers and low portion of flat top surface can lead to superhydrophobic surfaces.

2.2 Designing superoleophobic and superhydrophobic surfaces

After understanding the roles of surface energy, surface roughness and surface structure in designing superhydrophobic and superoleophobic surfaces, researchers have developed various methods to control the surface chemistry, increase the roughness, and create new structures to fabricate such anti-wetting surfaces.

2.2.1 Surface Structure

Overhanging structure

Recent research proved that superoleophobic and superhydrophobic surfaces can be fabricated through constructing micro-textures with overhanging structures. The overhanging structures can...
prevent liquids from penetrating into the texture due to the capillary force and a composite surface of air and solid in contact with the liquid droplets in a metastable Cassie state. The relationship between $\cos \theta^*$ (apparent contact angle) and $\cos \theta_c$ (Young’s contact angle) is shown in Figure 2.14. $\theta_c$ is the critical intrinsic contact angle. Inset (a) shows the Wenzel state; inset (b) represents the Cassie-Baxter state; while inset (c) is a representation of the metastable Cassie state, which is energetically unstable compared to the Wenzel state. However, liquid droplets may still contact a composite surface of solid and air due to the capillary force preventing them from entering into the substrates if the surface has overhanging structures as shown in inset (c).

Figure 2.14. Relationship of $\cos \theta^*$ with $\cos \theta_c$. The black solid line is the Wenzel state, the blue solid line is Cassie-Baxter state, the red dashed line is metastable Cassie-Baxter state when $\theta_c > 90^\circ$; the red dotted line stands for the metastable Cassie-Baxter state when $\theta_c < 90^\circ$.

Figure 2.15. Three cross-sectional profiles of water in contact with a solid indent consisting of overhanging structures. A critical parameter is the angle ($\theta_{overhang}$), which is the angle between the sidewalls of the indent and the horizontal line.
In Figure 2.15, when $\theta_{\text{overhang}}$ is greater than the intrinsic contact angle ($\theta_{\text{flat}}$), the water-air interface inside the indent is concave, shown in 2.15(a). The net force at the interface is toward the inside of the indent, which will cause droplets into complete contact with the solid. Image (b) shows the situation that $\theta_{\text{overhang}}$ is the same as $\theta_{\text{flat}}$, the water-air interface remains flat. When $\theta_{\text{flat}}$ is larger than $\theta_{\text{overhang}}$, the net force is toward the outside of the indent, which provides a force to prevent liquid droplets entering into the indent.

Gao \textsuperscript{67} reported a method to design and fabricate microtextures consisting of overhangs with well-defined geometries for inducing superhydrophobicity for a hydrogen terminated silicon surface with a Young’s contact angle of 74˚. They coated a silicon wafer with thermally grown silicon dioxide thin film and then the silicon dioxide film was patterned by photolithography, followed by HF aqueous etching. A Bosch deep reactive ion etching process was used to etch the SiO\textsubscript{2}-masked Si substrate, forming arrays of silicon pillars with vertical sidewalls. After that, they aligned a square pattern of silicon pillars on the flat silicon wafer. The silicon surfaces were exposed on the four sidewalls of each pillar, which then were etched in a potassium hydroxide aqueous solution. The exposed silicon surface underneath the top silicon dioxide mask formed overhanging sidewalls and the silicon dioxide mask was removed by HF, leaving a hydrogen-terminated Si surface. The pattern produced is a two-dimensional array of squares, in which the width of each square and the center-to-center distance between adjacent squares are the most critical parameters. After creating the overhang structures, they deposited Au nanoclusters onto the exposed silicon surfaces in an aqueous solution of HF and KAuCl\textsubscript{4}. Si nanowires were grown by a chemical vapor deposition method using silicon tetrachloride. \textsuperscript{72} Finally, the Au clusters were removed by HF and the samples produced were rinsed in deionized water and dried thoroughly in air.
The overhanding angle of the produced structures was around 54°, which is smaller than Young’s contact angle (smaller than 90°), while the static water contact angle on the produced surfaces with overhanging structure was around 160° even without any further coating with low surface tension chemicals. According to Gao’s explanation, the superhydrophobicity of the overhanging structures was due to the formation of a composite surface of solid and air making the water remain in a metastable Cassie state.

Gao’s group also prepared superoleophobic surfaces with overhang structures using layer-by-layer assembly process. They cleaned substrates by immersing them in piranha solution (3:1 mixture of 98 w.t. % H₂SO₄ and 30 w.t. % H₂O₂), rinsing with DI water and drying with a nitrogen flow.
Then the substrates were repeatedly immersed into alternative cationic and anionic aqueous solutions. Poly(diallyldimethylammonium chloride) (PDDA) was used to prepare the cationic aqueous solution and poly(sodium 4-styrenesulfonate) (PSS) was used to make the anionic aqueous solution. One bilayer was formed after treatment in cationic and anionic solutions. After five cycles, the adhesion of the subsequent layers was promoted for further coating of nanoparticles of polystyrene and silicon dioxide. They calcined the produced samples at 550°C, during which both the polystyrene particles and polyelectrolytes were removed and a nanoporous network of silica nanoparticles was formed. Finally, the samples were treated with (tridecafluoro-1, 1, 2, 2-tetrahydrooctyl) trichlorosilane and organic-inorganic nanocomposite coatings consisting of different numbers of layers were prepared.

They demonstrated that a highly oleophobic coating can be prepared based on a porous network of nanoparticles by first assembling an organic-inorganic nanocomposite and then removing the organic parts by calcination. In their study, the removal of the polystyrene particles made overhanging structures on the surface, which resulted in high oil-repellency of the coating although the intrinsic oil contact angle of the solid surface was smaller than 90°.

![Figure2.11. SEM images of the coatings. a) SEM image of coating before removing the polystyrene nanoparticles. b) SEM image of coating after calcination. The arrow 1 points to polystyrene nanoparticles which disappeared after calcination. Arrow 2 indicates silicon nanoparticles.](image-url)
Superhydrophobic and superoelophobic silicon surfaces with overhanging nanostructures were fabricated using anisotropic etching of silicon coated with a thin hydrophobic layer under certain etching parameters. Silicon is the most used material in microfabrication and anisotropic reactive etching. After etching, randomly ordered rods of silicon can be created. This process is an easy method to introduce roughness on silicon wafers, referred to as black silicon or silicon nanograss (SING) when using fluorine-based reactive etching ion process. In Ahuja’s experiment, he fabricated silicon nanograss using an inductively coupled reactive ion etching system under optimal process conditions. SF$_6$ and O$_2$ flow rate were controlled to change the angle of cone shaped nanograss rods. After this process, the surfaces were coated with heptadecafluoro-1, 1, 2, 2-tetrahydrodecyl trichlorosilane (PDTS) by molecular phase deposition. They also presented another method to improve the oil repellency. A thin layer of silicon dioxide was treated to form well-defined overhanging nanostructures at the apexes of the SiNG rods by using plasma enhanced chemical vapor deposition (PECVD). The produced samples showed high contact angles and low slide angles for water and rapeseed oil because of the overhanging structures.

Figure 2.12 The SEM images show the overhanging structures fabricated by varying the ratio of flow of SF$_6$ to O$_2$ to a) 50/80 and b) 99/80.
Ahuja et al. proposed and experimentally demonstrated a new and simple method relying on surface topography to achieve superhydrophobicity and superoelophobicity of surfaces. Instead of attempting to keep the Cassie-Baxter state at minimum-energy state, they created a system in which the energy barrier that separates the metastable Cassie-Baxter state from Wenzel state was high enough to lock the liquid in the desired non-wetting state. According to this idea, they created a special type of 3D overhanging structures, a nano-nail structure coated with low-surface-tension fluoropolymer, which could inhibit transitions from the Cassie-Baxter state to the Wenzel state. In their work, a honeycomb with overhanging structure was also created using reactive-ion etching. Then an oxide layer was grown on the structures using a thermal oxidation process. Finally, the samples were coated with a smooth layer of fluoropolymers using a chemical vapor deposition process. A wide range of low surface-tension liquids showed very large contact angles and small roll-off angles on the produced surface.

The reason that the nanonails, one kind of overhanging structure, can effectively prevent the transition from non-wetting Cassie-Baxter state to the wetted Wenzel state was given by Ahuja. To achieve smaller advancing contact angle (smaller than 90°), the liquid surface would have to sag in between neighboring nanonails, leading to a liquid-air interface with curvature of several inverse micrometers. Unless high pressure was applied, the liquid would stay on the top of the nanonails and would not penetrate inside and wet the surface.

In summary, overhang structures can prevent oils with low-surface-tension from penetrating into the texture because of the composite surface of air and solid in contact with liquid droplets. Such structures can provide an energy barrier, which may be caused by a capillary force, to separate the
Wenzel state and Cassie state. Quantitative evaluation of the stability of the metastable Cassie state still needs to be studied further.

Figure 2.13. Overhanging nanostructured substrate topography. a) Schematic representation of the overhanging geometry. Solid substrate is shown in red while the liquid is in blue. b) SEM image of nanonails with stem diameter 280 nm. c) SEM images of nanonails with stem diameter 383 nm. d) Side view of the honeycomb substrate. 75

Re-entrant structure

In order to achieve high contact angles and low hysteresis, SH and SO surfaces should have a composite solid-air interface to support liquid droplets, such as the air-solid composite interface formed in overhanging structure reviewed before.7 However, the composite interface may be unstable and have the irreversible trend to be transformed into a homogeneous interface. Recently, re-entrant structures with grooves were proposed to construct stable superhydrophobic and superoleophobic surfaces.76,67,7,77 Herminghaus first pointed out that the constituents on the leaves of some superhydrophobic plants, such as wild cabbage, are hydrophilic and the surprising
superhydrophobicity is because of the reentrant surface texture, in which a vector projected normal to horizontal plan intersects the texture more than once. Nosonovsky studied the stability of composite interface and he argued that the creation of a stable composite interface requires two criteria. One is that the local texture angle must equal the equilibrium angle. The other is that the differential quantities corresponding to changes in the solid-liquid contact area and the local contact angle of the liquid should have opposite signs.

Motivated by the understanding of re-entrant structure, Cohen’s group fabricated surfaces with re-entrant structure. They used flat silicon wafer as substrate, which was treated by means of SiO$_2$ deposition followed by a two-step etching process including reactive ion-etching of silicon dioxide and isotropic etching of Si using vapor-phase XeF$_2$. A structure, which they called micro-hoodooos with undercut silicon pillars and troughs, was formed.

2.2.2 Surface Chemistry

Chemical compositions of surfaces determine the surface free energy and thus play an important role in fabricating SO and SH surfaces. In order to repel organic liquids with low surface tension, the surface energy of a solid substrate should be lower than that of test liquids. Because of the low surface tension, good chemical stability and low friction coefficient, fluorinated polymers are widely used as coating materials to prepare SO and SH surfaces. However, the design of versatile fluorinated polymers is still very challenging, which limits the fabrication of SH and SO surfaces

Synytska synthesized linear aromatic end-group functionalized oligoesters by melt polycondensation in vacuum using Ti(OBu)$_4$ as a catalyst. The fluorinated oligoesters produced have linear structures consisting of a sequence of terephthalate and neopentylglycol alternating
groups. Next the fluorinated oligoesters were modified with C$_8$F$_{17}$ perfluorinated tail attached to the main oligomer chain via ester bonds. The perfluoroalkyl end-functionalized oligoester films were fabricated by spin-coating and melt techniques. For spin-coating, the fluorinated oligoesters solution in CHCl$_3$ was filtered through a porous filter and then the solution was made into films by spin-coating. Melt films were prepared by melting of polymer grain on the substrate in a vacuum oven. The films produced from these two methods exhibited both superoleophobicity and superhydrophobicity. Based on their results, the surface energy of oligoester films could reach 11 mJ/m$^2$ when the fluorine bulk concentration was 10.7 wt%.

Scheme 2.1. Schematic of the synthesis of linear aromatic end-group-functionalized oligoesters.$^{79}$

Surface-initiated ring-opening metathesis polymerization (SI-ROMP) is a promising method to prepare partially fluorinated polymer films because of its mild reaction conditions and rapid kinetics to enable films with thicknesses of several nanometers up to a few micrometers. Generally, fluorinated polymers are deposited onto a surface by spin-coating $^{80}$, dip-coating $^{81}$, solution-casting $^{82,83}$ or chemical adsorption $^{84}$. However, spin-coating and solution-casting do not provide a direct attachment of the polymer to the surface and chemical adsorption yields non-conformal,
low density polymer films. SI-ROMP can enable controlled growth of polymer chains attached directly to a surface and can produce conformal thin films on surfaces of different geometries. Faulkner et al.\textsuperscript{85} fabricated partially fluorinated polymer films with tunable thicknesses using SI-ROMP of NBFn on gold substrates. The produced films exhibited both superoleophobicity and superhydrophobicity. Perfluoroalkyl chains can range in length from 4 to 10 carbons. According to their study, the growth rate of film and the critical surface tensions are dependent on the perfluoroalkyl chain length. Longer chains enabled faster surface-initiated growth, greater thickness, and decreased critical surface tension. Upon exposure to air, the fluorocarbon chain segments will seek the air/polymer interface, resulting in the enhancement of the surface hydrophobicity and oleophobicity.

![Scheme 2.2](image)

Scheme 2.2. Schematic of SI-ROMP of 5-(perfluoro-n-alkyl)norbornenes on a gold substrate. A gold surface is modified with mercaptobutanol and further treated with trans-5-norbornene-2,3-dicarbonyl chloride for 30 min. The initiator is activated by Grubbs second-generation catalyst, denoted as [Ru], and exposed to the NBFn monomer solution (R2 = -C4F9, -C6F13, -C8F17, or -C10F21). R1 represents CHPh.\textsuperscript{85}

Block copolymers with one block containing fluorinated groups have been investigated extensively in fabricating SH and SO surfaces. Meskini\textsuperscript{86} synthesized and characterized one series of copolymers based on vinylidene cyanide and vinyl ether containing a fluorinated group, shown in Scheme 2.3. They used 1H, 1H, 2H, 2H-perfluorodecyl vinyl ether as the fluorinated...
comonomer. These copolymers showed superhydrophobicity and superoleophobicity. However, in many cases the use of such block copolymers results in dramatically altered surface properties, which limits its usage. An alternative and attractive strategy is the use of the functionalized polymer chains as additives. Aryl ether moieties carrying four C₈F₁₇ fluoroalkyl groups were used as initiator in the copper mediated living radical polymerization of both styrene and methyl methacrylate to yield such polymer additives in Jennings’ group. These multi-end – functionalized polymer could be used to modify the surface energy and properties, resulting in SO and SH surfaces. Wang synthesized a series of N-pentyl-perfluorooctaneamide end-capped semicrystalline poly (butylene isophthalate) films on silicon substrates and the produced films also presented both SO and SH properties.

Scheme 2.3. Synthesis of 1H, 1H,2H,2H-perfluorodecyl vinyl ether (FAVE8) and radical copolymerization of vinylidene cyanide (VCN) with 1H, 1H,2H,2H-perfluorodecyl vinyl ether in acetonitrile, initiated with tert-butyl peroxypivalate.
Figure 2.14. Controlled radical polymerization initiators carrying multiple fluoroalkyl groups.\(^87\)

Electrochemical polymerization of fluorinated monomers has been proven to be an effective method to fabricate SH and SO surfaces. A variety of electrodeposited polymer films with various morphologies were prepared from semifluorinated thiophenes, ethylenedioxythiophene (EDOT), pyrrole, 3,4-ethylenedioxyxpyrroles (EDOP) and 3,4-propylenedioxyxpyrroles (ProDOP). As mentioned above, the use of hydrophobic material and formation of surface roughness are two required conditions to make SH and SO surfaces. Experiments showed fluorinated tails not only can decrease the surface tension but can also force the formation of surface structures. Nicolas reported an easy processing method to get SH and SO surfaces of conductive polymers by electropolymerization of perfluoroalkyl ethylpropanoate thiophenes.\(^88\) Zenerino tried to synthesize a series of original monomers with short perfluorinated chains with less time consuming synthesis step. They produced 3, 4-ethylenedioxyxpyrrole derivatives containing respectively 4 and 6 perfluoromethylene units following a short synthetic method. After the electropolymerization step, the surface showed SH and SO properties because of the low surface tension of highly fluorinated polymers and the rough structure created. The conductive polymers play an important role in the
fabricating surfaces with nanoporosity and they provided a choice tool to modulate surface morphology and wettability.

![Chemical structures of the synthesized monomers by electropolymerization of perfluoroalkyl ethylpropanoate thiophenes.](image)

Figure 2.15. Chemical structures of the synthesized monomers by electropolymerization of perfluoroalkyl ethylpropanoate thiophenes. 88

2.2.3. Approach for designing SH and SO surfaces

Surface chemical compositions and surface structure are two major considerations in creating SH and SO surfaces as reviewed above. Therefore, researchers have tried to develop various methods to achieve the low surface energy, high roughness and overhanging or re-entrant structure.

Atom transfer radical polymerization (ATRP)

ATRP is a controlled radical polymerization technique which has been proven to be useful for the synthesis of functional macromolecules with controlled and complex architectures. This method is widely used for the formation of polymer brushes via surface initiated polymerization. Nystrom et al. 89 fabricated SH surfaces with a micro-nano-binary surface structure via the surface-confined grafting of glycidyl methacrylate, using 2-bromoisobutyryl bromide as initiator. A “graft-on-graft” architecture was obtained when GMA was polymerized from the initiating groups on each graft, followed by post-functionalization to obtain fluorinated brushes. The produced surface showed
very high water contact angle and self-cleaning property. Because of the high cost of fluorine-containing compounds, they further created SH and SO surfaces using reduced amounts of fluorine or even complete replacement of fluorine with other hydrophobic compounds such as poly(dimethylsiloxane) (PDMS).\textsuperscript{90} Highly oleophobic and hydrophobic cellulose surfaces were prepared by using ATRP methods and subsequent modification with pentadecafluorooctanoyl (C\textsubscript{7}F\textsubscript{15}), showing a contact angle up to 144° for sunflower oil. What’s more, the self-cleaning property of the produced surface was demonstrated by applying carbon black power on the surfaces.

Scheme 2.4. Synthetic approach for functionalization of cellulose substrate. Conditions: Synthetic approach for functionalisation of cellulose substrate. Conditions: (i) pentadecafluoroctanoyl chloride, TEA, DMAP, DCM, room temperature (RT); (ii) 2-bromoisobutyryl bromide, TEA, DMAP, THF, RT; (iii) GMA, CuCl, CuBr\textsubscript{2}, PMDETA, toluene, 30 °C; (iv) HCl(aq), THF, RT.\textsuperscript{91}

Figure 2.16. The self-cleaning ability of a C\textsubscript{15}H\textsubscript{31}-modified graft-on-graft surface using ATRP.\textsuperscript{90}
Although ATRP is an effective way to fabricate SH and SO surface, there are some disadvantages. First, ATRP method is time consuming because of the long step of synthesizing the monomers and polymers. Secondly, the conditions of ATRP are hard to control. Each ATRP reaction needs one specific series of reaction conditions. Thirdly, ATRP requires specific substrates. Therefore, it is still challenging to use ATRP in creating SH and SO surfaces.

Casting method
Casting has been proved to be a simple but effective way to make SH and SO surfaces. Jiang Lei reported a simple one-step casting process from two easily synthesized or commonly available polymer materials poly (methyl methacrylate) (PMMA) and fluorine –end-capped polyurethane (FPU) without any further modification. The as-prepared polymer films exhibited both SH and SO properties because of the micro-protuberances covered by nanostructure of low surface energy polymer chains, which is similar to the structure of lotus leaf. According to their analysis, after dissolving the PMMA and FPU in dimethylformamide, the DMF began to evaporate. As the concentration of polymers starts to increase during the initial evaporation period, the PMMA began to precipitate into a sponge-like structure and then the FPU starts to deposit onto the surface of the PMMA micropapillae to form the nanoscale structure on the surface of the PMMA substrate. Because of the low surface energy of fluorocarbons, the fluorine component in FPU will self-enrich on the topmost surface of the polymer film.
Loth et al. described a technique to fabricate SO and SH surfaces by spray casting nanoparticle-polymer suspensions to produce hierarchical nanotextured surface morphology. Nanocomposites are fabricated using solution-processable mixtures of ZnO nanoparticles to create nanoroughness and waterborne perfluoroalkyl methacrylic copolymer as low surface tension binder. According to their study, acetone was shown to be an effective compatibilizing cosolvent to construct hierarchical nanotextured surface morphology. Various substrate materials, including glass, can be coated using this method. This method was also proved to be versatile for the fabrication of SH and SO surfaces using a mixture of ZnO nanoparticle and organosilane quaternary nitrogen compounds.
Figure 2.18 SEM images of the composite surface of both ZnO nanoparticles and PMC cells.\textsuperscript{92}

Xue reported a facile one-step method to prepare SH and SO coating with a corealline-like structure by spraying nanocomposites composed of fluorinated multi-wall carbon nanotubes (MWCNTs) and fluorinated polyurethane without additional surface treatment with commonly used low surface energy materials.\textsuperscript{93} The MWCNTs played a role in creating both microscale and nanoscale roughness and fluorinated PU was the low surface energy binder. The produced films showed high contact angles for water and hexadecane because of the cavity and pole-rich hierarchical structure similar to the re-entrant curvature structure or the overhanging structure mentioned when talking about the structure impact of the wettability. In this method, they can control the surface wetting behavior by changing the proportions of toluene in the solvents.

Scheme 2.5. Grafting of perfluoroalkyl groups to MWCNTs.\textsuperscript{93}
Casting method is another simple and effective method to fabricate SH and SO surfaces, which can be applied to various substrates, such as glass, paper, etc. Usually, fluorinated chemicals are used to cast onto the surface to create low surface energy and high degree of roughness at the same time. Additional treatment using common low surface tension materials is not needed to get SO and SH surfaces. Therefore, casting is widely used in industry and academic laboratories.

Chemical Vapor Deposition (CVD)

Chemical vapor deposition is another chemical method used to produce non-volatile, high purity and high-performance solid material. Recently, CVD has been shown to be an effective method to fabricate SH and SO surfaces. Gleason described a new synthetic scheme to fabricate nanoporous-basalt-like poly(3,4-ethylenedioxythiophene) (PEDOT) by introducing a new oxidant CuCl₂ to the CVD process. The surface morphology and nanostructure of the resultant films could be controlled by changing substrate temperature and the concentration of oxidant. After modifying with the fluorinated polymer through an oxidative CVD approach, the as-fabricated films showed high contact angles for water and ethanol because of the nanoporous structure. This behavior can be interpreted by Cassie-Baxter theory and utilizing this mechanism, SH and SO silicon nanowires were fabricated by CVD, which can repel most of the existing nonpolar liquids as well as many polar liquids according to Boukherroub. In his study, silicon nanowires are synthesized on a silicon substrate using CVD methods using the following procedures. A silicon dioxide layer is deposited thermally on the silicon substrate, and then coated with a layer of gold. The substrate was heated to 500°C to form gold nanoparticles acting as catalysts for silicon nanowire growth. Then, silane gas was injected onto gold, forming a AuSi liquid eutectic, which introduced the
directional growth of nanowires with the gold nanoparticle on top. Finally, the surfaces were treated with 1H, 1H, 2H, 2H-perfluorodecyltrichlorosilane (PFTS).

Figure 2.19 The SEM image of nanowires produced by using CVD.  

Willis et al. created SH and SO poly(tetrafluoroethylene) surfaces with micro-roughened structures using oxygen plasma treatment. After deposition of a low surface energy plasma polymer coating, 1H,1H,2H,2H-heptadecafluorodecyl acrylate, through the plasma enhanced CVD process, the liquid repellency of as-fabricated micro-roughened PTFE substrates towards water and oil solutions was apparently improved. In summary, CVD is also an effective treatment method which is applied to various substrates to create SH and SO surfaces.

Dip-coating

Dip-coating is a simple method for depositing a uniform thin film of liquid onto a substrate, especially small slabs and cylinders for solidification into a coating. Thickness and uniformity can be controlled by flow conditions in the liquid bath and gas overhead. Dip coating process can be divided into five stages: immersion, start-up, deposition, drainage, and evaporation. Recently dip-coating has been widely used to fabricate SH and SO surfaces. Santucci et al fabricated crack
free and smooth surfaces of poly[4,5-difluoro 2,2-bis (trifluoromethyl)-(1,3 dioxole)-co-tetrafluoroethylene] (TFE-co-TFD) thin films by wet chemical dip coating on polished quartz and glass slide substrates. After annealing at different temperatures, different morphologies and elemental compositions can be obtained. The experiments showed that as the annealing temperature increased nano-hemisphere-like structures were grown, which can increase the contact angle of water and oil liquids on the surfaces.

Figure 2.20. General stages of dip-coating processes: (a)-(e) batch; (f) continuous.

Figure 2.21. Structure of the fluorine-based block-co-polymer used as a precursor for the preparation of TFD-co-TFE films by a wet chemical dip coating technique.
Liu’s group produced multiple facet supported alumina nanowires in a short time via high field anodization followed by a dip-coating process of perfluorosilane. In their experiments, cleaned Al foil was first treated with Na₂SO₄ solution at room temperature, creating fractal morphology with numerous facets. Then the sample was dipped into a solution of 1H, 1H, 2H, 2H-perfluorooctadecyltrichlorosilane in hexane and curing at 120°C, which resulted in tight covalent binding of a silane layer on the surface. After the post-modification with perfluorosilane, the multiple facets and the nanowires in horizontal and vertical orientations created large energy barriers to prevent liquid wetting. The produced alumina nanowire surfaces showed high contact angles for a broad range of liquids including water, water emulsion, glycerol, and alkanes. According to the authors, it was demonstrated that the SH and SO behavior can be observed even under conditions where there was no air between the surfaces and droplets.

Carins’s group used the dip-coating method to fabricate wear resistant polysiloxane coatings. Cleaned transparent soda-lime float glass slides were coated with alkoxide-synthesized sols by dip-coating in air at ambient conditions. The deposited films were then cured using an oven to form a dense three-dimensional film structure by thermally induced self-condensation reactions within the coating materials, bonding the structure together to the underlying substrate. The coatings obtained showed water and oil repellent properties. SH and SO surfaces were also fabricated in low-surface-energy fluorodecyl polyhedral oligomeric silsesquioxane (POSS) solution on various substrates using dip-coating methods developed by Cohen’s group. They developed a simple and benign dip-coating process which can provide a flexible and conformal coating of extremely low-surface-energy fluorodecyl POSS molecules on any surface, including those that have re-entrant textures, such as duck feathers, lotus leaves, or commercially available
fabrics. The produced re-entrant nano-textures, the surface energy of fluorodecyl POSS, and the surface roughness enabled the dip-coated surfaces to support a composite interface even for low-surface-tension liquids.

Figure 2.22. (a) Multi-facet aluminum by first step anodization in 60 mM Na₂SO₄ and 4 V bias for 3 h. (b–h) High field anodic oxidation for different time periods, resulting in nanowire forests on a multi-facet mattress. (i) Schematic depiction of the evolution of surface morphology from nanopores to nanowires during anodization.⁹⁸
Fu’s group also fabricated transparent SH and SO surfaces with improved stability using dip-coating. A transparent SH coating was first prepared with polydimethylsiloxane (PDMS) and hydrophobic silicon dioxide (SiO$_2$) nanoparticles. Then the samples were sintered to degrade the PDMS into SiO$_2$ and then oxidized into silanol, followed by the treatment with 1H, 1H, 2H, 2H-perfluorooctyl-trichlorosilane (PFTS). The produced coatings exhibited transparency, low adhesive SH and SO properties with high contact angles and low contact angle hysteresis, and good stability under high temperature.

Scheme 2.6. Fabrication procedures of superamphiphobic character PFTS treated coating, showing the change in the surface chemical composition.

**Electrospinning method**

Electrospinning is a simple but versatile method to generate fibers down to nano-size. Recently electrospinning has been widely used in synthesizing various polymers and been demonstrated to provide the appropriate surface roughness for SH and SO surfaces. He et al. fabricated large area SH and SO titanium membranes with high adhesive forces by electrospinning.$^{136}$ They fabricated fabrics with different morphologies by electrospinning of Ti(OBu)$_4$ precursor solutions for different time. Then microscope slide glasses covered with the nanomembranes via electrospinning were treated with acid solutions to create hierarchical micronanostructures, followed by 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane (POTS) modification. By changing the electrospinning conditions, they obtained surfaces showing different wettability. Kim created
multifunctional hybrid fabrics with thermally stable SH and SO properties by electrospinning methyltriethoxysilane (MTES).\textsuperscript{137} MTES was used to prepare organically modified silicates by adding HNO\textsubscript{3} under rigorous stirring at room temperature. After reaction for 48 hours, the linear polymerization was accelerated by adding aqueous aluminum acetylacetonate solution. The produced viscous solution was electrospun into a fibrous web under high voltage with a collecting distance of 15 cm between the tip of the needle and the collector. According to their data, all electrospun MTES surfaces exhibited water contact angle greater than 150°, even after heat treatment at 500°C.

Figure 2.23. (a) SEM image of a lotus leaf illustrating its surface texture. The inset shows that droplets of rapeseed oil easily wet the surface of a lotus leaf. (b) SEM image of a lotus-leaf surface after the dip-coating process. The inset shows that the dip-coated leaf can repel rapeseed oil. (c) SEM image of the polyester fabric. In spite of the presence of the re-entrant curvature, hexadecane can readily wet the fabric surface (inset). (d) SEM image of the dip-coated polyester fabric. The inset shows the elemental mapping of fluorine obtained using energy-dispersive X-ray scattering. (e) Super-repellency of a dip-coated polyester fabric against various polar and nonpolar liquids.
Cohen’s group reported another method to create SH and SO surfaces by randomly deposited electrospun fibers using PMMA and POSS. Different fabric morphologies were produced by changing the concentration of PMMA and POSS solution for spinning. A beads-only structure formed at the low concentration; the beads-on-strings structure formed at moderate solution concentration, and the fibers-only structure formed at high concentration. All three morphologies had re-entrant structure and the same low surface tension energy. These fabrics showed SH and SO properties towards decane, heptane, and octane.

Figure 2.24. Controlling the morphology of electrospun surfaces. (A–C) SEM micrographs of the various electrospun fabric textures for the PMMA + fluorodecyl POSS+ 44wt% blend, produced by varying the concentration of the electrospinning solution. The insets show droplets (droplet volume V ~ 2μL) of hexadecane (γLV = 27.5 mN/m°) on each electrospun surface. Coaxial electrospinning is an evolution from electrospinning, which is based on a spinneret consisting of two coaxial capillaries with different diameters. In a typical coaxial electrospinning process, the electrospinable polymer will act as a guiding material for nonelectrospinnable polymer and facilitate spinning by forming a compound Taylor cone from a combination of the core solution and the sheath solution. Therefore, compared with traditional electrospinning process, coaxial electrospinning can be applied to more polymers, even ones with low dielectric constant values. Steckl produced SH and SO surfaces by coaxial electrospinning for the first time. He used Teflon amorphous fluoropolymer(AF) with poly(ε-caprolactone) (PCL) as core materials to fabricate core-sheath-structure nano/microfibers, which combined different
properties from individual core and sheath materials. The morphology of the produced fibers can be controlled by changing the concentration of PCL core solution. The produced fibers showed high contact angles and very low sliding angles for water and oils.

Figure 2.25. Comparison of PCL-Teflon membranes by electrospinning and sol-gel processes: (a) a Teflon AF spin-coated PCL membrane, (b) a Teflon AF dip-coated PCL membrane, and (c) a coaxially electrospun PCL/Teflon AF membrane.102

Sigmund used coaxial electrospinning of poly(vinylidene fluoride) (PVDF)-Teflon amorphous fluoropolymer(AF) and Teflon AF-PVDF core-sheath nanofiber mats to fabricate surfaces with SH and SO properties.103 In their experiment, PVDF was dissolved in dimethylformamide and a Teflon AF solution in perfluoro compound FC-75 2,2,3,3,4,4,5-heptafluoro-5-(1,1,2,2,3,3,4,4,4-nonafluorobutyl)-tetrahydrofuran) was used.

Figure 2.26. Coaxial electrospinning setup showing how the core needle (red) was inserted within the sheath needle (pink). The inside and outside diameters of the sheath needle were 0.965 and 1.245 mm, respectively. The core needle was inserted all the way through the sheath needle. The assembly was done in such a way that the core needle slightly protruded out of the sheath needle to avoid the mixing of the core solution and the sheath solution.102
In summary, electrospinning is a versatile technique for producing desired micro and nanofibers with SH and SO properties from many kinds of polymers. Coaxial electrospinning expands the versatility of electrospinning by enabling the formation of core-sheath-structured micro/nanofibers of nonelectrospinable polymers. Compared to other fiber formation methods, coaxial electrospinning has many advantages, such as simple one-step process for the conformal coating of polymer fiber with low surface energy material; a large variety of available materials and high cost-effectiveness. Therefore, coaxial electrospinning method has been used to fabricate SH and SO by many groups. However, mechanical adhesion between substrates and electrospun fibers should be further improved.

**Etching**

As reviewed before, the overhanging or re-entrant structure is necessary to prevent water and oil from wetting the substrates. Etching was proved to be effective for creating such structures. Porous silicon films were fabricated in Gao’s group by a convenient gold-assisted electroless etching process. The treated films showed an overhanging structure because of the hierarchical porous structure, making the silicon surfaces superhydrophobic. Tuteja created nanostructured substrates with nanonail topography and honeycomb structures using reactive-ion etching of silicon. The treated silicon substrates were then coated with a smooth layer of fluoropolymer through chemical vapor deposition, making the surface possess overhanging structure. The as fabricated surfaces showed high contact angles for water, methanol, ethanol, and other liquids. Lindstrom showed that nanocrystalline cellulose can grow on structured and flat silicon surfaces and the surfaces produced showed SH and SO properties after coating with low surface energy materials. In their study, polished silicon wafers were thermally oxidized and patterned using standard photolithography followed by anisotropic plasma etching using SF$_6$ and C$_4$F$_8$ gases. After
modification with fluorinated trichlorosilanes, silicon surfaces exhibited SH properties because of the combination of surface overhanging structures and low surface energy materials. Furthermore, they coated the structured silicon substrates with cellulose nanocrystals using a polyelectrolyte multilayer technique. The fabricated surfaces showed highly nonwetting properties for a number of oil liquids, such as decane and hexadecane.

Scheme 2.7. Schematic representation of the buildup of electrostatically adsorbed multilayered films. The polyelectrolyte, PEI, is shown as highly branched molecules, and colloidal cellulose nanocrystals are represented by a straight rod; counterions have been omitted for clarity.\textsuperscript{105}

Kumar et al. used anisotropic etching process followed by a thin hydrophobic heptadeca fluoro-1,1,2,2-tetrahydrodecyl trichlorosilane CF\textsubscript{2}-(CF\textsubscript{2})\textsubscript{7}(CH\textsubscript{2})\textsubscript{2}SiCl\textsubscript{3} (FDTD) coating to fabricate SH and SO surfaces with overhanging structures.\textsuperscript{106} In order to investigate the effect of surface geometrical shape on wettability, Wong’s group used liquid-based metal-assisted etching treatments.\textsuperscript{107} Etching conditions, including etch time and etch solution concentration, influenced the reentrant structures and the wettability greatly. Recently, Kim produced a dual structure of microtextured surface onto which a layer of TiO\textsubscript{2} nanotubes were coated. The microtexturing was done by electrochemical etching, and the nanotube layer was formed by a hydrothermal process. The fabricated surface showed high contact angles for water and glycerol droplets. Nanostructures
introduced by hydrothermally grown TiO$_2$ nanotubes provided an effective air trapping structure in enhancing the surface SO and SH properties.$^{108}$

Figure 2.27. Schematic illustration of the experimental steps to fabricate SH and SO surfaces having a dual micro-and nanostructured TiO$_2$ arrays. (a) the hydrothermal processed for $\sim$8-nm-diameter TiO$_2$ nanotube deposition on Ti foil and (b) the microtextured and hydrothermal processed Ti foil.$^{109}$

Zhou reported a simple method to achieve hierarchical textured surface morphology on aluminum substrates by HCl etching and boiling water treatment. The aluminum substrates exhibited high contact angles even for the low surface tension liquids, such as hexadecane and decane because of the re-entrant structures on the surfaces.$^{110}$ Another fabrication method of new SH and SO surfaces using reactive ion etching followed by a vapor deposition of trichloro(1H, 1H, 2H, 2H-perfluorooctyl) silane was reported. In the experiments, etching was performed in an electrotech plasma, twin deposition/etch system, using a silicon wafer. A uniform etching rate was maintained with a ceramic plasma shower and the high concentration of SF$_6$ resulted in anisotropic silicon etching. Nanostructures with a well-defined concave shape and homogeneous sidewalls were produced as shown in Figure 2.33. After coating with trichloro(1H, 1H, 2H, 2H-perfluorooctyl) silane under vacuum, the surfaces showed SH and SO properties.
In summary, the etching process has been widely used by researchers to fabricate rough surfaces, including reactive metal-assist etching, reactive-ion etching, and acid/base etching. It is a simple and effective way to make SH and SO surfaces.

**Layer by Layer (LBL) assembly method**

LBL assembly technique is currently widely used to fabricate nanostructured thin films with excellent properties, such as special mechanical, electrical and wetting properties. Gao’s group also prepared superoleophobic surfaces with overhang structures using layer-by-layer assembly process. They demonstrated that a highly oleophobic coating can be prepared based on a porous network of nanoparticles by first assembling an organic-inorganic nanocomposite and then removing the organic parts by calcination. In their study, the removal of the polystyrene particles made overhanging structures on the surface, which resulted in high oil-repellency of the coating although the intrinsic oil contact angle of the solid surface was smaller than 90°.
Polymerization

Polymerization is necessary for designing new coating materials with low surface tension. Hong’s group synthesized a new diblock copolymer containing a poly[3-(triisopropyloxysilyl) propyl methacrylate]-block-poly[2-(perfluorooctyl)ethyl methacrylate] by sequential anionic polymerization. The synthesized polymer was used to coat silica particles, making the new surfaces exhibit high contact angles with water, cooking oil, and hexadecane. This approach was demonstrated to be versatile for the fabrication of SH and SO surfaces on silica particles, cotton fabrics and other materials with high stability.\textsuperscript{112}

\[
\text{CH}_2\text{CH}_3
\]

\[
\text{CH}_2\text{OCH(CH}_3\text{)}\text{CH}_3\text{Si(OCH}_3\text{)}\text{CH}_3\text{OCH}_2\text{CF}2\text{CF}_3
\]

**PIPSMA-\textit{b}-PFOEMA**

Electropolymerization has been shown to be an effective method for deposition of conductive polymers on conductive electrodes, such as gold, platinum and stainless steel. Following the electrochemical conditions and the chemical structure of the monomer, SH and SO surfaces can be achieved directly. Using this method, superhydrophobic polypyrrole, polythiophene, poly(3,4-ethylenedioxythiophene) films showing exceptional non-wetting properties were reported. Kofman synthesized a conductive polymer PEDOP and coated it on micropatterned gold surface consisting of cylindrical micropillar arrays by combining electropolymerization and lithography methods.\textsuperscript{113}
Figure 2.29 (a) SEM image of the micro-pillars surface and (b) monomer used for the electropolymerization of PEDOF.\textsuperscript{113}

Micro- and nanospheres with superamphiphobicity were prepared by the conventional dispersion polymerization of perfluoroalkyl methacrylates in methanol by Yoshida.\textsuperscript{114} The cooperation of the spherical structure and the surface fluorine with a high concentration was responsible for the SH and SO properties. The polymerizations of 2,2,2-trifluoroethyl methacrylate (TFMA) produced microspheres with an average 4.12-μm diameter, while that of 2-(perfluorooctyl)ethyl methacrylate (POMA) provided nanospheres with a 679-nm diameter. The perfluoroalkyl chains and trifluoromethyl groups were concentrated on the top of the sphere-coated surfaces. The produced surfaces showed high contact angles over 150° for both water and diiodomethane.

Figure 2.30. The FE-SEM images of PTFMA the particles obtained by the dispersion polymerizations of TFMA and POMA.\textsuperscript{114}
Recently, a patternable, electrically conductive superamphiphobic coating on fabrics has been fabricated by one-step vapor-phase polymerization of polypyrrole in the presence of a fluorinated alkyl silane (FAS).\textsuperscript{115} The resultant fabrics exhibited a high static water contact angle and a low sliding angle for both water and hexadecane, demonstrating the important applications in the multifunctional self-cleaning clothing. In their experiments, patterned polypyrrole (PPy)-FAS coating can be generated simply by using a screen-printing technique to quench the polymerization reaction in the unneeded fabric area. Polyester fabrics were mainly used as a model substrate. The resulting fabrics exhibited high contact angles and low sliding angles for both water and hexadecane. In summary, polymerization method, including electropolymerization, vapor-phase polymerization and dispersion polymerization, has been proven to be effective and simple way to fabricate SH and SO surfaces.

![Figure 2.31. Procedure for making PPy-FAS patterns on fabrics.\textsuperscript{115}](image)

**Pyrolysis**

Jiang Lei’s group reported that the nanostructured aligned carbon nanotube (ACNT) films can be treated to show superhydrophobic and superoleophobic properties.\textsuperscript{116} ACNT films can be prepared by pyrolysis of metal phthalocyanines on quartz plates. Water contact angle on a film of carbon nanotubes lying on the surface is around 136°, while the water contact angle on the films with
ACNT alligned normal to the surfaces is around 158°, which demonstrated that the aligned structure of ACNT can increase the superhydrophobic properties. In order to get superoleophobic surface, ACNT films were treated with fluorinated compounds. They immersed oxidized ACNT films in a methanolic solution of hydrolyzed fluoroalkysilane and obtained surfaces with large contact angles for water and rapeseed oil.

![Figure 2.32. The images of packed ACNT films (left top view and right cross-sectional view).](image)

**Template**

Natural materials and artificial structured materials can be used as templates for SH and SO surfaces with hierarchical structures. PDMS is widely used as a base material to replicate the structures of templates. After solidification, the complement of the template surface pattern was transferred on the solid negative replica. Similarly, a negative replica was used as the template to fabricate a positive PDMS-replica. PDMS-based biomimetic replica was prepared by using the dry natural colocasia leaf as a template. After further modification with silica nanoparticles followed by chemical vapor deposition of fluorocarbon materials, the resultant -CF$_3$ terminal, silica-modified PDMS-replica exhibited both high oil-repellent and superhydrophobic properties.$^{117}$ The performance of produced surfaces can be controlled by its surface chemical composition.
Zhou reported a replication strategy for imprinting sophisticated binary micro/nanostructures into surface coatings to realize SO and SH properties using Al and Al$_2$O$_3$ as template.\textsuperscript{118} A series of polymeric replicas, including polyurethane (PU), polytetrafluoroethylene (PTFE) and polydimethylsiloxane (PDMS), were prepared. These surfaces exhibited SH properties without further modification. After modification with perflouro chemicals, these replica surfaces showed SO property for a number of oils, such as glycol, glycerol and ionic liquids.
Scheme 2.8. Schematic illustration of the polymer replication procedure for the Al$_2$O$_3$ mold with complicated irregular micro/nano hierarchical structures.$^{118}$

Inspired by the promising morphology of soot, Vollmer developed a simple way to make robust, transparent, SH and SO coating using candle soot as a template through chemical vapor deposition of tetraethoxysilane catalyzed by ammonia.$^{119}$ In the experiments, the soot-coated substrates were placed into a desiccator together with two open glass vessels containing TES and ammonia to form silica shell by hydrolysis and condensation. A porous deposition of candle soot was coated with silica shell. After calcination and silanization, the coating became transparent and showed SH and SO properties. The coated surfaces were sufficiently oil-repellent to cause the rebound of impacting drops of hexadecane. Even low-surface tension drops of tetradecane can roll off easily when the surface was tilled by 5°. The coating was transparent and could be applied to a variety of heat-resistant surfaces, such as aluminum, copper and stainless steel.

**Spray**

Spray-coating has been demonstrated to be an effective construction approach of SH and SO surfaces with re-entrant structures.$^{120}$ Loth reported a technique to fabricate SH and SO coating by spray casting nanoparticle-polymer suspension for the first time.$^{121}$ They used ZnO nanoparticles blended with a waterboron perfluoroacrylic polymer emulsion using cosolvents. Acetone is shown
to be an effective compatibilizing cosolvent to produce self-assembled nanocomposite with hierarchical nanotextured morphology upon curing. What’s more, the coatings can be applied to large and/or flexible substrates by spray coating with ease and require no additional surface treatments of commonly used hydrophobic molecules such as fluorosilanes.

Figure 2.34. SEM images of nanocompostion coating with different scale bars.\textsuperscript{121}

Zhu described a simple method to synthesize copper perfluorooctanoate and fabricate SO coating by spraying a copper perfluorooctanoate suspension onto substrates.\textsuperscript{122} By chemical etching of engineering metals in perfluorocarboxylic acid solutions to generate metal perfluoroalkanates \textit{in situ} to get SO properties have been achieved on metal substrates. However, this etching method is time-consuming and limited to particular metal surfaces. By spraying a copper perfluoroctanoate suspension, many substrates can be used to produce SO surfaces with re-entrant structures.

Cohen’s group also fabricated microtextured SO surfaces using solution spray coating of a blend of poly(methyl methacrylate) (PMMA) and the low surface energy molecule 1H,1H,2H,2H-heptadecafluorodecyl polyhedral oligomeric silsesquioxane (fluorodecyl POSS) using an air brush.
with a pressurized nitrogen stream.\textsuperscript{123} The solution concentration and molecular weight of the dissolved polymer can be altered to control the morphologies of microtextured surfaces. In summary, spray-coating is an alternative low cost technique to rapidly and conformally coat large areas on a variety of substrates, including glass, metal, and soft textile materials.

Figure 2.35 SEM images of the copper perfluorooctanoate coating at (a) low and (b) high magnification. The inset shows a schematic diagram of re-entrant geometries. (c) Droplets of water, ethylene glycol, rapeseed oil, hexadecane and dodecane on the superoleophobic coating. (d) The high hexadecane repellency of the superoleophobic coating when kept in a petri dish with hexadecane (colored with oil red O).\textsuperscript{123}

Scheme 2.9. Schematic of spray apparatus and the chemical structure of PMMA (A) and the FluoroPOSS cage molecule sprayed under a constant temperature and a range of relative humidity.\textsuperscript{123}
**Sol-gel method**

The sol-gel process with alkoxy silanes can be used to prepare organic-inorganic silicon-based hybrid materials with a size on the order of nanometers.\(^{124}\) Using this method, Savada prepared fluoroalkyl end-capped vinyltrimethoxysilane oligomeric nanocomposites having biphenylene units. The produced nanocomposites were applied to the surface modification of PMMA to exhibit high contact angles for some oils. In their experiments, fluoroalkyl end-capped vinyltrimethoxysilane oligomer reacted with biphenylene-bridged ethoxysilanes under alkaline conditions to yield the corresponding composites in good isolated yields.

Chen’s group prepared SO silica sphere stacking layers with one- and two-tier roughness on transparent glass substrates using a sol-gel method followed by fluoroalkoxy silane treatment.\(^ {125}\) In their experiments, uniform silica spheres were synthesized in colloidal solution using a sol-gel method that consisted of tetraethoxysilane in an alcoholic medium, followed by the base-catalyzed polycondensation of silicic acid group, leading to the formation of giant silica macromolecules. To reduce the surface energy, a fluoro-containing mixture of perfluoroalkyl methacrylic copolymer and distilled water was coated onto the sphere arrays using a spin coater. The produced surfaces can repel a variety of liquids including sunflower oil, red wine, and coke etc.

![Figure 2.36. Photographs of surface repellency toward different types of liquids, (a) sunflower oil, (b) red wine, (c) dilute juice water, (d) soy sauce, (e) coke, (f) milk, (g) coffee, and (h) water, on silica surfaces.](image)

\(^{125}\)
**Solution-immersion**

Solution-immersion method is a simple way for the fabrication of SO surfaces on various substrates. SH and SO surfaces, including zinc, aluminum, iron, nickel, were prepared through simply immersing these materials into an ethanol solution of perfluorocarboxylic acid at room temperature.\textsuperscript{126,127} This method did not need special rigorous equipment and further surface modification. The rough structures can be controlled by altering the chain length, concentration of perfluorocarboxylic acid and the process time. Ming prepared SO cotton textile with multi-length-scale structures based on the woven structures.\textsuperscript{128} The cotton textiles firstly were coated with a layer of silica particles by subsequent chemical modification. The treated sample was placed into a solution consisting of methanol, 2-propanol, ammonia, and tetraethylorthosilicate.

Scheme 2.10. Schematic Illustration of the procedure for the preparation of dual-size structure onto the surface of woven cotton fibers, combining an *in situ* Stöber reaction with the subsequent adsorption of silica nanoparticles.\textsuperscript{128}
Figure 2.37. SEM images and contact angle profiles of prepared films on different substrates: (a) aluminum plate; (b) nickel plate; (c) Zn–Fe alloy plate; (d) iron plate. Profiles of water and oil droplets are shown in the upper and bottom insets, respectively. The additional inset in (d) is its magnified SEM image.\(^\text{128}\)

Recently, Jiang synthesized a new bi-functional copolymer containing catechol groups and perfluoroalkyl groups by free radical polymerization.\(^\text{127}\) After immersion in the fluorinated polymer solution, self-assembly films were formed on steel, silicon, and glass using catechol groups as multivalent H-bonding anchors. The surfaces exhibited SH and SO properties. This method also can be used to construct SH and SO cotton fabrics after soaking in POSS-based terpolymers solution.\(^\text{128}\)
Scheme 2.11. Synthesis of (HFPO)_{3}MA.

2.3 Literature Review Summary

With the increasing demand for materials with special wettability, designing superoleophobic and superhydrophobic surfaces has attracted a great deal of attention because such surfaces have a wide domain of applications. A variety of artificial self-cleaning superhydrophobic and superoleophobic surfaces have been fabricated using different approaches reviewed above. Cellulose fibers with superoleophobicity and superhydrophobicity were prepared and used in anti-bacteria field. Anti-reflective films with oleophobicity also have been fabricated using dip-coating process. Superoleophobic and superhydrophobic surfaces also have been used to resist heat, chemicals and corrosion. What’s more, SH and SO surfaces have promising applications in antistatic, abrasion resistance, and many other fields.
Although great progress has been made in developing superhydrophobic and superoleophobic surfaces, there are some common issues that need to be solved. First and the largest problem is the aging and decay of the coating. Fabrications are still needed with increased lifetime of the coating, such as fabricating superoleophobic surfaces with self-healing abilities. Secondly, the superoleophobicity and superhydrophobicity can be destroyed by mechanical abrasion. Therefore, methods to fabricate SH and SO surfaces that can endure friction are still needed. What’s more, there is still no easy, cheap and highly productive fabrication method to create SH and SO surfaces based on textile materials.
CHAPTER 3 EXPERIMENTAL

3.1 Materials

Nylon 6,6 film (Mn: 12kD), nylon 6,6 nonwoven fabric (Nonwovens Institute, Raleigh, NC), polyacrylic acid (PAA, Mw: 450kDa, Aldrich), ammonium hydroxide (NH₄OH, Mallinckrodt Chemical, Raleigh, NC), trichloromethylsilane (TCMS, Aldrich), (heptadecafluoro-1, 1, 2, 2-tetrahydrodecyl) trimethoxysilane (C8-FS, Gelest), methanol (Sigma-Aldrich), isopropyl alcohol (Sigma-Aldrich), toluene (Aldrich), deionized water (surface tension $\gamma = 72.8$ mN/m, from NCSU), Kaydol (surface tension $\gamma = 31.0$ mN/m, CBM group, INC. NC), dodecane ($\gamma = 25.35$ mN/m, Sigma-Aldrich, St. Louis, MO), methanol ($\gamma = 22.70$ mN/m, Sigma-Aldrich), heptane ($\gamma = 20.14$ mN/m, Sigma-Aldrich), hexane ($\gamma = 18.43$ mN/m, Sigma-Aldrich) were used as received.

3.2 Grafting of PAA onto non-woven nylon surface

PAA was grafted onto cleaned nylon fabric to increase the density of reactive functional groups (-COOH). In order to remove the grease and other contaminants on the fabric surfaces, the fabric was immersed in isopropyl alcohol and rubbed uniformly with gloved hands every 30 minutes. After 2 hours, the fabrics were dried in an oven at 120°C. Then each fabric was immersed in water and rubbed uniformly by hand for another 2 hours followed by oven drying at 120°C. The cleaned fabrics were immersed for at least 4 hours into a 4g/L aqueous PAA solution. In this process, the fabrics were rubbed by hand to remove the air bubbles so that PAA could be absorbed uniformly. Then the fabrics were cured in an oven at 175°C for several minutes; the curing time depended on the mass of the fabric. Then the fabrics were washed with distilled water three times followed by oven drying at 120°C.
3.3 Grafting nanoparticles onto PAA-grafted nylon surface

A series of trichloromethylsilane anhydrous toluene solutions with different TCMS concentrations was prepared. Then the fabrics were immersed into the prepared solution at room temperature for 2 hours. Next the fabrics were washed using toluene, ethanol, ethanol and DI water mixture (1:1 in volume) and then distilled water in sequence, followed by padding to remove excess solvent and oven cured at 150°C. The sample was labelled as Nylon-PAA-TCMS fabrics. In order to study the impact of gas generation compounds on the surface formed during the process, the NaHCO₃ was used in steady of DI water in the final washing step.

3.4 C8-FS treatment of Nylon-PAA-TCMS fabrics.

The Nylon-PAA-TCMS fabrics were immersed in a solution consisting of 7 wt % C8-FS and 1 wt % NH₄OH in isopropyl alcohol and allowed to be soaked overnight at room temperature. After the excess solution was squeezed out, fabrics were cured in an oven at 150°C. Finally, the fabric was washed twice with isopropyl alcohol in an ultrasonic bath to wash off the physically attached molecules and subsequently dried at 120°C.

3.5. Zein nanoparticles as superhydrophobic coating

Zein was dissolved in 20 mL alcohol aqueous solution with a concentration of 70% in volume. Then 40 mL DI water was added drop by drop to the mixture solution. After formation of the zein nanoparticles, a PET and a nylon nonwoven fabric were dipped into the solution for 5 minutes. Finally, the coated fabric was cured at 130° in an oven for 30 minutes.
3.6. Water contact angle and roll-off angle measurement

The water contact angle on fabricated non-woven fabrics were measured at room temperature using a lab-built goniometer. The images of 10\(\mu\)L liquid droplets on the prepared surface were obtained using a digital camera (Canon EOS EF-S 18-55IS). The contact angle values were obtained from at least three measurements at different locations.

The roll-off angle of 50\(\mu\)L water droplet was measured by placing a specimen on a level platform mounted on a Newport 495 rotation stage and inclining the specimen. The stage was rotated and the angle of the stage was recorded when each droplet rolled off. The values of roll-off angle were measured three times using different spots for each sample.

3.7. Martindale Abrasion.

Martindale abrasion test was performed using a commercial Martindale abrasion tester following Standard ASTM D4966. The fabric samples were mounted on a dynamic disk which was brought into contact with an abradant underneath. The abradant was mounted on a separate motionless disk. Pressure was applied by adding weights onto the upper shaft. During testing, the dynamic disk was rotated on its axis, at the same time following a circular path across the abradant surface. Heal’s Martindale abradant wool fabric was used as the abradant. During the test, 12 kpa loading pressure was employed, which is often used to evaluate coated fabrics for heavy duty upholstery usages.

3.8 Other characterization.

3.8.1. Scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDX)

The nontreated and treated nylon surfaces were examined with scanning electron microscope, Hitachi S-3200N and Verios, operated at 2kV with magnification from 25x to 20,000. The surface roughness and morphology change can be obtained through the analysis of SEM images. The Energy-dispersive X-ray spectroscopy (EDX) was used to examine the distribution of the elements.
3.8.2. Air Permeability: Air permeability was examined by using an FX 3300 air permeability tester according to ASTM D737-96 standard test method. All air permeability values reported represent the mean of ten measurements.

3.8.3. Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) was used to determine the chemical structure change of the treated and untreated nylon fabrics.
Nylon, PET and cotton fabrics are well known to possess hydrophilicity due to the existence of polar functional groups. To form an anti-wetting fabric surface based on these materials, a coating leading to low surface tension rough surfaces is needed. Take nylon as an example. Firstly, PAA was used to chemically treat the nylon surface to increase the density of reactive functional groups. Then TCMS was used to provide a low surface tension surface composed of nanoparticles, which can provide nanoscale roughness. Finally, perfluorosilane was used to further decrease the surface tension of the surface, making it superhydrophobic and even superoleophobic. A water droplet easily rolled off from the surface at a low tilting angle.

4.1. TCMS treatment

Nylon 6,6 surface has a large surface tension (40.8 mN/m) making it easily wetted by water and oils. The treatment of the nylon 6,6 surface is hindered by the limited number of reactive sites. Therefore, before performing TCMS treatment, nylon fabrics were treated with PAA to increase the reactive functional groups (–COOH) using a modified method developed by Michielsen’s group. During the treatment, the –COOH groups were attached to the nylon 6,6 through the condensation reaction between –NH₂ at the end of the nylon 6,6 chains and –COOH groups from PAA. According to their study, the PAA thickness formed is around 10nm. Due to the higher polarity after PAA treatment, the fabric became more easily wetted.

To fabricate textile surfaces with robust superhydrophobicity, low surface tension and high degree of surface roughness with multi-scale structures are needed. In this study, a simple, commercially available silane, trichloromethyl silane, was used. Because of the product of the polymerization reaction of trichloromethyl silane catalyzed by water is not soluble in water, polymer micro/nano structures can be produced in large amounts of water. First, TCMS was dissolved into toluene. After being immersed into the TCMS and toluene mixture solution, the fabrics and film were wetted because of the low surface tension
of the TCMS/toluene liquid. When the samples were removed from the solution, there was a solution layer containing TCMS formed on each sample. The concentrations of the TCMS in these layers were the same as the bulk system. When the samples were washed using water, the condensation reactions of TCMS with water, substrates and TCMS itself took place at the same time, leading to nanoparticles chemically attached. After air drying at room temperature, the samples were cured in an oven at 130 °C. The superhydrophobicity can be controlled via varying different reaction conditions, such as TCMS concentration in toluene solution, the immersion time in water during washing step, ultrasonication and adding gas generation agents.

SEM images can provide the morphological information of the non-woven nylon surface before and after coating. Without coating, the surfaces of nylon fibers were smooth. However coated fibers had very rough surfaces caused by the nanoparticles formed during the treatment. The nylon fibers can provide the micro-size roughness. What’s more, the nanoparticles along the fibers formed the hierarchical structure. The morphology of the surface was quite similar with the lotus leaves.

After treatment under the optimum conditions, the hydrophilic nylon fabrics were successfully converted to superhydrophobic ones, which showed significant improvement in repelling water. As shown in Figure 4.1a and b, water wets a nonwoven surface immediately because of the high surface tension of the nylon surface and the hydrogen bonding between the substrates and the water. After coating, water droplets can sit on the top of the surface as a sphere with a contact angle larger than 150°. The contact angle hysteresis of the coated surface was also studied by measuring the water roll-off angles. For the most superhydrophobic sample, the contact angle was so small that it was very challenging to place water onto the surfaces. To show the excellent water repellency, a water droplet was placed on the treated non-woven nylon fabric. The contact angle change with time was recorded. It was observed that the water contact angles on the surfaces showed no change with time. To show the robustness of the prepared surface, a water droplet (30 µL, 0.03g) was dropped onto the surface from 10 cm height. The water droplet bounced off
the treated surface, leaving the surface completely dry. Furthermore, a treated non-woven nylon fabric was immersed in water, but remains dry for several days.

Figure 4. 1. a) The mechanism of the treatment; b) the SEM image of untreated nonwoven nylon fabric and a piece of fabric wetted by water; c) the SEM image of treated non-woven nylon fabric and a spherical water droplet on treated nonwoven nylon fabric.

4.1.1. Effect of parameters

TCMS concentration in toluene solution

To illustrate the effect of TCMS concentration in toluene solution on the superhydrophobicity of fabricated nonwoven nylon surfaces, a series of toluene and TCMS mixture solutions containing different concentration of TCMS were prepared, including 0.01 wt%, 0.25 wt%, 0.5wt%, 0.75wt% and 1wt%. The results showed that 1.0 wt% is the best concentration choice when other factors were fixed. When TCMS concentration was too low, the fabric surfaces were only partly covered by nanoparticles and low surface tension materials, leading to low water contact angle. When the TCMS concentration was too high, one thick and relatively flat coating layer was formed, making water contact angle drop dramatically. When the TCMS concentration was 1.0 wt%, the fabricated sample showed the highest water contact angle. According to the SEM images of produced fabrics,
the one treated with 1.0 wt% showed the highest coverage and uniform distribution of formed nanoparticles.

![Graphs showing water contact angle and roll-off angle vs. TCMS concentration](image)

**Figure 4.2.** The relationship between TCMS concentration in toluene solution with (a) water contact angle and (b) water roll-off angle.

![SEM images of non-woven nylon fabrics](image)

**Figure 4.3.** SEM images of non-woven nylon fabrics treated with different concentrations of TCMS. a) 0.25wt%; b) 0.5wt%; c) 0.75wt%; d) 1.0wt%.

**Immersion time**

The immersion time of fabric in TCMS toluene mixture solution is another critical factor that can affect the wettability of the treated fabrics. The relationship between water contact angles of treated
fabrics with immersion time is shown in Figure 5. When the immersion time increased from 0-2 hours, the WCAs increase. Because longer immersion time would increase the number of TCMS molecules adsorbed onto the nylon surface. When the immersion time was between 2 to 4 hours, the WCAs were the largest. When the immersion time was larger than 8 hours, the water contact angles decreased dramatically. The reason may be that too long immersion time resulted in too many TCMS molecules adsorbed around the nylon fabric surface. When the fabric was washed with water, most of the reaction took place before the water reacted with the nylon surface to condense with the TCMS molecules adsorbed onto the nylon surface.

Figure 4. The relationship between immersion time of nylon fabric in toluene/TCMS solution with water contact angles on the treated non-woven nylon fabric.

The addition of NaHCO$_3$ in washing step

The addition of NaHCO$_3$ also showed tremendous effects on the morphology and the wettability of the prepared fabric. NaHCO$_3$ was dissolved in DI water at a concentration of 1g/100mL and used to replace pure DI water to wash the fabric that was immersed into toluene solution containing TCMS 1 wt%, followed by oven curing at 130°C. The prepared non-woven fabric showed increased water contact angle, even though the roll-off angle had no obvious change. Also the fabric was able to endure more cycles of abrasion in
Martindale abrasion test. The reason may be that NaHCO₃ can decompose at 70°C. During the curing process at 130°C, the gas generated by the decomposition of NaHCO₃ would have some influence on the formation of the coating by generating regular nano-scale wrinkle structure as shown by the SEM images. Through the SEM images of TCMS coating, when NaHCO₃ was used, we can see a rough surface containing nanoparticles distributed along and between the wrinkle structures. The multi-scale structure played a critical role in increasing the water contact angle and abrasion durability.

![SEM images of TCMS coating](image)

Figure 4. 5. SEM images of TCMS coating when NaHCO₃ was used during washing procedures. Compared the fabrics without NaHCO₃, the surface possess winkles everywhere along the fibers. These winkles can increase the surface roughness further.

4.1.2. Abrasion stability test.

Abrasion stability is a critical requirement for the coating to be applied commercially. Most existing methods to create superhydrophobic textiles have low mechanical durability. Two strategies were used in this study to increase the abrasion stability. The first one is introducing chemical bonds between the coating and fabric substrate. The other one is to create multi-scale structures. Martindale abrasion test was used to indicate the abrasion durability of the fabricated superhydrophobic surface under a load of 12 kPa using Heal’s Martindale abradant wool fabric as abradant. The change of water contact angle with abrasion cycles was recorded.
For the samples treated with 1.0 wt% TCMS and using NaHCO3 during wash step, their superhydrophobicity persisted without changing water contact angle and roll-off angle to 2000 abrasion cycles. From 2000 to 5000 cycles, the water roll-off angle increased with more abrasion cycles, even though the water contact angle did not change much. The water droplet was still in Cassie-Baxter state, which was stable with time. From 5000 to 15,000 cycles of abrasion, the water contact angles remained larger than 160° when the water droplets were dropped onto the surface. However, the roll-off angle increased with more cycles of abrasion. What’s more, the droplets became unstable on the treated nylon surface. A droplet placed onto the nylon surface with 2000 cycles of abrasion would stay for a long time period until the evaporation off of the droplet. However, after 5000 cycles, the contact angle of the droplet decreased and would wet the nylon surface after a period of time. The time period in which the droplet would wet the surface continued to decrease with more abrasion cycles. If the sample was treated only with TCMS and without NaHCO3 in washing step, the roll-off angle began to increase even before 2000 cycles’ abrasion. The nylon fiber surfaces still possessed enough nano-scale roughness after 2000 cycles to keep the water contact angle and roll-off unchanged. While after 2000 cycles’ of abrasion, the nano-roughness was lost more and more with the increasing abrasion cycles, leading to the increasing of roll-off angle and transition from Cassie-Baxter states to Wenzel states. Compared with the sample produced without using NaHCO3, the nano-scale wrinkle structure can slow down the destroying of the superhydrophobicity by possessing multi-scale structure.
Figure 4.6. a) water contact angle change with increasing abrasion cycles; b) water roll-off change with the increasing abrasion cycles; c) the time dependency of water contact angle on treated nylon fabrics with different abrasion cycles; d) the SEM images and EDS spectrum for the whole image of treated nylon fabric after 2000 cycles’ abrasion.

4.1.3. Base/acid durability test

Nylon fabric can be easily destroyed by strong acid and base. When strong acid and base droplets were placed on the treated fabrics, both of the droplets remain on the top surface with nearly spherical shape. For longer time (>20mins), the contact angles for strong acid and base liquid had no obvious changes. To study the acid and base durability further, two pieces of prepared nonwoven nylon fabrics were immersed into strong acid (H2SO4) with pH value of 1 and strong base (NaOH) with a pH of 14 for a period of time separately by external forces. Neither acid nor
base solutions wet the treated non-woven nylon fabric. A bright reflection layer was formed on the fabric surface, showing the existence of trapped air. After releasing the external forces, both fabrics floated to solution top surface, even though the fabric had larger density than acid and base solutions. Then the two fabrics were left on the top surfaces of base and acid solutions separately for extended time. After around one hour, the fabric in strong base solution began to be wetted and dropped to the bottom of the solution. However, the fabric was restored to its superhydrophobicity after water rinsing, air dry and oven dry at 130 °C. While the fabric in strong acid solution remained dry after 1 day and night. When the fabric was taken out from the acid solution, the fabric surface contacting with the solution began to be wetted and the surface exposed to air still remained superhydrophobic. Both surfaces of the fabric restored their superhydrophobicity after water rinsing, air dry and oven dry at 130 °C. For comparison, two non-treated nylon fabrics were immersed into strong acid and base solutions. Both fabrics were wetted and dropped to the bottom immediately.
4.1.4 Long Term stability

Aging is a common problem that limits the life time of superhydrophobic coatings. To investigate the long term stability of the prepared non-woven fabrics, the water contact angle was monitored for a long period of time. Two fabrics using different storage methods were tested. The first sample was stored in a sealed plastic bag and the other one was stored open to air under lab conditions. After 1 year, both fabrics still kept the superhydrophobicity. Therefore, this method can prepare superhydrophobic nonwoven nylon fabrics with long life time (Figure 4.8.).
4.2. Modification of C8-FS treatment

After TCMS treatment, the TCMS-PAA-nylon surface exhibited superhydrophobicity and oleophobicity for some oils, such as Kaydol. To repel oils with very low-surface tension, C8-FS was attached to the surface by its condensation reaction with itself and the incompletely condensed -OH and –COOH groups remaining after TCMS treatment. C8-FS was dissolved in isopropyl alcohol solution with a concentration of 7 wt%. Ammonium hydroxide was added into the solution as a catalyst. After C8-FS treatment, nano-size particles were covered by a smooth low surface tension polymer layer.

After coating, as shown in Figure 4.9, the non-woven nylon fabric exhibited a considerable increase in its ability to repel water and super-low tension oils, such as dodecane, methanol and even heptane. Water, methanol and heptane droplets formed round balls on treated nylon surface
with a contact angle of 178.0º(±2º), 152.0º(±1º), and 148.0º(±2º), respectively. These results indicate that FS-TCMS-PAA-nylon surface is superamphiphobic. The contact angle hysteresis of the coated fabric was also studied by measuring the roll-off angles of test liquids. The roll-off angle for water was so small that it was quite challenging to put the water droplet onto the surface. For oils, the roll-off angle increased with decreasing surface tension.

![Chemical formulas and mechanism diagram](image)

Figure 4. 9. The chemical formula of a) TCMS and b) FS. c) The mechanism of forming rough low surface tension surfaces.

To demonstrate the excellent liquid repellency of the coated fabric, water, Kaydol, dodecane, methanol and heptane droplets were placed and left on the surface for extended periods of time. The contact angle change with time was recorded, which is shown in Figure 2C. It was observed that the contact angles for water and dodecane had no significant change with time until the droplets evaporated completely. For methanol, the contact angle had no change for the first 6 minutes and then decreased slowly with time until droplets evaporated completely after 12 minutes. However, the contact angles for heptane and hexane droplets decreased with time down
to around 90° before evaporation. The super-repellency was also examined by immersing the coated fabric in test liquids for certain period of time. The coated fabric immersed in water by force remained dry for many days. When the force was released, the fabric would float to water surface immediately. In dodecane, the fabric was wetted after 20 minutes. However, the repellency was restored after it was allowed to dry at room temperature or oven dried.

![Figure 4.](image)

**Figure 4.** 10. (a) Dependency of contact angle on the surface tension of the liquids. (b) Dependency of roll-off angle on the surface tension of the liquids. (c) The time dependence of contact angles of water, dodecane, and methanol on fabricated fabric surfaces with time. (10μL droplet)

It is well-known that that low surface energy, multi-scale roughness and re-entrant surface structure are important in creating a non-wetting surface. The morphology and chemical composition of coated non-woven nylon fabric are shown in Figure 4.11. SEM images can provide the morphological information of the non-woven nylon surface before and after coating. Without coating, the surfaces of nylon fibers were smooth. However coated fibers had very rough surfaces caused by the nanoparticles formed during the treatment. The nylon fibers can provid micro-size roughness, therefore a surface structure with multi-scale roughness was formed after the treatment. EDX gave detailed information about the distribution of elements along the fibers. Based on the EDX images, fluorine atoms were distributed uniformly across the whole fabric surfaces. Before
coating, there were no F atoms and Si atoms along the nylon fiber surfaces. C and O are the two main elements of the original fiber. After TCMS/FS treatments, the atomic percentage of F atoms can reach more than 16% and the content of Si became much greater. The EDX result confirmed that the fabric was covered with fluoroalkyl groups after the coating process.

![SEM images](image)

Figure 4. 11. SEM images of a) coated fabric surface; b) uncoated fabric surface; c) SEM image of sample treated only with C8-FS; d) methanol (red), water (blue) and heptane (clear) droplet on uncoated surface (top row) and on uncoated surface (bottom row).

According to Tuteja’s study, optimal superoleophobic surfaces require both $D^{*} \gg 1$ and $A^{*} \gg 1.21$. From the parameters measured from SEM images, both $D^{*}$ and $A^{*}$ can be calculated. The average value of $D$ is about 6 times $R$. Therefore, $D^{*} \sim 7 \gg 1$. To calculate the value of $A^{*}$, dodecane was used as an example.
\[
D_{cylinder}^* = \frac{R + D}{R}
\]

Equation 1

\[
A_{cylinder}^* = \frac{l_{cap}}{R(D_{cylinder} - 1)} \frac{(1 - \cos \theta)}{(D_{cylinder} - 1 + 2 \sin \theta)}
\]

Equation 2

The measurement of Young’s contact angle on a fluorinated nylon film surface using FS(C-8) showed that \( \theta_e \) for dodecane is 75º. For the fiber, \( R = 10 \) μm; \( D \) is around 60 μm. So \( A \) for dodecane is around 4.6, which is higher than 1. Therefore, the fabricated surface is a robust superamphiphobic surface according to these two parameters.

To illustrate the function of TCMS, a nylon fabric treated only with C8-FS was prepared using the same conditions and procedures. The fabric treated only with C8-FS showed smaller contact angles and higher roll-off angles for test liquids. The contact angle for dodecane on such a coated surface decreased dramatically with time, which showed that the droplet was not in Cassie-Baxter state. According to the SEM images, the C8-FS treated nylon showed smooth fiber surfaces.

4.2.2 Mechanical stability

Martindale abrasion test was used to test the mechanical durability of the fabrics under a load of 12 kPa using Heal’s Martindale abradant wool fabric as abradant. The change in liquid repellency with abrasion cycles is shown in Figure 4.12. After the first 5000 abrasion cycles, the water contact angle on the fabric did not change. Interestingly, the contact angles for dodecane and methanol increased to 163º and 156º respectively. The roughness of the fibers was only slightly decreased but some pills were formed on the fabric surface because of the abrasion. This increased the
roughness factor of the fabric surface resulting to increased contact angles for dodecane and methanol. After 5000 cycles, both the roughness and nanoparticles along the fibers decreased because of the abrasion. Even though the water contact angle still showed little change, the contact angle for dodecane reduced to 151º and the contact angle for methanol was reduced even more. The roll-off angle was affected by the abrasion greatly due to the loss of nanoparticles and low-surface tension coating because of the abrasion.

The SEM images and EDX spectrum (Figure 4.12) showed the change of the coating during abrasion. The EDX spectrum showed that there is good coverage by F atoms on the coated fabric surface before abrasion with an atomic percentage of 18.1%. After 5000 cycles of abrasion, the F content on the surface reduced to 16%, while the roughness of the fibers was still high. After 15000 cycles of abrasion, the F atoms content on the surface reduced to 5.2% because of the loss of the coating material due to the abrasion. However the F-atom content was still high enough to be an oleophobic surface. Meanwhile, the nanoparticles on the fibers surface were destroyed, which reduced the contact angles and increased roll-off angles. However, even after 15000 abrasion cycles, the fibers on the fabric surface still possessed some nanoparticles. What’s more, the multi-scale roughness of the fibers inside the fabric still existed, preventing the low surface tension liquid from wetting the surface. The coating also exhibited some ability to heal. After heating the abraded sample at 130ºC, the surface attempted to take the lowest free energy state by moving more F atoms to the surface, which can be verified by the EDX spectrum. The F atom percentage increased to 7%, as shown in Figure 4.13.
Figure 4. 12. a) The change of contact angle for water, dodecane, and methanol on coated nylon surface with abrasion cycles using Martindale Abrasion tester; b) the visual surface of the coated fabric and that after 5000 cycles of abrasion; c) the SEM images of fibers in the coated fabric and that after 15000 cycles of abrasion; d) EDX spectrum of coated fabric; e) EDX spectrum of coated fabric after 15000 cycles of abrasion.

Figure 4. 13. The EDX spectrum of non-woven nylon fabric after 15000 cycles abrasion followed by heating at 130°C.
4.3. Transform Hydrophilic cellulose-based materials to Superamphiphobic Surfaces

Most cellulose-based materials are hydrophilic materials because of the abundant surface polar functional groups. To perform superhydrophobic modification of the cellulose fiber surface, TCMS was utilized to form various nano structures. The hydrolysis and condensation reactions of TCMS formed the strong acid HCl, which can destroy cellulose-based fabrics at high temperature. It was shown during the experiments, room temperature was sufficient for formation of SH coating in this study. The wettability of the treated surfaces, including sticky or roll-off SH surface, can be controlled by the formation of different nano morphologies, including flat coatings with a small amount of nanoparticles, nanoparticles and nanofilaments. After TCMS modification, hydrophilic cellulose-based materials became superhydrophobic and also oleophilic, which can be used to separate oil/water mixtures.

Briefly, filter papers and cotton fabrics were immersed into the TCMS/toluene solution. The low surface tension of solution permits the TCMS to penetrate into the paper fiber network. After 10 minutes immersion, the filter papers were rinsed twice with water, followed by air drying at room temperature. To study the influence of repeated treatment times on the wettability of the coated surfaces, the coating procedure was repeated twice and three times. After coating, the wettability of the surfaces by water was characterized by measuring the WCA and water roll-off angle, which can illustrate the static and dynamic behavior of water droplets on the surfaces.

After treatment, the filter paper showed considerable increase in water repellency. While changing treatment conditions resulted in different wetting behaviors of water droplets on coated surfaces because of the various nanostructures formed. The concentration of the TCMS in coating solution
had an influence on the surface energy. Different concentrations led to different coverage, leading to different surface tension values of the substrates. From Figure 4.14b, the optimal TCMS concentration was 0.25wt% for getting larger WCAs. Because different substrates composed of different materials have various abilities to adsorb the toluene/TCMS mixture solution, the optimal TCMS concentration for them may not be the same.

Figure 4. 14. The continuous procedure to transform hydrophilic cellulose-based materials to SH surfaces. b) The dependence of water contact angle on TCMS concentration. c) Water wets the non-treated filter paper d) A water droplet on SH filter paper surface with a spherical shape.

All samples treated with one, two and three times using TCMS showed large contact angles to water, but for samples treated only once, the water droplet on the coated surface did not roll-off easily with a sliding angle larger than 90° as shown in Figure 4.15. Surfaces exhibiting this behavior is referred to as sticky SH surfaces. The SEM images showed that only a flat coating with a small amount of nanoparticles formed, as shown in Figure 4.16a, b. When the filter paper was treated twice with TCMS under the optimal conditions, water contact angle did not show obvious
change. However the roll-off angle of a water droplet decreased dramatically to 3° (±1). It is well known that multi-scale roughness plays an important role in enhancing the superhydrophobicity by increasing the contact angle and reducing the contact angle hysteresis. From the SEM images of the twice TCMS treated filter paper, uniformly distributed nanoparticles are attached to the microscaled fibers, forming multiscale structures along the fabric. When a water droplet (~ 0.03g) dropped onto the coated surface within 5 cm, the water droplet bounced off. When the filter paper was treated three times with TCMS under the optimal conditions, the water contact angle and roll-off angle had no obvious changes compared with the one treated twice with TCMS. However, the droplet dropped onto the coated surface within 8 cm bounced off from the surface without penetrating, which showed higher degree of robustness due to the formation of nanofilaments as shown by SEM images (4.16).

Figure 4. 15. Water roll-off angles on samples with different repeated TCMS treatment times.
In order to prove the differences in wettability between samples treated with different number of treatment cycles, a water droplet (100 µL) was placed onto each sample. The WCAs were recorded with time (Figure 4.17). There was no change with WCAs for all three samples, even for the sticky superhydrophobic one. However, when all the samples were immersed into water, the sample treated with TCMS twice and three times remained dry for longer time. This can be explained by the discrepant wetting models. With a relatively flat coating, the droplet on its surface took a stable Wenzel state, leading to large contact angle and roll-off angle at the same time. For 2xTCMS sample, the nanoparticles along the fibers reduced the solid-liquid area fraction dramatically. The water droplets on it would form a stable Cassie-Baxter state.

Figure 4.16. SEM images of coated filter papers with TCMS once (a, b), twice (c, d) and three times (e, f).
For 3xTCMS sample, the nanofilaments created pores, which reduced the solid-liquid area fraction and increased the robustness factor further.

![Graph](image)

Figure 4. 17. a. The WCA dependence on time when a water droplet was placed on the coated surfaces; b. The air layer formed when the cotton fabric treated with TCMS twice was immersed into water.

Although the samples treated twice and three times with TCMS possessed similar superhydophobicity, they showed different physical properties, such as air permeability. According to the results shown in Table 4.1, the fabrics treated once and twice with TCMS did not have significant influence on the air permeability. While the air permeability of the fabric treated with TCMS for three times showed a dramatic decrease compared to the original cotton fabric. For the samples treated once and twice with TCMS, the coating was on the fiber but not on the fabric scale. However, the nanofilaments formed on the fabric treated three times with TCMS blocked some gaps of the fabric, leading to the decrease in air permeability.
Table 4.1. The water contact angles, roll-off angles and air permeability comparison of untreated cotton fabric and treated cotton fabrics with different repeated times of TCMS.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Untreated</th>
<th>1xTCMS</th>
<th>2xTCMS</th>
<th>3xTCMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>WCAs(10μL)</td>
<td>0º</td>
<td>171º(±2º)</td>
<td>174º(±2º)</td>
<td>175º(±2º)</td>
</tr>
<tr>
<td>Roll-off angle (50 μL)</td>
<td>NA</td>
<td>&gt;90 º</td>
<td>3º(±1)</td>
<td>2 º(±1)</td>
</tr>
<tr>
<td>Air Permeability (ft^3)/(min/(ft^2))</td>
<td>77.1</td>
<td>76.6</td>
<td>76.1</td>
<td>62.6</td>
</tr>
</tbody>
</table>

Note: 1 (ft^3)/(min/(ft^2))=4.38 x 10^-5 m^3/s

Figure 4.18. The XPS spectrum of cleaned filter paper and 2xTCMS treated filter paper.

The chemical components of the coating layer were characterized by XPS, which is shown in Figure 4.18. The uncoated filter paper surface only possesses C and O. However, the treated filter paper shows Si peaks. What’s more, the percentage of O atoms increased dramatically,
while the percentage of C atoms dropped. The comparison between treated and untreated filter papers illustrates the existence of condensation reaction.

**Coating stability**

The coated fabric and filter paper have high durability to strong base, strong acid, and organic solvent, which is shown in Figure 4.19. When a strong acid (H$_3$NO$_3$) droplet with a pH value 1 was placed on the treated cotton fabric and filter paper surfaces, the acid droplet remained on the top surfaces with a spherical shape. For longer time, the contact angles had no change and the droplets fall off the surfaces when the fabric or filter paper were tilted slightly. When a strong base (NaOH aqueous solution) droplet with a pH value 14 was placed on the treated cotton fabric and filter paper surfaces, the same behavior was observed. When a piece of coated fabric was immersed into the strong acid or base solutions and held there with tweezers, a bright reflection layer was formed on the fabric surface, showing the existence of trapped air. After releasing the fabric or paper, the fabric and filter paper floated to top of the solution. When the coated fabric and filter paper were immersed into methanol solution, both the fabric and filter paper were wetted because of the low surface tension of methanol. However, the samples restored their superhydrophobicity after drying at room temperature, which illustrated the solvent stability of the coating.
Figure 4.19. The figures of NaOH droplets on TCMS treated cotton fabric (a), filter paper (b), an acid droplet on TCMS treated cotton fabric (c) and filter paper (d). Both the fabric and filter paper were treated twice with TCMS.

**Water/Oil separation**

The coating of the filter paper and cotton fabric with trichloromethylsilane resulted in the changes of their wettability. As shown in Figure 4.20, the uncoated filter papers are superhydrophilic and superoleophilic. However, the coated filter paper is superhydrophobic and superoleophilic and can only be wetted by low surface tension oils. When hexadecane droplets were dropped onto a TCMS coated filter paper surface, the filter paper was wetted immediately. However, the water droplet exhibited large contact angles and small roll-off angles, which is very promising as materials that can be used for water/oil separation. To compare with the TCMS treated samples, a hexadecane droplet was placed on the untreated cotton fabric and it wetted the fabric immediately too. But a water droplet on the hexadecane wetted spot had a quite small water contact angle.

When a mixture of water and hexadecane was poured onto the coated filter paper, the oil quickly penetrated through the filter paper while the water colored with blue dye collected on the surface of the filter paper. After each oil/water separation experiment, filter paper was dried and the water contact angle on the surface restored to 170°. Therefore, the repeatedly wetting by oil had no
influence on the wettability of the coated filter paper, which is an important factor for practical applications.

![Images of droplets on fabrics](image)

Figure 4. 20. A hexadecane droplet on TCMS treated woven cotton fabric; b) a water droplet on the TCMS treated woven cotton fabric wetted by hexadecane; c) a hexadecane droplet on untreated woven cotton fabric; d) a water droplet on the untreated woven cotton fabric wetted by hexadecane; e) the separation of water from water/hexadecane mixture solution.

Although the samples treated with TCMS are superhydrophobic, they can easily be wetted by low-surface-tension liquids, such as dodecane. To modify the superhydrophobic samples to superamphiphobic further, perfluorosilane can be utilized. In this research, (heptadecafluoro-1, 1, 2, 2-tetrahydrodecyl) trimethoxysilane was used. The fluoroalkyl long chain provides the low surface energy to the coated surfaces. After modification with (heptadecafluoro-1, 1, 2, 2-tetrahydrodecyl) trimethoxysilane, samples showed superhydrophobicity and superoleophobicity spontaneously, characterized by large contact angles of dodecane, which is shown in Figure 4.21.
4.4. Zein nanoparticles as superhydrophobic and oleophobic coating

Natural polymers are renewable, biodegradable and inexpensive. Most natural polymers are hydrophilic and water absorbing. However, Zein, a major protein of corn, is an amphiphilic, possessing both hydrophobic and hydrophilic properties. Many applications of zein are related to its self-assembly ability. For instance, evaporation-induced self-assembly results in microspheres, packed spheres, and films, depending on zein concentration and the ethanol-water ratio of the solvent. Zein is classified as prolamine because it is insoluble in water and only soluble in 40-90% aqueous alcohol. Therefore, the dissolution and precipitation can be controlled by varying the concentration of alcohol aqueous solution. Zein and zein-based coatings have been used in various industrial applications, for example paper coating for glossy magazine covers, grease-proof paper, floor coatings, biodegradable films and plastics, and microspheres to control the drug release. However, as far as we know there is no report on the developing superhydrophobic and oleophobic coating using zein particles.

Robust, superhydrophobic, and self-cleaning textile fabrics were fabricated via nanoprecipitation of zein. Fabrics were coated with zein nanoparticles through a simple dipping process. Poor wear resistance is a common problem with superhydrophobic coating, limiting the large-scale utilization
of superhydrophobic coating. The conventional strategy employed to improve the durability of coating involves crosslinking the coating layer, establishing chemically covalent bonding between coating and substrates, and creating multi-scale roughness. Inspired by the fact that cross-linking reaction will happen when zein is heated to 130°, the zein coated fabrics were heated to 130° to form a cross-linked coating to endure mechanical abrasion. This heating induced cross-linking process can avoid the usage of toxic crosslinking agents.

We developed a facile coating process by using the nanoprecipitation of zein to fabricate superhydrophobic textile surfaces. The optimal condition was studied by varying parameters, such as the concentration of zein in alcohol aqueous solution, the composition of the alcohol aqueous solution, and the number of repeats of the treatment. The formed coating was characterized using SEM and XPS to illustrate the morphology and chemistry of the coated surface. The cross-linked coating had strong durability to strong acid/base, abrasion and organic solvents.

![Figure 4.22. The scheme of superhydrophobic zein coating process](image)

**Effect of Zein concentration**

To illustrate the effect of zein concentration on the wettability of the coated fabrics, a series of zein solutions with concentrations 0.25, 0.5, 0.75, 1.0 and 2.0 mg/mL in ethanol (70% volume) and DI (30% volume) water mixture. The WCAs and roll-off angles were measured and shown in Figure 4.23. The fabric treated with 0.25 mg/mL zein solution showed a small improvement in
hydrophobicity compared to original one. However the water droplets wetted the fabric surface immediately. For all the other 4 selected concentrations, the treated fabrics showed superhydrophobicity with contact angles as 149.9°, 168.5°, 155.1°, and 145.6° from 0.5 mg/mL to 3.0 mg/mL. The maximum WCA appeared when the zein concentration was 0.75 mg/mL. The differences on the superhydrophobicity can be explained by the surface chemistry and surface roughness of the formed zein coating.

![Graph](image.png)

Figure 4.23. The dependence of water contact angle and roll off angle.

### 4.5. 3D Light-Weight Porous Superamphiphobic Bulk Material with Coral Structure

We utilized heptadecafluoros-1,1,2,2-tetrahydrodecyl) trimethoxysilane (FAS) and 3-aminopropyl triethoxysilane (APTES) to fabricated a 3D rigid and low density foam-like material with superamphiphobicity. The process contains several steps, as shown in Figure 2 a. Firstly, silica covered with siloxane network was formed by the co-hydrolysis of tetraethyl orthosilicate (TEOS), FAS and APTES under basic conditions in ethanol. Then PAA aqueous
solution was added into the system, followed by curing in an oven. After the evaporation of the solvent, material with bulk superamphiphobicity was formed. The long fluoroalkyl chain on FAS provided the low surface tension. The polysiloxane networks and the chemical bonds formed between amino, carboxyl group and PAA as a binder provided the rigid structure of the material. The fabricated materials showed super wetting repellency against water, polar liquids with low surface tension (acetone and methanol), and nonpolar oils with low surface tension (dodecane and octane) without any post modification.

![Chemical formula of FAS and APTES](image)

Figure 4. 24. Chemical formula of FAS and APTES

As shown in Figure 4.25, not only all the surfaces of the material but also the body part cannot be wetted by the water (dyed blue), dodecane (clear) and methanol droplets (dyed red) because of the inherent superamphiphobicity. All the droplets stayed on the top of the contacting surface with a spherical shape. Because of the high roughness of the surface, contact angles were difficult to measure accurately. In the report, roll-off angles and residues are good indications of anti-wetting properties. The roll-off angle for water and dodecane were less than 2° and no residue was left on the material after the sliding of droplets. Methanol droplet had a relative large roll off angle (around 5°) but no residue was observed.
Figure 4.25. a) the scheme of the process to fabricate material with bulk superamphiphobicity; b-d) water, dodecane and methanol droplets on the fabricated superamphiphobic material; e) a methanol droplet on exposed surface after abrasion.

The SEM image, shown in Figure 4.26 (a) and (b), indicated that the prepared superamphiphobic material possessed multi-scale roughness and a highly porous structure, which can form Cassie-Baxter state when a droplet was placed on it. The EDX spectrum showed the existence of a large amount of F (24.77%) and Si (30.03%) besides O, N and C elements. The high concentration of fluorine, combined with the re-entrant structure and multi-scale roughness, results in the bulk material showing intrinsic superamphiphobicity. What’s more, to identify the chemical composition of the material, Fourier Transform Infrared Spectrum (FT-IR) was also used to characterize the sample, as shown in Figure 4.26 (d). The peaks of 1069 and 800 cm\(^{-1}\) correspond to the asymmetric and symmetric vibration of Si-O-Si respectively. Peaks at 1202 and 1145 cm\(^{-1}\) are the characteristic of C-F stretching vibrations. The broad peak around 3300 cm\(^{-1}\) indicates the N-H stretching. The existence of \(-\text{CONH}-\) was proved by the peak around 1636 cm\(^{-1}\).
To indicate the stability of the liquid repellency, the water, dodecane and methanol droplets were left on the surface of the produced superamphiphobic material for a period of time. All the liquid droplets maintained their spherical shapes well on the surface, including the exposed surface after damaging of the surfaces. The roll off angle for liquids had no change and no residue on the material was observed after the drops rolled off. To further prove the excellent repellency, the porous foam produced was completely immersed in a clear water fluid and the wettability was observed. Without an external force, the bulk material kept floating on the water surface. An external force was needed to immerse the superamphiphobic material into water. The material kept dry with the superamphiphobic ability maintained after 2 weeks. This can be explained by the existence of air gap formed between water and superamphiphobic material, which resulted in the mirror-like phenomenon at the surface of bulk material immersed in water. In comparison, the bulk superamphiphobic material was immersed into dodecane and methanol solution separately.
Without external force, the foam also floated on the fluid surface without being wetted. When the material was immersed into dodecane, it remained dry after 2 days and the mirror-like phenomena was observed also. The one immersed in methanol was attached by some small droplets. However, after the evaporation of methanol, the superamphiphobicity was restored. Although the red color was left on the surface of the material after drying, the water (blue), dodecane (clear) and methanol (red) droplets stayed on its surface with spherical shapes, shown by Figure 4.27(f). According to the calculation based on the measurement of volume and weight, the prepared superamphiphobic material had a density of 0.87g/mL, which is smaller than the density of water but larger than methanol’s density. However, it would float on the methanol fluid surface, which also indicated its super anti-wetting property to methanol.

![Figure 4.27](image)

Figure 4. 27. Superamphiphobic material was immersed in water (a) and dodecane (b) with an external force; Superamphiphobic material floated on the surfaces of water (c), dodecane (d) and methanol (e); the sample taken out from methanol after 1 hour of immersion and the droplets of water (blue), dodecane (clear) and methanol (red) on the dried sample wetted by methanol during immersion.
The produced superamphiphobic foam was very stable in strong acid and base solutions. When droplets of aqueous H$_2$SO$_4$ with a pH value 1 and an aqueous NaOH solution with a pH value 14 placed on the surface of the produced foam, they remained stable with spherical shape and could easily roll off the surface. When the superamphiphobic foam was immersed in a H$_2$SO$_4$ and NaOH solution by external force separately for 1 day, it showed no change in its superamphiphobicity. When the external force was released, the bulk material floated to the surface of the solutions immediately.
CHAPTER 5 CONCLUSION

5.1. Design of abrasion resistant anti-wetting fabric using TCMS and C8-FS

Superamphiphobic surfaces made from randomly oriented fibers have been found to be nontrivial to fabricate. In this dissertation, a novel wet-chemistry method to fabricate robust, superamphiphobic surfaces based on nonwoven nylon fabric has been developed. Trichloromethylsilane was used to form well-distributed nanoparticles along the nylon fibers via its condensation with water, -COOH groups on polyacrylic acid treated nylon fiber surface and itself. After (heptadecafluoro-1,1,2,2-tetrahydrodecyl) trimethoxysilane (C8-FS) treatment, the nanoparticles were covered by a flat polymer layer with low surface tension by its reaction with the incompletely condensed –OH groups. The fabricated fabrics have excellent repellency to low surface tension liquids without impacting the physical properties of the fabrics, such as air permeability. Martindale Abrasion test showed the coating had high mechanical durability.

5.2. Transform Hydrophilic cellulose-based materials to Superhydrophobic and Superamphiphobic Surfaces

Cellulose is naturally hydrophilic. However, for many applications, such as packaging, it would be beneficial if cellulose was able to repel water and oils. Tunable superhydrophobic cellulose-based materials have been prepared by a wet chemistry method based on the condensation and polymerization of organosilane. After trichloromethylsilane treatment, the fabricated filter papers showed wettability ranging from sticky superhydrophobicity to superhydrophobicity where the droplets easily roll off depending on the morphologies formed by the coating. The robust superhydrophobic cotton fabrics and filter papers showed superoleophilic properties as well, which can be used to separate water/oil mixtures. After further modification with perfluorosilane, the
superhydrophobic materials can be switched to superamphiphobic ones, showing superhydrophobicity and superoleophobicity simultaneously.

5.3. Zein nanoparticles as superhydrophobic and oleophobic coating

Robust, superhydrophobic, and self-cleaning textile fabrics were fabricated via nanoprecipitation of zein, a major protein of corn. Zein is an amphiphilic protein, possessing both hydrophobic and hydrophilic properties. Due to high content of nonpolar amino acid residues, zein is insoluble in water and alcohol but soluble in an aqueous alcohol solution in a certain concentration range. By adding water as anti-solvent under stirring, zein nanoparticles can be formed. Fabrics were coated with zein nanoparticles through a simple dipping process followed by oven curing at 130 °C. The produced superhydrophobic coating had high mechanical stability because of the crosslinking structure formed under high temperature.

5.4. 3D Light-Weight Porous Superamphiphobic Bulk Material with Coral Structure

We utilized heptadecafluoros-1,1,2,2-tetrahydrodecyl) trimethoxysilane (FAS) and 3-aminopropyl triethoxysilane (APTES) to fabricate a 3D rigid and low density foam-like material with superamphiphobicity. The process contains several steps. Firstly, silica covered with siloxane network was formed by the co-hydrolysis of tetraethyl orthosilicate (TEOS), FAS and APTES under basic conditions in ethanol. Then PAA aqueous solution was added into the system, followed by curing in an oven. After the evaporation of the solvent, material with bulk superamphiphobicity was formed. The long fluoroalkyl chain on FAS provided the low surface tension. The polysiloxane networks and the chemical bonds formed between amino, carboxyl group and PAA
as a binder provided the rigid structure of the material. The fabricated materials showed super wetting repellency against water, polar liquids with low surface tension (acetone and methanol), and nonpolar oils with low surface tension (dodecane and octane) without any post modification.

In summary, to design SH/SO surfaces with high abrasion durability, several important requirements need to be met. First, the surface tensions of the coated surfaces must be low; next the surface structure must be multi-scale. Additionally, the coating and substrate should be chemically bonded, not just simple physical deposition or adhesion. Textiles can provide micro scale structure on which nanostructures can be created. This combination of 3D micro and nanostructured system can improve the abrasion resistance. The fabricated SH/SO fabrics can be used for oil/water mixture separation, as discussed in the previous text. Without using textiles, 3D bulk SH/SO materials are also another choice to increase the abrasion resistance.
6. FUTURE WORK

To continue the project, we need to do more research on fabricating antiwetting surfaces without long fluoralkyl chains chemicals due to the potential environmental and health problems. Compared to chemicals having no fluoralkyl chain or short fluoralkyl chain, the main advantage of longer fluoralkyl chain is that they are easy to align and form special structures which can enhance the antiwetting properties. Without using chemicals with long fluoralkyl chain (larger than 8), repelling oils with low surface tension would be difficult.

Therefore, one future work would be searching ways to prepare superhydrophobic and superoleiphobic surfaces using short fluoralkyl chains. Insertion of stiff functional groups would be a choice, such as benzene ring; Secondly, ways to improve the washing durability need be developed.
7. REFERENCE


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