

Advancements in Non-fluorinated Durable Water Repellent (DWR) and Stain-Resistant Coatings

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Abstract. Fluorinated compounds are commonly used to produce durable water repellent (DWR) coatings, but they also have adverse environmental impacts, which has led to the exploration of alternative environmentally friendly products. This study illustrates that biomimetic hydrophobic coatings provide new ideas for solutions by describing some natural materials, such as lotus leaves and cactus thorns. However, scalability challenges and poor durability also limit their application. Although etching and photolithography can replicate natural structures, they are costly and require high industrial scale. Therefore, this study illustrates the shortcomings of these current technologies and future research directions. Innovative materials need to have similar functions as fluorinated coatings, but without the adverse impact on the environment. This study also emphasizes that future coatings need to perform well in multiple aspects such as waterproofing, self-healing, antibacterial, and UV resistance to meet the needs of more industries.

Keywords: Fluorinated coatings, DWR coatings, scalability, nanotechnology

1. Introduction

Durable Water Repellent (DWR) and stain-resistant coatings have high water and grease resistance, so they are widely used in various fields, such as outdoor equipment, daily clothing, and the automotive industry [1]. For outdoor equipment or daily clothing, DWR coating can effectively repel water, keep clothing dry, and ensure that clothing D has strong breathability. Car seats and carpets are also often coated with DWR and antifouling coatings to repel water or grease. The reason why durable water repellent (DWR) and antifouling coatings have strong waterproof and antifouling properties is that there are strong, difficult-to-break carbon-fluorine bonds in this coating. Based on this, people began to study this chemical bond and discovered the important role of fluorine. For example, many products with added fluorine often have strong oil and water repellency, so they are now widely used in chemical products [2].

Although fluorine products perform well in terms of water resistance and antifouling, adding fluorine elements to products is not good for the environment. One of the main problems with traditional fluorinated DWR coatings is their persistence in the environment, that is, they are difficult to degrade in nature [3]. At the same time, these coatings contain highly persistent and mobile perfluoroalkyl and polyfluoroalkyl substances (PFAS), which causes fluorinated coatings to penetrate soil and groundwater and pollute drinking water [4]. Furthermore, PFAS will also

accumulate through the food chain. After many animals drink fluorinated water or eat fluorinated animal meat, fluorine will continue to accumulate in their bodies until it reaches a high concentration [5]. Through the food chain, humans will eventually become victims of fluorine. PFOA (Perfluorooctanoic Acid) and PFOS (Perfluorooctane Sulfonate) are two of the most famous representatives of the PFAS family, which are both “long-chain” perfluorinated compounds [6]. Due to the high stability of the C-F bond, they are difficult to degrade and are extremely harmful to the human body. They may damage the human immune system and even cause various diseases [6]. Therefore, current researchers are developing new non-fluorine materials to replace traditional fluoropolymers to minimize the negative impact on the human body [4]. Fluorine-free DWR coatings use alternative technologies (such as silicone-based or plant-based materials) to provide water-repellent and stain-repellent properties without relying on PFAS. These alternatives are biodegradable and do not pose similar risks to human health or the environment as traditional fluorinated DWR coatings.

This paper is focused to solve such problems and minimizing the cost of the non-fluorine materials to ensure the non-fluorine material will have the opportunity to bring on stream. This paper reviews the process of preparing the materials with superhydrophobic surfaces in both physical and chemical method and why the materials can have the same characteristics as the traditional ones. Moreover, the paper also gives some examples of the superhydrophobic materials in nature to mimic such eco-friendly advantages to prevent the conditions that are difficult to degrade. Finally, this paper analyzes the current limitations of non-fluorine materials and their future developments.

2. Theoretical background

2.1. Contact angle definition

According to figure 1, a contact angle is the angle between the surface and the liquid drop which lie on the surface, the surface tension attracts the water drop to form a quasi-semicircle shape. In other words, it is the surface tangent of the drop. In some cases when surface tension is strong enough or the drop is small enough, the shape will turn into a ball-up shape. In a standard system, the solid, liquid, and vapor has only contact angle. However, when transitioning from the maximum advancing contact angle to the minimum receding contact angle, contact angle hysteresis occurs. By measuring the size of the contact angle, the wettability of the material can be basically determined. For example, the contact angle of a super hydrophilic material is 0 degree. The contact angle of a hydrophilic material is 0-90 degrees. The contact angle of a hydrophobic material is 90 degrees-150 degrees, and the contact angle of a super hydrophobic material is greater than 150 degrees.

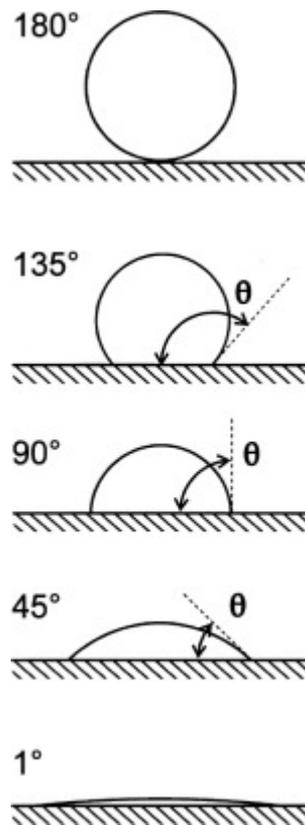


Figure 1. Contact angle definition and simulation

The well-known equation (1) Young–Laplace equation defines the three phases of connection of gas, liquid, and solid in the figure 2 below:

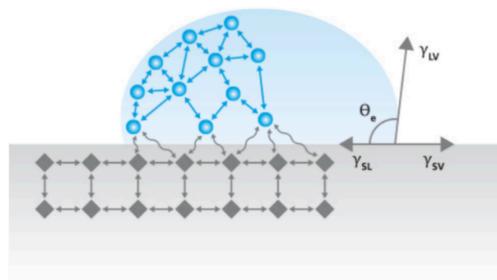


Figure 2. Three-phase contact point where solid, fluid, and fluid meet

Source: <https://www.nanoscience.com/techniques/tensiometry/contact-angle-measurements-and-wettability/>

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta_Y \quad (1)$$

In equation (1), the interfacial tension γ_{sv} represents the surface tension of the liquid, γ_{sl} represents the interfacial tension between the solid and the liquid, and γ_{lv} represents the surface tension of the solid, that is, the surface free energy [7]. The resulting Young's contact angle θ_Y is the equilibrium contact angle of wetting, as shown in figure 2. The validity of this formula must be based on the following conditions: the surface is smooth, non-reactive, insoluble, hard and chemically uniform.

2.2. Heterogeneous interfaces and the Wenzel and Cassie-Baxter equations

2.2.1. Definitions of the Wenzel and Cassie equations

The Wenzel equation was proposed by Robert Wenzel in 1936, and this model describes the wetting state of a liquid drop on a rough solid surface and assumes that the contact angle (θ_w) of the liquid on the rough surface is related to the static contact angle (θ_0) of the liquid on the smooth surface [8]. According to equation (2), r is the surface roughness coefficient. When $r > 1$, if the solid itself is hydrophilic, then the roughness will further enhance the hydrophilicity. Conversely, if the solid itself is hydrophobic, then the roughness will further enhance the hydrophobicity.

The core formula of the Wenzel equation is:

$$\cos \theta_w = r \cos \theta_0 \quad (2)$$

The Cassie equation, proposed by A.B.D. Cassie and S. Baxter in 1944, considers situations where air is partially trapped in a structure with a rough surface, i.e., the liquid does not completely wet the surface.

The core formula of the Cassie equation is:

$$\cos \theta_c = f_1 \cos \theta - (1 - f) \quad (3)$$

However, equation (3) is the most commonly used case of the Cassie–Baxter equation, which is only applicable to flat-top column geometries and without liquid penetration [9]. In general, the original form of the Cassie–Baxter equation, $\cos \theta_c = f_1 \cos \theta_1 - f_2$ should be used, which has a wider range of applicability. It should be noted that $f_1 + f_2 \geq 1$. Therefore, the Cassie–Baxter model describes the Cassie state of a droplet on a rough surface, that is, a non-complete wetting state, in which the droplet is suspended in the air and the solid surface instead of completely filling the rough structure. The assumption of this model is that the roughness of the solid surface, such as the nanoscale, will form a large number of tiny gaps that trap air, making it difficult for the liquid to completely wet the surface [10].

2.2.2. Range of applicability of the Wenzel and Cassie equations

The Wenzel equation is often used when the droplet completely wets the surface, penetrates the roughness, i.e. the roughness of the solid without trapping air pockets, ensuring full contact between the liquid and the solid indentations, and the liquid is uniformly wetted. The Wenzel equation is an approximation, and its accuracy increases when the droplet size significantly exceeds the roughness scale. The Wenzel equation is often used for hydrophilic surfaces. However, for surfaces with high roughness or porosity, the right-hand side of the Wenzel equation may exceed 1, which makes the Wenzel equation no longer applicable and requires the Cassie-Baxter model [11].

When talking about Cassie equation, it is used to denote the situation where a rough (heterogeneous or homogeneous) surface is not completely wetted by the liquid and there is residual vapor beneath the droplet. The term “Cassie” is specifically used to denote the situation where a heterogeneous (smooth or rough) solid surface is completely wetted by a liquid. At this point, the droplet is in a mixed wetting state, which applies to both hydrophobic and superhydrophobic surfaces, where air entrapment increases the contact angle [12]. This model can explain the low adhesion properties of lotus leaves and artificial superhydrophobic coatings.

However, the Wenzel and Cassie equations are only theory in ideal situation, due to the droplets not always fills completely between nanopillars of surface, the estimate might be not accurate at all time. As a result, hydrophobicity is also critically related to surface energy and roughness. In contrast, the Wenzel model is more applicable when surface roughness enhances wettability, while the Cassie-Baxter model explains why roughness leads to water repellency and low adhesion [12].

2.3. Contact angle hysteresis

Contact angle hysteresis (CAH) refers to the change between the advancing contact angle and the receding contact angle, and is also an important representation of the wetting behavior of liquid on solid surfaces. The size of the contact angle hysteresis determines the difficulty of the droplet rolling off the solid surface. The more severe the hysteresis, the more difficult it is for the droplet to roll off. Mathematically, it is equation (4):

$$CAH = \theta_A - \theta_R \quad (4)$$

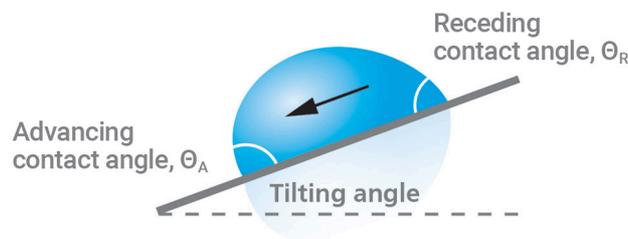


Figure 3. Contact angle hysteresis

Source: <https://www.nanoscience.com/techniques/tensiometry/contact-angle-measurements-and-wettability/>

2.4. Stability of a composite interface and role of hierarchical structure

Composite interface refers to the interface formed by two or more materials. This composite material has stronger physical, chemical or mechanical properties than a single material [13]. The stability of composite materials will be affected by some external factors, such as the use environment of the composite material, external pressure, etc. [14]. Hierarchical structures are often used in composite material design to provide a basis for the material matching and introduction of composite materials. Different purposes of use will determine the differences in hierarchical structures [15]. For example, nanoparticles or coatings with customized surface properties can be introduced at the interface to enhance wettability, adhesion and other related properties.

3. Natural examples

3.1. Natural water repellent

In nature, there are two suitable examples of introjection, lotus leaves and cactus Spines. These two surfaces contain a microstructure that leads to high contact angle, low roll angle, and chemical properties that lead to a good self-cleaning effect to avoid water droplets to conglutination, as a embody of hydrophobicity. Compared to normal materials, their most conspicuous advantage is eco-friendly and can be utilized in different industries to reduce the cost of cleaning and chemical

pollution. On the following topic, we will discuss the principle of well hydrophobicity, the chemical and corrosion resistance, and the most suitable industry they can put into use.

3.1.1. Lotus leaves

Lotus leaves are concerned with altering hydrophobic materials for their self-healing ability [16]. That mostly depends on its microstructure of papillae and the dense waxes covered on its surface, and as a result, the droplets easily slip down and bring the ash away from the leaves [17]. Neinhuis and Barthlott's study observed the micromorphological characteristics of 200 plants and obtained scanning electron microscope (SEM) images of different waterproof plants, one of which was the lotus leaf according to figure 4. Their research confirmed that the contact angle of the lotus leaf was relatively high, reaching more than 160 degrees [18]. They find that the outer layer of the lotus leaves surface forms small papillae and nanoscale hair-like structure, like figure 4 shows the SEM picture of lotus leaves from 1 to 10^6 . We can see that the distinct papillae are of varying heights, and much smaller than epidermal cells. Moreover, the tip of each nipple is not the shape of spherical but arched, just as figure 5. The surface is mainly composed of carbon and oxygen elements, forming an organic wax with extremely low surface energy [19]. Simultaneously, when droplets roll on the surface, the advanced angle is larger than the receding angle, as a phenomenon of contact Angle lag (CAH). So, drops can readily settle at the vertices of arch's meanwhile bubbles will valley floor between the nipples below. This demonstrates why droplets can maintain a small contact area to display the hydrophobic characteristic of lotus leaves [20].

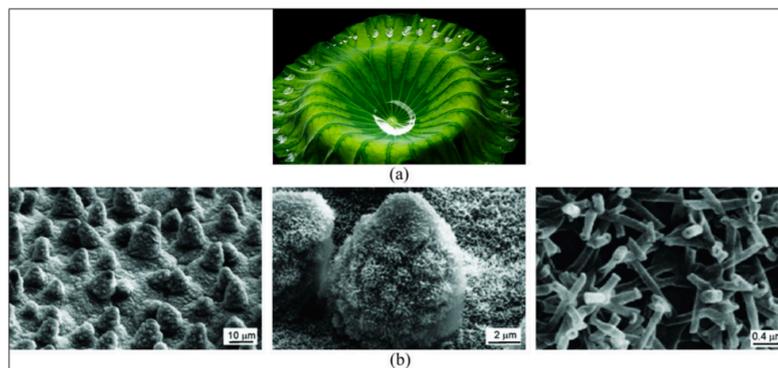


Figure 4. Lotus: (a) Magnification of one. (b) Morphological micro- and nanostructures showed in three different magnification of SEM images

Source: <https://www.sciencedirect.com/science/article/pii/S1631072111001860>

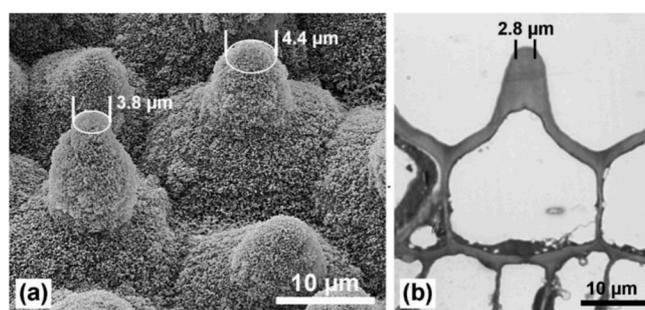


Figure 5. Epidermal cells on the upper side of the leaf have papillae and are densely covered with wax tubes. (a) SEM image after freeze-drying. (b) Light microscopy (LM) image of a thin section of the embedded sample

Source: <https://www.beilstein-journals.org/bjnano/articles/2190-4286-2-19>

Moreover, the contact force is also a factor of contact angle hysteresis. When the raindrops reach leaves with an initial velocity, it contains force. Under higher pressure, water penetrates deeper between papillae and forms a meniscus on the still super-hydrophobic coating of the wax tube. When losing contact, it generally forms a receding angle on few higher papillae and exhibits stronger adhesion. It can be deduced that our artificial materials with lower adhesion are better to control height of each papilla to an ideal level to reach a relative smaller CAH. Secondly, examining the self-recovery mechanism can better explore and mimic the surface function of lotus leaves. Such techniques can be applied in infrastructure elements including transmission lines, towers and turbines to avoid being humid and quickly recover from erosion.

3.1.2. Cactus spines

The reason why cactus thorns can obtain water in the desert is related to their hydrophilic and hydrophobic structures [21]. The hydrophilic tip of the cactus thorn is used to capture water; the hydrophilic-hydrophobic gradient structure in the middle allows water to move from the hydrophilic tip to the base. The hydrophilic base allows the water droplets to eventually enter the cactus body for storage [22].

From a physical principle point of view, the formation mechanism of the hydrophilic-hydrophobic gradient of cactus mainly depends on Laplace pressure, surface wetting gradient and capillary action. Surface pressure can push water droplets from the hydrophilic end of the cactus thorn to the base, and Laplace pressure is expressed in equation (5) mathematically [23]. The micro- and nano-scale textures on the surface of cactus spines form a rough surface that can trap air and minimize contact with water, thereby enhancing its water-repellent ability and exhibiting superhydrophobic behavior. The presence of wax in some areas of the surface of cactus spines can reduce the surface energy, prevent water from diffusing, and instead cause it to condense into beads, which makes it hydrophobic [23]. The components of cactus spines, including specific types of cetyl alcohol and lignin, are mainly non-polar in nature. This lack of polarity hinders interaction with water, further enhancing their hydrophobicity. The hydrophilic end allows the cactus spines to naturally capture moisture from the air and form tiny droplets. The hydrophobic gradient allows such droplets to freely and directional move from the hydrophilic end to the base. The capillary network formed by the grooves on the cactus spines builds a capillary action to guide the water droplets downward and ensure that the water can be fully absorbed by the cactus spines.

$$\Delta p = - \int_{R_1}^{R_2} \frac{2\gamma}{(R+R_0)^2} \sin \alpha dz \quad (5)$$

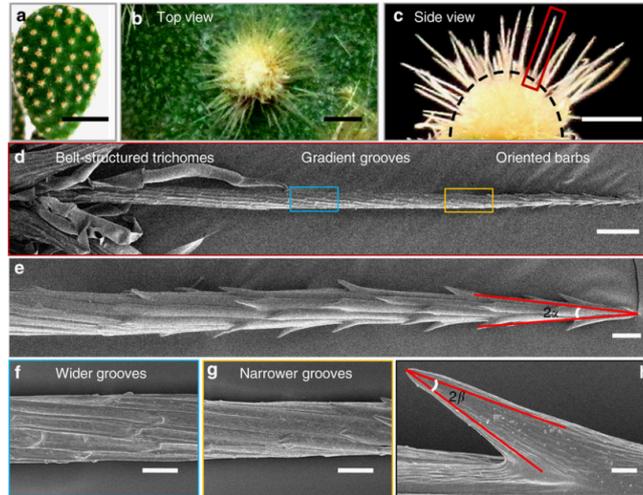


Figure 6. Hydrophilic-hydrophobic gradient structure of cactus spines
 (a) cactus spines (b) top view (c) side view (d) Microstructure (e) Microstructure (f) wider grooves
 (g) narrower grooves (h) angels

Source: https://www.researchgate.net/figure/Appearance-and-surface-structures-of-the-cactusa-Optical-image-of-a-plant-of-O_fig2_233849188

3.2. Natural stain-resistant

Except for the two examples above, there are more natural stain-resistant such as duck feathers, insect wings, spider silk, palm leaves and other possible inimitable stain-resistant materials. However, the cost to research and develop them is necessary to be considered and some of them are supposed to be a substantial amount of budget. Besides, natural stain-resistant mainly obtains micro-roughness and chemical matter, for instance, the papillae waxes and air interlayer are the most common constituents to reduce contact area. There are some special ingredients to introduce:

3.2.1. Natural stain-resistant of spider silk

The spider silk obtains spider silk protein with extremely low surface energy. It consists of long, thin filamentous chains that make up the protein fibroin, a large quantity of nonpolar hydrophobic acids. Fibroin proteins are very water insoluble and therefore help to make spider silk water-resistant [24].

From the perspective of chemical structure, the amino acid composition of silk protein is different from that of general cell enzymes according to figure 7. According to figure 8, spider silk protein has many repeated amino acid sequences, especially in the core region. Current research shows that the spider silk expressed in transgenic goat mammary gland by Canadian Nexia Biotechnologies is the most special. It uses goat mammary gland as a biological carrier to produce high-strength spider silk protein, but the concentration of soluble protein in goat milk is low, making it difficult to effectively purify the protein for thorough analysis [25].

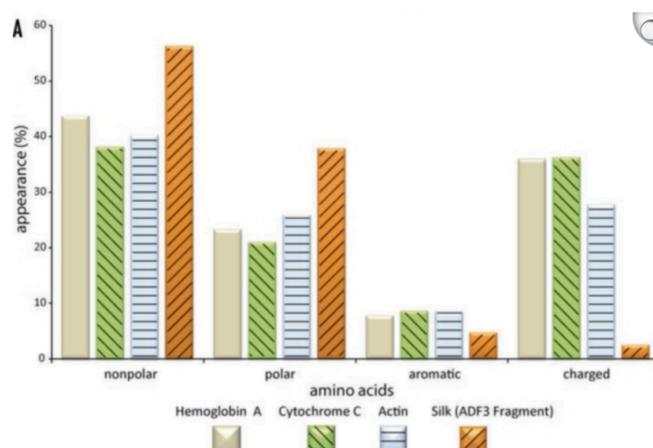


Figure 7. Comparison of the amino acid composition of three common proteins with spider silk

Source: <https://www.ncbi.nlm.nih.gov/pmc/articles/PMC2658765/>

	protein origin	amino acid sequence	putative structure	property
motifs	MA	(GA) _n / A _n	β-sheet	strong
	MA	(GPGQQ)	β-spiral	elastic
	Flag	(GPGGX)	3 ₁₀ -helix	elastic
	MA/Flag	(GGX)	3 ₁₀ -helix	elastic
	Flag	spacer	unstructured	elastic
termini	MA/Flag	NR ₁ -domain	helical	signal sequence and unknown assembly
	MA/Flag	NR ₂ -domain	helical	signal sequence and unknown assembly

Figure 8. Amino acid motifs of silk protein

Source: <https://www.ncbi.nlm.nih.gov/pmc/articles/PMC2658765/>

3.2.2. Natural stain-resistant of water striders

The reason why water striders have the property of water resistant is that their body and legs are covered by substantial amount of elaborate hair, the hair has special structure to avoid water to penetrate its body [26]. According to figure 9, these are needle-shaped, with diameters from 3 micrometers down to several hundred nanometers. Most Length of state is about 50 um and forms the inclined angle about 20 degrees above the surface [27]. This property can thus help water striders to process activities underwater, withstanding bubbles and breathe. Also, the contact angle can be as large as 167.6 4.4° [27]. According to the experiment, we also find that water striders secrete a kind of wax on its surface. Which increase its capability of water resistance. So such characteristics can be designed as a breathable surface, according to the physical structure. Besides, it separates its mass into a relatively large area, depending to high surface tension and low surface energy of water, water strider can easily float on water.

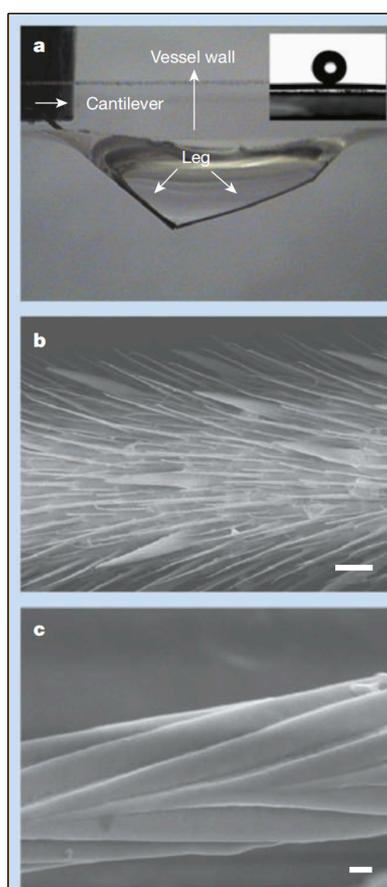


Figure 9. Body structure of water striders

3.3. Chemistry and texture in the design of these natural surface

Numerous materials take cues from the natural world. Indeed, humans' exploration of anti-pollution substances has been influenced by these natural inspirations. The biological structures previously discussed play a vital role in creating hydrophobic surfaces. Organisms and plants, such as the lotus, exemplify nature's inherent ability to resist pollution through their distinctive textures and chemical properties. These organisms not only maintain cleanliness and grace in contaminated environments but also serve as significant sources of inspiration for humanity. Below are some examples of organic materials and inorganic material.

3.3.1. Natural wax

Wax is a class of organic compounds composed of ester compounds of long-chain fatty acids and alcohols, usually solid, with good hydrophobicity. Waxes contain saturated or unsaturated long-chain fatty acids, usually between 16 and 36 carbon atoms in length. For example, the structure of beeswax is mainly myricetin palmitate ($C_{30}H_{60}O_2$), while carnauba wax contains cerotic acid ($C_{26}H_{52}O_2$) and myricetin ($C_{30}H_{62}O$). Waxes also contain long-chain alcohols, which combine with fatty acids to form wax esters. On the surface of plants and animals, waxy components can form a protective film to prevent water loss. For example, leaves such as lotus and cabbage have cuticular wax, which helps to repel water [28].

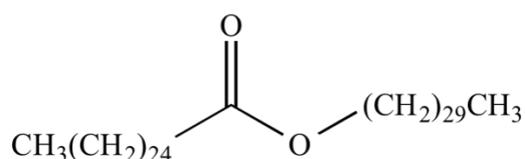


Figure 10. Chemistry structure of wax

The superhydrophobic properties of wax are primarily attributed to the following factors. The first one is low surface energy, the chemical composition of wax is characterized by low surface energy, which impedes the adhesion of water droplets on its surface, leading to a high contact angle (generally exceeding 150 degrees) and showcasing distinct superhydrophobic traits [29]. The second one is surface roughness: Many natural waxy surfaces feature micro- and nano-scale textures; this roughness, combined with the inherent smoothness of wax, significantly increases the contact angle for water droplets. The third one is rolling effect of water droplets: The superhydrophobic nature of wax promotes the easy rolling of water droplets across its surface, effectively removing dirt and dust while demonstrating self-cleaning properties [29]. Finally, natural waxes, including carnauba wax and paraffin wax, can be extracted to make hydrophobic fabrics and prepare super-hydrophobic coatings [30]. Waxes can be applied directly to fabrics, made into wax particles, or mixed with other nanoparticles.

From the several types of natural waxes, beeswax and carnauba wax are two kinds of wax can use in daily life because of its eco-friendly property and low cost. Because they do not need to undergo the process of chemical refine, which will cause a pollution to the earth. Chemically, beeswax consists mainly of esters of fatty acids and various long-chain alcohols. After adding beeswax, the water vapor transmission rate (WVTR) was significantly reduced to 20 g/m².day.atm, while the water contact angle (WCA) increased to 111° when the beeswax addition was 10 wt.% [12]. Furthermore, it has been experimentally proven that paint containing a mixture of beeswax and tung oil in a 1:5 ratio performs better than all other paints [31]. The conclusion shows that beeswax itself possesses a moisture-retaining properties and antimicrobial properties. To reach the superhydrophobic state, it needs to combine with oil to increase the WCA.

Another natural wax that can be used in producing hydrophobic coatings is carnauba wax. Compared to the main components of carnauba wax are long-chain fatty acids and alcohols (such as tricolons), and these long-chain molecules form a highly hydrophobic membrane on the surface. The non-polar nature of long-chain fatty acids makes it difficult for water molecules to bind to the wax surface [32]. Moreover, carnauba wax is also more stable than other waxes. It contains a higher melting point and greater hardness, making it more durable in practical production. The chemical resistance can also withstand more erode such as UV light, heat, and moisture. This stability contributes to the longevity of the coating.

Candelilla Wax and rosin wax are two typical examples as well. Candelilla Wax is widely used in waterproof coatings and cosmetics, and has high wear resistance and lubricity. After mixing with other waxes, it can enhance its hydrophobicity, so it is widely used in waterproof mascara and waterproof lipstick [33]. In a humid environment, the effect of candelilla wax is more significant. Rosin wax has a relatively low surface energy and hard physical properties, so it is also often used in wear-resistant and waterproof surface treatment [34]. Rosin wax is widely used in hull coatings and waterproof paper.

3.3.2. Cellulose

Cellulose is a polysaccharide structure that uses single glucose units connected by glycosidic bonds. As can be seen from figure 11, the chemical structure of cellulose includes a large number of hydroxyl groups (OH), that is, cellulose appears to be hydrophilic. However, cellulose can also be hydrophobic due to its unique physical structure and biodegradability [16]. Although cellulose itself is hydrophilic, it can be given super hydrophobicity by specific treatments and modifications. The super-hydrophobic surface of cellulose-based materials generally has two characteristics, namely, first, the surface structure of the coating is a micron structure. Second, the chemical properties of the coating are medium-low surface energy chemical properties [16]. Based on this, if we want to improve the hydrophobicity of the super-hydrophobic surface, we can use a micron or nanometer-level surface structure, or try to reduce the surface energy by introducing hydrophobic functional groups, such as long-chain alkyl and fluorinated groups. In addition, cellulose can also be combined with other hydrophobic materials, such as polymers, nanoparticles, etc., to form composite materials to improve super-hydrophobic properties. For example, Liu et al. (2016) create a super-hydrophobic coating with a contact angle as high as 150° by forming micro-nano structures on cellulose, and control the rolling angle at 3° to ensure the cleaning effect [35].

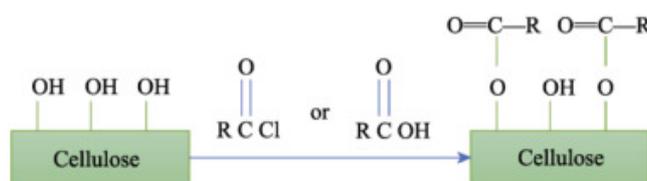


Figure 11. Esterification reactions of cellulose

3.3.3. Thermoplastic Polyolefin (TPO)

TPO is made of blend of polypropylene and ethylene-propylene rubber. Both can be recycled at their end of lifespan. TPO is typically free from harmful chemicals like chlorofluorocarbons (CFCs) and halogens, characterizing by the outstanding chemical property and long durability about 25 years. TPO offers better reflectivity and insulation, reducing cooling costs in warm climates [36]. From the perspective of environmental protection, TPO can reduce environmental cooling costs because it can absorb heat from the surrounding environment by reflecting sunlight. TPO roofing systems are increasingly marketed for their sustainability, with manufacturers emphasizing recyclable materials and energy efficiency [37]. However, it is less flexible in extremely cold weather.

3.3.4. Ethylene Propylene Diene Monomer (EPDM)

Ethylene Propylene Diene Monomer (EPDM) is a synthetic rubber formed by polymerization of ethylene, propylene and a small amount of diolefin (usually ethylene or propylene). It does not have harmful element. Although EDMP itself cannot be recycle, some manufacturers offer recycling programs that can reprocess it into other products. It has excellent durability, highly resistant to UV radiation and weathering. Moreover, it is highly flexible, even in low temperatures. EPDM shows better resistance to a wide range of chemicals, such as oils and solvents, compared to TPO [38].

By comparing the two kinds of inorganic materials, TPO is highly reflective, reduces cooling costs and sustainable with active recycling programs. On the contrast, it can degrade under extreme temperature swings, and its initial cost is high. EPDM is flexible in extreme temperatures and has lower cost. But it has limited energy efficiency without coatings. Studies highlight that TPO

membranes may leach more pollutants than EPDM during rainwater runoff, though both are within acceptable limits [39]. In addition, EPDM is easier to repair due to adhesive seam technology, whereas TPO requires specialized heat-welding repairs [40]. In conclusion, TPO is best for buildings in warmer climates where reflectivity and energy efficiency are priorities, while EPDM is suitable for colder climates or where flexibility and low-cost installation are desired.

3.3.5. Silicone

Silicone itself is an element does not contain the ability of hydrophobic. However, silicone and certain silicon-based materials can exhibit hydrophobic properties. First, its chemical structure of containing silicon, oxygen, carbon, and hydrogen, often forms a structure with a repeating siloxane backbone ($-\text{Si}-\text{O}-\text{Si}-$) with organic side groups like methyl ($-\text{CH}_3$) attached to the silicon atoms. These organic groups are nonpolar and shows the ability of repelling water. Silicone improved hydrophobicity and chemical resistance of poly (lactic acid) membranes, ideal for water treatment [41]. Secondly, silicone-based coatings can form a barrier between water and surface. As a result, water can hardly penetrate inside surface. Silicone improved water resistance in polyurethane-acrylate hybrid coatings, enhanced mechanical strength and reduced water permeability in industrial coatings [42]. Thirdly, silicone has a low surface energy, so water will tend to maintain the shape instead of spreading out on surface, according to the Wenzel and Cassie-Baxter equations mentions above, this status is hydrophobic. Hyperbranched silicone resins demonstrated superior thermal stability, flame resistance, and water repellency [43].

3.3.6. Graphene

Graphene is a single, two-dimensional material made of carbon atoms arranged in a hexagonal honeycomb pattern, and the water resistance is mainly because of the close pack of C atoms [44]. Meanwhile, the C-C bond is covalent bond, making it a smooth and nonpolar surface. Since H_2O is a polar matter, and graphene do not have an obvious polar properbility, that makes water can hardly wetting the surface. Furthermore, the C atom inside graphene forms a large quantity of cloud of π -electron. That means the cloud obstruct the intermolecular force between H bond in water, other bond inside water and surface [44]. That structure remarkably enhances the hydrophobicity of graphene. Graphene aerogels exhibited super-hydrophobicity with water contact angles up to 150° , indicating excellent water resistance suitable for applications like oil spill remediation [45]. Pristine graphene membranes showed low water permeability, while graphene oxide's functional groups facilitated water transport, highlighting the tunable water resistance properties of graphene-based materials.

However, the large scale of producing graphene is still a tough road. First, it is of great difficulty to produce it with a high quality. Due to the traditional method such as mechanical stripping's output is very low, so it can hardly put into large scale of factories. On the other hand, Chemical Vapor Deposition (CVD) method can reach the standard of high quality, but it is burdensome to peel off the substrate and transfer to the target material as a reason of its complexity and high cost [46]. Secondly, Consistency and purity is uncertain. Different group of graphene have their individual variation in thickness, crystal structure and defect density, influencing the property of the final material.

In general, although graphene is a potential material to replace water resistant coats with fluorine in market, the lack of technology and cost is the main obstruction of it to be the major material.

4. Preparation methods

4.1. Etching and lithography (Si, C)

4.1.1. Technical introduction

Etching and lithography are both key technologies for manufacturing micro-nanoscale surface structures. According to figure 12, etching includes dry etching and wet etching. Wet etching utilizes chemical solutions to dissolve and remove materials from silicon wafers, while dry etching employs plasma or ion beams to achieve material removal [47]. Owing to the “isotropy” of the liquid, that is, all directions of the surface in contact with the chemical agent are etched at the same rate, resulting in an uncontrollable etching speed. Conversely, the dry method is more controllable and precise.

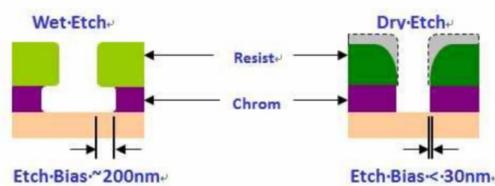


Figure 12. Wet etching and dry etching

Source: (Shen, 2013)

https://www.researchgate.net/figure/Wet-etching-and-dry-etching_fig7_259809585

According to figure 13, photolithography, also called optical lithography or ultraviolet lithography, is a patterning technique that uses light to transfer a geometric pattern from a photomask to a photosensitive material called a “photoresist” that has been coated on a substrate. The term “photolithography” merges the prefix “photo-” (indicating light) with “lithography,” which is a printing process [48]. This method involves selectively exposing certain areas of the photoresist to light, triggering chemical reactions that alter the solubility of those regions—making them either more soluble (in the case of positive photoresist) or less soluble (for negative photoresist) in developer solution [40]. Following development, either the exposed or unexposed portions of the photoresist are removed, thereby revealing the intended pattern on the substrate.

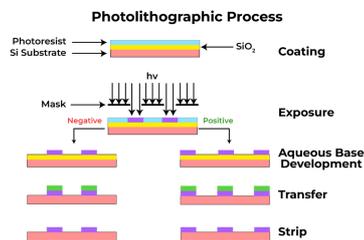


Figure 13. Photolithography process

Source: (GeeksforGeeks, 2024)

<https://www.geeksforgeeks.org/what-is-photolithography/>

Kang et al. (2024) explored wet etching techniques using KOH and TMAH for fabricating porous silicon nitride (SiN) membranes with applications in extreme ultraviolet lithography (EUV). The

conclusion is that wet etching processes are prone to undercutting, affecting the accuracy. Moreover, limited compatibility with certain materials and designs is also a negative perspective.

4.1.2. Technical steps

We use etching and photolithography to mimic the roughness of the surface of the lotus leaf mentioned above. First, we need to prepare the substrate, usually by applying an anti-corrosion coating (wax or resin) on the metal plate (Cu, Zn or Pb). Then, we use a sharp tool to carve the shape and expose the metal plate, that is, the metal area that needs to be etched. Next, we start etching. If we use wet etching, we need to put the metal plate in an acid solution such as KOH or TMAH to corrode the engraved part. If it is dry etching, we need to use plasma or ion beam to selectively remove the material [49]. Finally, after we remove the metal plate, we use a solvent to remove the residual photoresist and we can get the shape.

4.1.3. Technical features

The advantage is that etching can realize the manufacture of complex patterns, and the dry etching technology has high precision. Photolithography combined with etching technology can achieve complex micro-nano patterns, which is suitable for the production of some high-precision structures, such as integrated circuits, sensors, etc. However, the disadvantage is that wet etching may cause lateral corrosion (undercutting), which is not conducive to maintaining high precision. At the same time, the equipment cost is high and the etching process is complicated and troublesome. In the future, etching will still have high applicability. For example, etching can be applied to bionic super-hydrophobic surfaces, and the technical precision can be improved by optimizing etching conditions.

4.1.4. Technical cases

The first case is a super-hydrophobic surface based on the micro-nano structure of lotus leaves. Researchers used photolithography and dry etching techniques to create micro-nano structures that can simulate the surface of lotus leaves, thereby making the silicon surface super-hydrophobic [50]. Adjustment of etching parameters can also help control the surface structure morphology, achieve self-cleaning and anti-pollution. For another example, photolithography and etching are also widely used in the field of micro-electromechanical systems (MEMS). The manufacture of pressure sensors or accelerometers requires the use of photolithography technology to determine the basic structural pattern, and dry etching can remove unnecessary materials to ensure the high performance and accuracy of the pressure sensor [51].

4.2. Layer-by-Layer (LBL) assembly method

Layer-by-layer deposition (LBL) can be used to build nanoscale thin films by repeatedly depositing alternating layers of material [52]. After processing the substrate, LBL can be performed to deposit each layer of the film one by one and repeat the process [52]. Finally, the substrate needs to be cleaned and dried according to Figure 14.

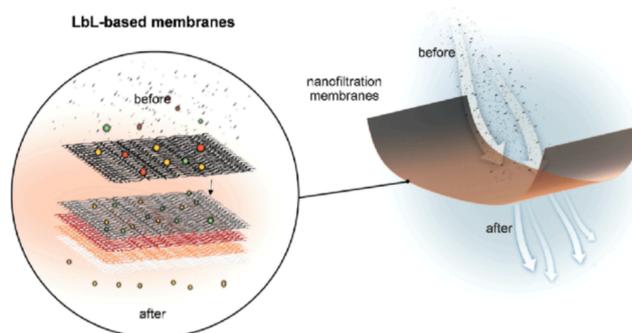


Figure 14. Layer-by-Layer (LbL) assembly can be used for membranes for gases and liquids

Source: https://www.researchgate.net/figure/Layer-by-layer-LbL-assembly-can-be-used-for-membranes-for-gases-and-liquids_fig4_333364619

LBL technology is very simple, low-cost, and has relatively high precision, so it is widely used in life. It can control the number of layers and the structure of the film. The flexibility of design also makes LBL self-assembly an effective and efficient way to form multilayer films and produce films with specific functions, which may include intelligent responsiveness, permeability, etc. In the biomedical field, LBL technology has been used in many aspects, including drug delivery, biosensing, biocompatible scaffolds, etc., and has great application potential in the future [53]. However, LBL technology also has limitations. For example, it is extremely time-consuming, and each layer requires a separate deposition and stabilization step, so it may not be suitable for industrial industries that value efficiency. In the future, it may be possible to consider using flexible materials such as rubber to improve its hydrophobicity, or to increase the deposition rate by optimizing the material.

4.3. Electrochemical reaction

Electrochemical methods to improve water resistance mainly involve applying protective coatings and changing surface chemical properties, such as electroplating, anodization, and electrochemical polymerization. Electrodeposition can form a waterproof surface by adding a thin layer of metal or polymer. Anodization forms an oxide layer on aluminum or titanium to improve corrosion resistance according to figure 15 [54]. Electrochemical polymerization can build a hydrophobic polymer layer. These technologies are widely used in many industries, such as construction, shipbuilding, electronics, etc. The advantage is that they can be mass-produced and are corrosion-resistant, but the disadvantage is that some materials are expensive, such as titanium oxide and graphene, and the process is complex and requires high precision control. Some new innovations include nickel-graphene coatings, which do not require chemical modifiers to have good waterproof and anti-corrosion functions [55].

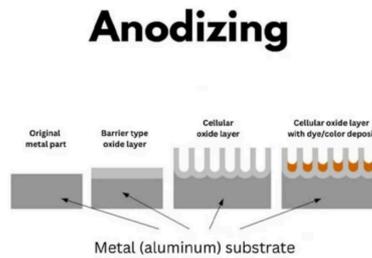


Figure 15. Anodization

Source: https://www.google.com.hk/url?sa=t&source=web&rct=j&opi=89978449&url=https://www.dekmake.com/everything-you-should-know-about-anodized-aluminum/&ved=2ahUKEwiN7t67r9SLAxWSADQIHbY8N_QQh-wKegQIWRAD&usg=AOvVaw3Nj22jhSJ7xZE_-uCw7YJH

4.4. Deposition and growth on template-substrate

Directed growth of crystalline materials occurs on single crystal substrates of different materials. The film material is deposited at a high temperature, allowing atoms to move to favorable positions [56]. The process begins when atoms or molecules nucleate on the substrate, and the film's composition and microstructure can be modified by ion bombardment during deposition. Chemical Vapor Deposition (CVD) is a bottom-up approach in which gaseous or liquid reactants are introduced into a reaction chamber. Chemical reactions occur on the substrate surface due to factors like temperature, plasma, or light [57]. Sputtering involves the ejection of atoms from a solid target's surface by the impact of gaseous ions, which are then deposited onto the substrate. Evaporation is performed in a vacuum chamber, where the material to be deposited is heated until it evaporates and condenses on surfaces within the chamber [58]. Recent research has focused on developing water-resistant materials using deposition techniques. Superhydrophobic surfaces produced via chemical deposition exhibit enhanced durability and water-repellent properties [59].

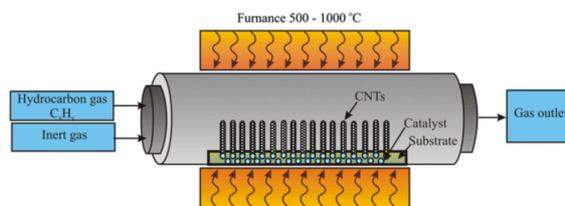


Figure 16. Chemical Vapor Deposition (CVD)

Source: <https://www.google.com.hk/url?sa=t&source=web&rct=j&opi=89978449&url=https://www.sputtertargets.net/blog/what-is-chemical-vapor-deposition-cvd.html&ved=2ahUKEwinmq-Wr9SLAxXNHjQIHS8aD4EQh-wKegQIVxAD&usg=AOvVaw3ae2RCTv5K1NVNr4D6OG7M>

5. Limitations and outlook

5.1. Limitations

Although fluorinated compounds are widely used in today's chemical products, fluorinated DWR coatings can cause serious environmental problems, and the harmful effects of PFAS mean that the demand for environmentally friendly alternative solutions continues to increase. Natural non-

fluorinated alternatives, such as lotus leaves and cactus spines, have provided some important insights and inspiration, but face scalability challenges [60]. The most promising methods for replicating these natural microstructures are etching and lithography, but these technologies are relatively expensive to implement and difficult to implement on a large scale, especially in the industrial and textile industries. Compared with fluoride DWR coatings, some biomimetic hydrophobic materials do not perform well in terms of durability and functionality. For example, although the surface texture is hydrophobic, the actual effectiveness may be reduced in harsh environments. In addition, some preparation techniques, such as dry etching and electrochemistry, can perform better in terms of precision, but it also means that more investment resources, higher precision professional equipment, and richer reserves of professional knowledge are required. On the other hand, wet etching involves a large number of isotropic processes, which makes it difficult to effectively control the reaction rate and make it difficult to keep the microstructure and hydrophobic properties consistent. The use of metals such as copper, zinc or lead in the etching process may cause environmental pollution and metal poisoning. Unless effective protection measures are taken, some materials may be susceptible to corrosion, which will weaken the advantages of hydrophobic coatings.

5.2. Outlook

First, future researchers may conduct more in-depth research on biomimetic hydrophobic coatings, especially sustainable and biodegradable materials, because these materials have less harmful impact on the environment. Advances in polymer science and nanotechnology can help scientists explore more durable and effective alternatives that have the performance of fluorinated coatings but do not have the harsh environmental impact. At the same time, future scientists also need to prioritize methods such as dry etching, electrodeposition and anodization to ensure the scalability of materials and reduce costs. Automating these processes and integrating corresponding manufacturing systems are important for the large-scale application of these materials in industries such as textiles and automobiles. In addition to water repellency, the next generation of coatings needs to have some corresponding additional functions, such as self-healing, antibacterial, and UV resistance [61]. These performance innovations can expand the application range of materials and enhance their commercial value. Researchers also need to focus on improving the stability of hydrophobic surfaces in different environments to avoid the degradation of their hydrophobic properties, such as adding wear-resistant layers or performing advanced surface treatments to ensure the long-term performance of materials.

As regulation advances and people's demand for alternatives to fluorinated compounds continues to increase, governments may provide financial incentives to encourage the development and production of environmentally friendly alternatives for commercial and large-scale manufacturing. Academic researchers, industry regulators, and policymakers should form an effective balance and actively cooperate to promote innovation in the corresponding fields. Scientists also need to continue to explore natural hydrophobic surfaces. For example, based on the conclusions drawn from lotus leaves and cactus thorns, new chemical mechanisms or chemical structures can be used to enhance existing designs [62]. Advanced computational modeling and simulation can also enable scientists to study these natural phenomena more deeply and promote the development of high-performance, innovative hydrophobic coatings.

6. Conclusion

Fluorinated compounds are commonly used to produce durable water repellent (DWR) coatings, but they also have adverse effects on the environment. Although lotus leaves and cactus thorns provide new ideas for material research, they face challenges in scalability, durability, etc. To overcome these challenges, researchers need to improve the durability and functionality of hydrophobic coatings. In addition, the scalability and low cost of materials can be improved through automated manufacturing processes. Policymakers and industry regulators need to work together to promote the research and development of innovative materials and develop environmentally friendly solutions.

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