Bio-Inspired Surfaces for Fouling Resistance

Yingfei Huang[1], Zehua Wang[2], Tom Chen[3]

1 University of New South Wales, Sydney, Nsw, Australia
2 The University of Teesside, Middlesbrough, TS1 3BX, UK Email: W9148982@live.tees.ac.uk
3 Ykpao School, Shanghai City, 200000, China

ABSTRACT. Each type of fouling, including marine fouling, biofouling, ice fouling, clathrate fouling, inorganic scaling, dust fouling, paraffin formation, and polymers fouling and how these types of fouling formed also described in this article. The current developed anti-fouling methods, for example, chemical control, physical cleaning, coatings, and biocides. After reviewing the necessary background of fouling and methodology against it, this article also explains the theory and reasoning under the phenomenon with young's equation, Wenzel model, Cassie & Baxley model, roughness, hydrophobicity, and hydrophilicity. Moreover, the phenomena of nature anti-fouling surface are illustrated, then the properties of different types of anti-fouling are summarized. Methods against biofouling under specific biomedical condition are discussed. Lastly, this report is going to evaluate different ways of anti-fouling to help other researchers to study the previous study under the topic of "bio-inspired surfaces for fouling resistance".

KEYWORDS: Bio-inspired surface, Fouling, Biofouling, Antifouling, Medical biofouling resistance

1. Introduction

Fouling can do physically or chemically damaged, includes corrosion, chemical accumulation, bio-organisms, or unwanted impurities, on the surface of a ship, on the side of the container, in the solution, or within the system. For example, the group of material scientists observed unique texture on the lotus, then inspired by the properties like levels of texture, usage of long- chain of hydrocarbons, and air pockets scientists invented a similar structure using silicon that this surface has the property of self-clean. The success of this waterproof surface encourages more researchers to study under the topic of fouling from lessons taught by nature. The surface on the rose petal, on the leg of pond skater, on the carapace of desert beetle's surface, and the skin of shark give researchers and material scientists excellent examples, so they conclude the following properties of a waterproof surface (hydrophobic surface): microscale texture, low energy surface energy, anti-wetting, low contact angles, low drug, low adhesion, glooming, and physics and chemical secretion[1]. Then some scientists focus on other fouling and its methodology of anti-fouling because other fouling is causing even worse economic loss and social welfare loss. The ice fouling caused airline delay, dust fouling caused water shortage, biofouling caused inflammation, or the marine fouling caused ship damages.

2. Background of Fouling

2.1. FOULING

2.1.1 Definition of Fouling

Fouling includes nine categories: marine fouling, biofouling, ice fouling, clathrate fouling, inorganic scaling, dust fouling, paraffin and wax deposition, protein fouling, and polymer fouling. Fouling is a process that the degradation of films properties causes suspended or soluble material is deposited on the outer surface, orifice or pore of films. Types of fouling and the effects of various types of fouling

(1) Marine Fouling

Marine fouling is "undesired growth of marine organisms such as micro-organisms, barnacles, and seaweeds on submerged surfaces [2]". When the clean surface of a ship submerges underwater, it immediately enters an environment full of micro-organisms. Some small bacteria, virus, protein, Protozoa, and diatoms colonies are floating in the water. If there is any chance to let those small organisms attach to the ship, they will create a more comfortable environment for more organic to grow. Once the process of fouling starts, more and more organisms from micro-organisms, unshelled sea animals, and shelled invertebrates create a micro-society on the wall of

ships, and their offspring enlarge it. Therefore, the part under the water becomes heavier and heavier and causes economic loss. So, marine fouling is one of the most undesirable fouling types, which cause millions of economic costs annually. Economists estimate the marine fouling would cost $56M per year for the entire DDG-51 class or $1B over 15 years due to the damage and speed lost [3].

(2) Biofouling

Biofouling in the medical field is the unwanted bacteria or organisms intruding human body that causes sickness such as eye infection, ventilator-associated pneumonia, periodontal disease, and failure from fibrous encapsulation. The micro-organisms came into the human body by different methods such as injection, blood transfer, surgery, medical machines, and implanted devices. Like currently, the coronavirus been found out that it can spread through human excrement, and they found this virus meanly diffuses by gasoline and air. Since the virus can also transfer from one infected patient to others through the machines, pipes, and needles, viruses, micro-organisms, and bacteria grow, invisibly, on the micro-texture or layers on the pipe. They are sub-micron, with sizes in the range of 100 nanometers, and they can survive under extreme conditions. They enter the human body quietly but dangerously since one report shows with more than 5000 annual deaths owing to infections [4].

(3) Ice Fouling

Steam or liquid water froze under zero degrees Celsius, and people in freezing places always face the problem caused by ice. Ice would block heat water, stop electricity, and cause blaze disaster. Aeroplanes in those freezing places close to the Antarctic always covered by ice that prevents them from operating functionally, which sensors were broken and became inaccurate. Moreover, due to the high adhesion of ice, it will be expensive to use a chemical to dissolve ice or physically melt the ice, but it will also be dangerous not to solve the ice on the winds.

(4) Clathrate Fouling

Clathrate fouling is defined as the fouling occurs when gas molecules become enclosed in the cage-like structures of water to form a crystalline material under conditions of high pressure and low temperature. Chemicals (propane, methane, cyclopentane, ethane and carbon dioxide) easily forms in those oil and natural gas industry, and their pipe system challenged by those chemical due to the downside of clathrate fouling (blockage, reduction in reaction speed, pressure and heat build-up, dangerous indexes, and economic losses). Since the formation of clathrate fouling is so easy that industries need frequently check and clean the undesired particles from transmission vents, the economic cost for cleaning would be expensive.

(5) Inorganic Scaling

Inorganic scale happens spontaneously, forming gases, oil, or salt precipitates on the wall of any container due to temperature, pressure, or concentration change to the fluid. This "self-scaling" might lead to slower flow speed, the uncontrolled reaction between liquid and precipitate, corrosion under the scale, and physical damage to the pipes. For example, the water desalination industry needs disinfection of the salt scale on every container that has contact with salty water. Generally, there are white scales on the containers which are NaCl that includes the very meal we have. Still, this precipitate in water desalination firms is a huge problem since the system cannot regularly stop running to clean those inorganic scales.

(6) Dust Fouling

Dust fouling caused by the formation of dust accumulation, and this normally happened in an arid climate where lack of rainfall, ground exchanging to sand, and frequent dust storms; furthermore, these places normally inappropriate for humans to live in to do regular checks. Therefore, the dust accumulation would destroy the water system, which is essential to survive in those arid areas. Moreover, space exploration technology also sees dust fouling as one huge challenge since the Moon and Mars are entire planets with dust [5]. Space crafts have to experience intensive sandstorms in extreme conditions so that they are facing to damaging dust fouling.

(7) Paraffins and Wax Deposition

Normally, crude oil will go through multiple steps to produce different products, and the transportation of oil through the process would produce paraffin and wax precipitates as byproducts. Those byproducts in the vent would slow down the transport efficiency while costing extravagant spending on regular cleaning. In the petroleum industry, firms need to add chemicals into crude oil to prevent the formation of waxes and paraffin. Disinfection would be extremely costly not only because of the expenditure of the chemical used but also due to the additional steps of the process. The chemical added might be dangerous to the engine, or it might produce waste or pollution in air; therefore, the firms need supplementary separation steps to separate the chemicals away from petroleum.

(8) Polymer Fouling

Polymer fouling occurs in the polymerization reaction, and the undesirable polymers would contaminate the organic reaction, including inefficient filtering, unwanted byproduct, and lower yield. The organic product like plastic formed from polymerization with exothermic reactions. Therefore, the reactor must be cooled down and transported to the next steps. When the polymer mixes with other components like dyes or molten plastics, polymers go through pipes and condense inside the vessel. During the transmission of polymers, the solution experiences a temperature change and a pressure change, so there will be polymer fouling occurs, including reaction to the pipe, loss of heat when needed melting polymers again, and undesired impurity in the end solution.

2.1.2 Overview of Fouling Species

To conclude, all the fouling types would potentially or directly damaging human health, limitation of technology, reduction in reaction speed, and economic loss; moreover, they can be classified as physical fouling (mostly accumulation), a chemical reaction (normally correction, replacement reaction, and decomposition), and conditional fouling (caused by pressure, temperature, or concentration change).

2.2 Antifouling Methods in Practice

2.2.1 Surface Coating Methods

All metal would react with oxygen to form the metal oxide, although some alloy like stainless steel or Nobel metals like rhodium, palladium, silver, platinum, and gold were inactive material [6]. Although ships can electroplate Nobel materials to the surface, those marine traffic ships have large surface area needed protection, so it will be impossible for any firm to build marines all using Nobel metals. Trying to find a cheaper way to solve, some companies use a thin coating with stable material to cover its main body to prevent corrosion. Or some scientists would use polymers with a unique property like glass-reinforced polyester [7] because they are much cheaper to industrialize, and its water-saturated state can guarantee its more stable than electroplating. However, the drawback is ignoring the complex condition underwater that there are millions of organisms trying to set down on the marine. Others focus on finding other coatings with the organic product to clean the organism or micro-animals underwater. One example of this method is AF enzyme that can react with the organism on the surface of a boat to drain the biofouling.
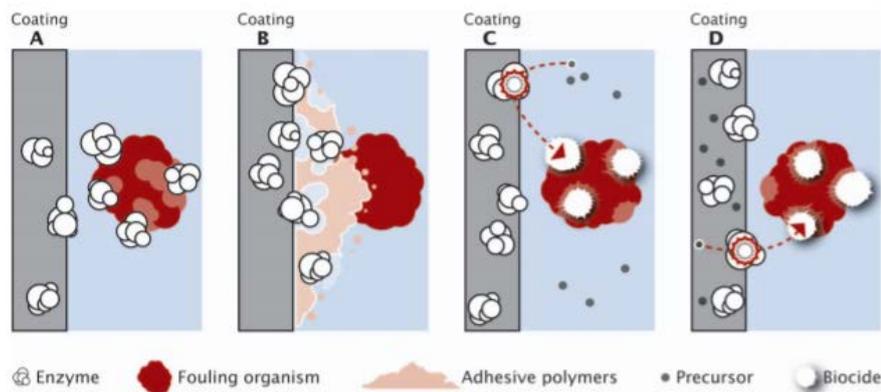

Figure 1 Enzyme coating mechanisms. Image reproduced from S. M. Olsen et al. [8]

As figure 1 shows, the enzyme (named AF) coating can have the following benefits in the report:

1) This enzyme reduces settlement of barnacle cyprids and reduce the adhesion strength of it;

2) The enzymes are active antifoulants in high concentration environment specially fit the marine condition;

3) Enzymes are stabilized in the coating while they still can clean the biofouling [8].

In total, the coating method is a viable advanced method against fouling biofouling especially, with different properties of special coating. However, the duration, ability against the extreme condition, and environment-friendliness still need further developments.

2.2.2 Chemical control

Chemical control includes biocides (releasing toxic or non-toxic) and vinegar (antioxidation or reaction to oxides). For the biocides, scientists have extensive use of Tributyltin (TBT) during the 1950s that the chemical is highly efficient to avoid protein or organisms on the surface of a ship because the release of TCT has a toxic effect on plants at all points in the food chain, even to the mammals [1]. However, the weak point is clear that reports show that medical has a direct effect on friendly mammals in multiple ways. First, the chemical would inhibit the Cytochrome molecule, which can disrupt the mating system by transferring male hormones to female hormones [9].

Moreover, the toxic particle can affect the vertebrates in all mammal that damage the immune system, and reports explains that immunosuppression has been detected in sea animals and transfer to human [10].

Since the massive success of TBT, scientists continually found other toxic products which are more efficient and longer life cycle of the coating, like Copper oxide. By exposed copper oxide underwater, the Cu2+ ions are released, and it has negative effects on organisms' ion regulation [1]. There are more toxic methods to kill organisms like chlorothalonil, dichlofluanid, and Irgarol until the current regulation control appeal via the toxic particle that anti-fouling uses. On the other side, vinegar usage is the method to avoid inorganic fouling that uses food coating and metal covering. There are various chemical uses as vinegar to react with oxygen and prevent the value part inside, including cane vinegar, Beer vinegar, and potato vinegar [11].

2.2.3 Physical cleaning and disinfecting

Compared to chemical control, the physical cleaning method was more commonly used in most industries and less damage to the environment. Physical cleaning (or called miscellaneous) anti-fouling includes grooming, burrowing, flexing, algae growing, and mechanical cleaning [1]. Grooming is highly useful to growing biofouling because it uses brush-like structures to directly clear the surface, which usually cooperate with low adhesion, low drag, or low surface energy surface. Burrowing is generally applying to the pipes which have been blocked by biofouling, dust fouling, or inorganic scaling, so this method is just merely digging a hole to dredge the canals. These two methods can use a high-pressure water beam to cut or clean the fouling. Algae growing is usually covering the object with fouling on it to the dark for months. The algae will spontaneously grow on the surface to slowing clean the surface by its chemical secretion. However, those physical methods are not efficient to use because most fouling has accumulation for months that are stabilized to the surface, so the mechanic cleaning methods are hard to remove them. Furthermore, the physical solution might take a long period and cost the user for significant time spending.

3. The basic theories for developing bio-inspired surfaces

3.1 Surface energy and surface tension

Liquids have two properties, cohesion and adsorption. They are the representation of the molecular attraction. Cohesion makes the liquid-resistant to the tensile stress, while adsorption makes liquid stick on other objects. At the boundary between two contacting phases, there is a change in free energy, which is caused by the molecular attraction force. The surface energy, γ (J/m^2), and the surface stress, σ_{ij} (N/m), of the interface, are two properties for achieving this equilibrium interface. The surface tension, σ, can be used to represent the equilibrium property of the interface when the surface stress is isotropic [12].

Surface energy is the amount of energy required to break the intermolecular forces while creating a surface. Surface tension is the change of internal energy caused by the change of the surface area of an object. Surface tension is due to the different environment of the surface particles and inside particles of the object. It means that particles have different energy [12].

For example, each ion inside the liquid is evenly surrounded by neighboring particles, counteracting the forces of attraction from different directions [12]. In contrast, particles on the surface of the liquid contact with air, which density is lower than the density of liquid. Therefore, the surface ions are less attracted by the air molecules and more attracted by particles inside the liquid. In this case, the surface molecules are subjected to pull toward the liquid interior. Works need to overcome the inward force for moving particles from the inside of the liquid to the surface. As these migrated particles form a new surface, this work is converted into potential energy of the surface particles. The excess energy of the surface particles over the inner particles is called the surface energy.

For the liquid, the value of surface energy per unit area is the same as the surface tension, but the physical meaning of these two is different. However, they are not the same for the solid. The Laplace's equation illustrates the relationship between the pressure difference (ΔP) and the mean curvature. Their proportionality constant is the surface tension (σ).

$$\Delta P = P_1 - P_2 = \sigma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \#(1)$$

In this equation, P_1 is the concave side pressure and P_2 is the convex side pressure. R_1 and R_2 are the principal radii of surface curvatures [12].

3.2 Young's relation

In the case where the boundaries of the three phases intersect at one point, the system has a contact angle that makes the sum of the three surface tensions be zero. This lets the system reach equilibrium. This relationship is shown in Young's Equation [12].

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} cos\theta_{eq} \#(2)$$

In equation 2, θ_{eq} is the contact angle of the system for the equilibrium. γ_{SV}, γ_{SL}, and γ_{LV} are the surface energies of the solid-vapor interface, solid-liquid interface and liquid-vapor interface, respectively [13]. Young's equation is a thermodynamic equation showing the relationship among surface energies. It is valid whether $cos\theta_{eq}$ is negative, positive or zero. However, if $\gamma_{SV} > \gamma_{SL} + \gamma_{LV}$, the equilibrium of the system is impossible. For the solid-liquid-vapor system, the sum of γ_{SV} and γ_{LV} is always larger than γ_{SL}.

Work of adhesion and work of cohesion need to be considered for discussing the forces mechanisms [13]. For an equilibrium solid-liquid-vapor system, the energy needs for effecting the phase separation is called the work of adhesion, W_A.

$$W_A = \gamma_{SV} - \gamma_{SL} + \gamma_{LV} \#(3)$$

In equation 3, the work of adhesion is always positive. Combined with equation 2, another relationship can be given, which is shown in equation 4.

$$W_A = \gamma_{LV}\left(1 + cos\theta_{eq}\right)\#(4)$$

3.3 Effect of surface roughness

Two models can simply described the contact angle on a real surface. The first one is the Wenzel model, and the other one is the Cassie-Baxter model. The chemical heterogeneity and surface roughness need to be considered for the real surface. The rough and chemical homogenous surface is considered for the Wenzel model, while the heterogeneous surface is for the Cassie-Baxter model consideration [14].

3.3.1 Wenzel model

Wenzel model is shown below.

$$cos(\theta^*) = rco\Box(\theta)\#(5)$$

In equation 5, r is the surface roughness ratio, which is defined as the ratio of the actual area to the projected area of the surface. θ is the equilibrium contact angle, which is given by the θ_{eq} in Young's equation and θ^* is the apparent contact angle [15].

From the Wenzel model, it is found that the surface roughness can influence the surface wettability because r is larger than 1 in all cases. If the flat surface is initially wetted by the liquid, the hydrophilicity of the surface can be enhanced by the amplified surface roughness. Also, if the surface is non-wetting initially, the enhancing roughness can make the surface more hydrophobic [15].

3.3.2 Cassie & Baxter model

For dealing with the heterogeneous surface, the Cassie-Baxter model needs to be considered.

$$\cos(\theta^*) = \sigma_1 cos(\theta_1) - \sigma_2 \#(6)$$

$$\cos(\theta^*) = \sigma_1 (cos(\theta_1) + 1) - 1 \#(7)$$

In equation 6 and 7, two fractions are composed in a heterogeneous interface. One of the fractions has the fractional area of solid under a drop σ_1 and Young's contact angle θ_1. Another one has σ_2 and θ_2. Also, the sum of σ_1 and σ_2 equal to 1 [15].

Also, Cassie's Law is proposed which modified two materials with different chemical properties on both smooth and rough surfaces.

$$\cos(\theta^*) = \sigma_1 cos(\theta_1) + \sigma_2 cos(\theta_2) \tag{8}$$

Equation 8 above can be combined.

$$\cos(\theta^*) = r_\varphi \varphi_s \cos(\theta) + \varphi_s - 1 \#(9)$$

In equation 9, $r_\varphi \varphi_s$ is the real liquid and solid contact surface area. φ_s is the solid-liquid contact interface area.

The Cassie-Baxter model considers that the surface is not only rough but also porous. This leads the model to consider two wetting modes: air entrapment and wicking. The water drops stay on the surface composite, and the air is trapped by the topography under the air entrapment wetting mode. For the wicking wetting mode, the liquid is attracted to the topography at the advancing edge, allowing the droplets to stay on the liquid and surface [16].

For air entrapment,

$$\cos(\theta^*) = \varphi_s(1 + \cos(\theta)) - 1 \#(10)$$

For wicking,

$$\cos(\theta^*) = \varphi_s \cos(\theta) + 1 - \varphi_s \#(11)$$

3.4 Bio-inspired Superhydrophobic surface

The surface is superhydrophobic when the contact angle is larger than 150°. The contact angle can determine the wetting of the material surface, and the value of that depends on the free energy of the solid surface. The surface is considered hydrophilic when the contact angle between the water droplets and surface is smaller than 90°, while the surface is hydrophobic when the contact angle is larger than 90° and less than 150 °. Young's equation illustrates the correlation between the surface energy and the solid-liquid-gas phase contact angle [17].

Two methods are considered for designing a superhydrophobic surface, including decreasing the material surface energy and increasing the surface roughness. Controlling the surface roughness to create superhydrophobic surfaces is more considered in the present study. Aside from that, the surface energy can also be controlled by modifying the surface with low surface energy elements.

Young's equation only applies to the smooth surface. When simulating the rough surface with homogeneity and heterogeneity, the Wenzel model and Cassie-Baxter model need to be taken into account. Based on these models, the results show that the wettability of the solid surface is related to both the surface structure and the composition of the surface. Furthermore, the contact angle is not constant and varies within a range on a rough or heterogeneous surface. The contact angle hysteresis, which is the difference between the advancing contact angle and receding contact angle, is strongly related to the behaviors of droplets on the solid [17].

3.5 Bio-inspired Underwater superoleophobic surface

The underwater superoleophobic surface is usually superhydrophobic in air. This is due to similar micro and nanostructure on superhydrophobic and superoleophobic surfaces. For underwater superoleophobic surfaces, water droplets trapped in the rough surface can resist the immersion of oil. In this situation, water has the same role as that of the air on superhydrophobic surfaces. With the increase of surface roughness, the contact angle of oil droplets in water increases and the adhesion force decreases [17].

Young's equation usually describes the wettability of solid surfaces by the contact angles. However, Young's equation is generally applied to a water/air/solid interface, where the liquid drops contact with solid surfaces in the air. This equation can be transformed to be suitable for describing the wettability of the surface when the oil droplets on the solid surface are in water [17].

$$cos\theta_3 = \frac{\gamma_{o-g}cos\theta_1 - \gamma_{w-g}cos\theta_2}{\gamma_{o-w}} \#(12)$$

In equation 12, γ_{o-g} is the oil and gas interface tension, and γ_{w-g} is the water and gas interface tension. θ_1, θ_2 and θ_3 are the contact angle of oil in the air, the contact angle of water in air and contact angle of oil in water, respectively [18].

Based on the equation, $cos\theta_3$ is negative when the solid surface is oleophobic in water. This indicates that $\gamma_{o-g}cos\theta_1$ is smaller than $\gamma_{w-g}cos\theta_2$. The surface can be superoleophobic in the air only when the surface tension of the water droplets is smaller than that of the oil droplets. For describing the state mentioned above, the concept of the contact angle in the Cassie & Baxter model can be presented. The Cassie & Baxter model for a water/oil/solid surface is shown below [17].

$$cos\theta_3^* = fcos\theta_3 + f - 1$$

In this equation, θ_3^* is the contact angle when the oil droplets are on the rough surface in water, while θ_3 is the contact angle when the oil droplets are on a smooth surface in water. f is the area fraction of the solid surface [17].

.4. Properties of bioinspired surfaces for antifouling

4.1 Superhydrophobicity and self-cleaning ability of the lotus leaf

Nelumbo nucifera is a semi-aquatic plant with roots planted in underwater soil and leaves floating on the water surface. The diameter of the lotus leaf is generally up to 80 cm, while the diameter of the flower is approximately 30 cm. The upper epidermal of lotus leaf has superhydrophobic and self-cleaning properties, which is known as "lotus effect", and is widely used as the nature reference in the design of antifouling surfaces. When the water droplets contact the upper epidermal of the lotus leaf, water does not wet the surface and drops from the lotus leaf. Based on this phenomenon, lotus effect means that water falling on a superhydrophobic surface can form water droplets due to the effect of surface tension and the contact angle between water and leaf surface is greater than 150 degrees. Then, the water droplets can simply roll off when the surface is slightly tilted and carry away any foreign material such as dust or dirt [19].

The reasons for the high-water repellency of the lotus leaves can be attributed to the special surface geometry and the ability to produce the unique epidermal wax. The surface structure of the lotus leaf is the combination of the complex nano-ultrastructure and micro-ultrastructure on the upper leaf surface and dense wax tubules with the special chemical composition [20].
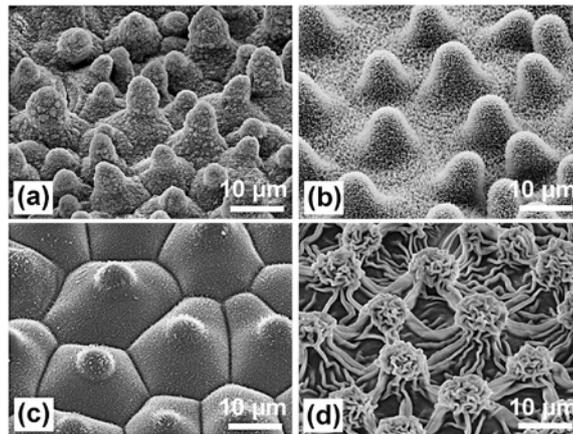

Fig. 2 Topography of lotus leaf. Image reproduced from Hans J. Ensikat et al. [20]

This hierarchical surface structure can be found in many natural plants, but the water-repellent properties of lotus leaves are much better when compared with other superhydrophobic plants Based on many studies. The excellent properties of lotus leaves derive from the small contact area between water and leaves, and the protection of epicuticular wax crystals by the papillae [21].

Papillae with varying height form on the epidermis cells of the upper lotus leaf side. The diameter of the papillae is around 10 microns which is much smaller than the diameter of epidermis cells, and the average space

of each papilla is 12 microns. Each papilla is formed by many nano-papillae with 200 nanometers in diameter. Also, the entire surface is covered with short wax tubules, which usually gather in clusters. Compared with the other plant with papillose surfaces, the papillae of lotus have the highest density and the smaller diameter, reducing the contact area with water drops. The minimization of the contact area is the primary cause of very low water adhesion, resulting in the small roll-off angles. Besides, the different height of each papilla further reduces the droplet adhesion to the surface because droplets only contact the highest papillae at low pressure. Even at higher pressure, the contact between the water and the papillae is deeper. However, there are still superhydrophobic wax tubules coatings, and the papillae release their contact with water one after another, which causes a small adhesive force [20] [21].

The robustness caused by the high density of the papillae is the basis of the lotus leaf surface protection. The pressure required for water droplets to invade between the papillae is determined by the distances between the hydrophobic wax crystals. Furthermore, the chemical property of the wax on the lotus surface needs to be considered. Lotus epidermal wax contains a high proportion of nonacosanediols, which provides a high melting point. This indicated that the high strength of hydrogen bonding in the lattice, which increases the stability of the lotus leaf surface protection [20].

These features make the lotus leaf a natural superhydrophobic surface which is often referred to in antifouling surface design.

4.2 Superhydrophobicity of rose petals

When water contacts a rose petal, it does not wet the surface, which is similar to the property of upper lotus leaf [22]. However, there are differences between the rose petal effect and the lotus effect. The rose petal effect shows that water droplets on the surface of these petals are spherical, which cannot roll off even when the petal is turned upside down [23]. This is because the surface of the rose petals has a periodic close array of micropapillae, with many nano-folds that exist on each papillae top. Superhydrophobicity is provided by the roughness of this hierarchical micro- ultrastructure and nano-ultrastructure. A high adhesive force between the water drop and petal surface is also given by this structure [24]. Figure 3 shows the shape of the water droplet on the rose petal surface in each condition.
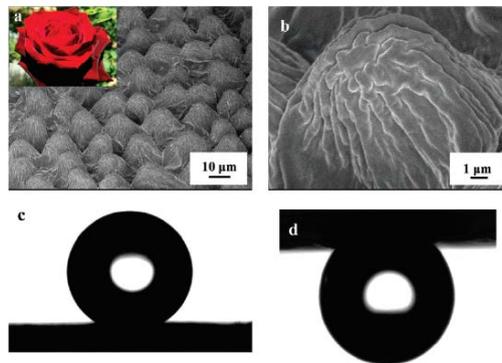

Fig. 3 (a, b) SEM images show the structures of the red rose petal surface. (c, d) The shape of a water droplet on the petal's surface when the surface is up and down, respectively [25].

The differences in the surface topography and sizes of the rose petal and lotus leaf result in different dynamic wetting. In the case of rose-petal effect, a high contact angle that is controlled by the nanostructure of the surface can coexist with strong adhesion between water and a solid surface (high contact angle hysteresis). Contact angle hysteresis can be controlled by the microstructure of the petal surface [25]. A key parameter for the petal effect is the size of the water droplets. The droplet can stick to the surface when its weight is smaller compared to the surface tension force [26]. However, the droplets fall when the size of the droplets is too large, leading to a balance of the surface energy and weight of the droplets. The water drops might enter the larger grooves of the petal instead of the small ones. This can form the Cassie impregnating wetting state on the rose petal surface [26].

Rose petal effect is often compared with lotus surface to provide a new design reference for the antifouling surface.

4.3 Superhydrophobicity of mosquito eye

The structure of the insect eye surface is often considered during the antifogging surface design. Mosquitoes can recognize targets quickly in fog. This is because their eyes have a good antifogging property which means the mist is hard to condense into water droplets on the mosquito eye [17]. The mosquito eyes are a composite structure of hundreds of tiny hemispheres, including a large number of nanoscale papillae distributed on each hemisphere[27]. The papillae are distributed regularly and uniformly, which is similar to the upper epidermal structure of the lotus leaves [17].

However, the upper surface of the lotus leaf does not have antifogging property. When the lotus leaves are exposed to a humid environment, the leaf surface might gradually become wet. This is caused by the uneven distribution of the structure of papillae on this surface. The drops are smaller than the gap, so they might adhere to the surface. This means that not all the superhydrophobic surfaces are suitable for antifogging design. Since the nanostructures of some materials are too far apart and the mist droplets have smaller diameters than it, the droplets tend to get trapped between the gaps. The ommatidia and papillae on the ommatidia distributed on the surface of the mosquito eyes are more closely aligned and can resist smaller water droplets [17].

As a superhydrophobic surface, the mosquito eyes compensate for the flaws of the lotus leaf surface and give a new design strategy for anti-fogging [17].
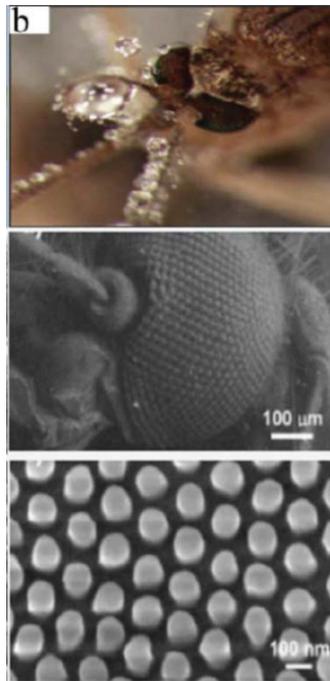

Fig.4 Topography of mosquito eye. Image reproduced from Zhihao Li et al. [17].

4.4 Superhydrophobicity of butterfly's wings

Butterfly wings, pigeon feathers, and lotus leaves are typically superhydrophobic nature surfaces. Butterfly wings have a specially arranged scale, which provides its unique characteristics. The superhydrophobicity of the butterfly wings is because of the neatly arranged and strongly overlapping scales on their wings and the side-by-side micro-grooves on the scales [17].

Special scales are found on the translucent portions of butterfly wings, which are ovate and much thinner than normal scales. Almost 30 special scales stand on the surface, leaving as much as 80 percent of their wings surface uncovered (Figure 5). Under the pressure of contacting water droplets, these special scales bend but do not collapse. The elastic recovery of the structure at the edge of the drop gives a high contact angle. This provides a design direction for a superhydrophobic surface with this special structure [28].
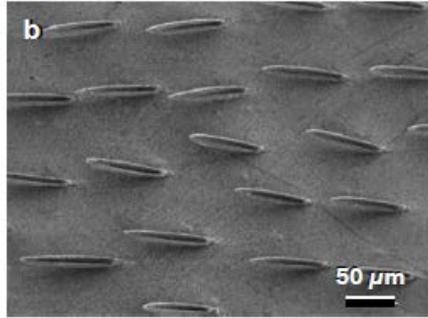
Fig. 5 Top view of specialized scales in the translucent zone of a butterfly wing [28]

Another observed phenomenon is that droplets on the wings of butterflies are anisotropic. The droplets easily roll from the inside to outside of the wings, whereas the droplets can adhere to the wings of the butterflies in the opposite direction. This is because of the flexible tip of the groove edge at the nanometer scale and the one-dimensional overlap on the micrometer scale. This leads to two different contact and motion states of water droplets on the wings of butterflies, resulting in different adhesion properties. This characteristic provides a new idea for the design of microfluidic directional transport and intelligent control fluid interface [17].

4.5 Micron sized ribbed structure on sharkskin

The shark's skin is covered with tiny denticles which can be flexed against each other because of the elasticity of the skin underneath [4]. The scales on the skins are overlain by the regular pattern of parallel ridges and grooves. These riblets with special size and spacing orient parallel to the swimming direction [29].

The antifouling properties of shark skin are due to its low resistance and microtexture. The low drag of shark skin is achieved by reducing the contact area between the vortices and the skin surface. Instead of contacting the vortices with the total surface area, shark skin only allows the vortices to contact with the tiny riblets tips. This decreases the total shear stress, thus reducing the drag force. Also, low drag enables the layer of water near the skin to move faster, which decreases the settling time of the micro-organism and help wash them away [29].

Furthermore, the microtexture of shark skin can also block certain micro-organisms. The reason is that these micro-organisms prefer to stick to the groove with specific widths and depths. This makes it difficult for microbes to attach and stick to the sharkskin [17].

Since shark skin surface has many benefits, for example, superhydrophobicity, self-cleaning, drag reduction, anti-fouling, and so on. It can be extensively applied in many aspects of design [17].

4.6 Fish scales which are superoleophobic in water and superoleophilic in air

Fish scales are composed of calcium phosphate, proteins, and a thin layer of mucus that causes their hydrophilic behavior [4]. However, fish scales have good antifouling and self-cleaning properties in oily water. This may be due to a large number of radially arranged micron level papillae distributed on the surface of the fish scales. They cooperate with mucus to give the fish scales antifouling properties. Nevertheless, when the scales are exposed to air, the superoleophobic properties they exhibit in the water change to superoleophilic properties. Studies have shown that the water around fish scales can cause a wettability reversal, causing these phenomena [17].

Based on the theory of superhydrophobicity surface, the air is trapped in the rough surface when this surface contacts with water. The water/air/solid interface is formed by these trapped stable air molecules that are existed on the surface of micro and nanostructure and give a high hydrophobicity. This means the superhydrophobic surfaces are derived from the formation of new composite surfaces [30].

The oil/water/solid interface is formed when water molecules are trapped in the micro and nanostructure fish scales which contact the oil droplets. This interface has the superoleophobic properties. This wetting behavior is similar to that of the superhydrophobic surfaces [30].

The surface of fish scales has high compressive and tensile strength, and a new method for antifouling and biological application is proposed [17].

5. Design strategies for antifouling bio-inspired surfaces

5.1 Surface properties

Scientists concluded the theories (the young's equation, Cassie-Baxter state, Wenzel State, shear-induced equation, and contact angle) from the phenomenon of lotus, rose petal, pond skaters, India canna's surface, desert Beetle's surface after rigorous mathematical modelling. So now, researches can use the previous study to create surfaces with levels of texture, designed air pocket, and pillars that can have properties of hydrophobic, omniphobic, anti-protein, and anti-fouling. One successful example is the structure with the re-entrant material forms a structure as Figure 6.
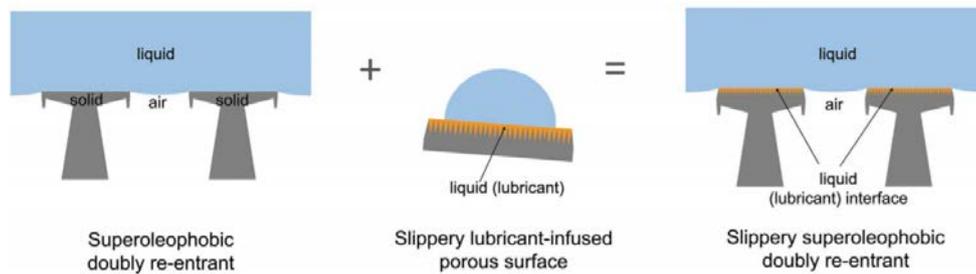

Fig. 6 Successful example is the structure with the re-entrant material forms a structure. Image reproduced by Zheqin Dong et al. [31].

The re-entrant material forms pillars to create a large contact angle and material angle. The material angle is greater than 90 degrees, and for this type of material, low surface tension liquid cannot wet the surface, the contact angle of liquid is greater than 90 degrees. On the other hand, if the liquid contact angle smaller than the material angle, the surface tension would cause the water to attach to the texture. The re-entrant texture, or we can say, re-entrant curved texture induces a vapor-liquid interface directly upwards, and this texture forms both apparent contact angle and the texture angle of the liquid. The re-entrant material always has a greater than 90-degree material angle. If the liquid-solid contact angle even greater than its material angle, this means the texture repels the liquids. So due to the unique property of the re-entrant surface, the pull-off force for this surface is nearly ten μN, which ice can be easily drive off [31].

As the definition of the superhydrophobic surface and the super hydrophilic surface illustrated. The difference between them is the contact angle (θ). Young's Equation ($\gamma_{sv} = \gamma_{sl} + \gamma_{lv} * \cos\theta$). For the same liquid, when the surface energy of the solid contacted with it decreases, the contact angle between them will increase correspondingly. On the contrary, when the surface energy of the solid in contact with them increases, the contact angle between them will decrease relevantly. Moreover, this relation has been illustrated in Figure 7 below.
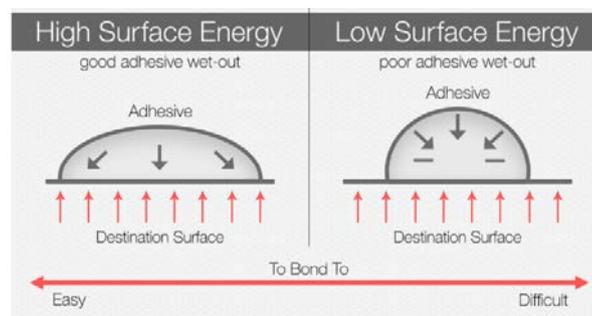

Fig. 7 relationship between surface energy and contact angle [31]

Therefore, it is an antifouling measure to select materials with low surface energy or to reduce the surface energy of materials as much as possible through artificial design to obtain superhydrophobic performance on the surface of materials and instruments.

5.2 Superhydrophobic surfaces

To a large extent, the superhydrophobic material is an ideal antifouling material. For example, a superhydrophobic dry gel was synthesized from a mixture of nanoscale fluorosilicone, fluorooxysilane and dorsal bone silane has been reported by Privett and others. In this report, the researchers studied the adhesion of Staphylococcus aureus and pseudomonas aeruginosa to the surface using a coating made from a mixture of fluoro silane, raloxifene and spinal silane and a coating made from a mixture of untreated silicones, raloxifene and spinal silane. The result is that the adhesion of Staphylococcus aureus and p. aeruginosa to fluorinated surfaces was significantly lower than that of the control group (untreated surfaces) [32].

At the same time, there is another example to prove the antifouling property of the superhydrophobic surface. Researchers hair using hydrophobic liquid injected into porous poly (butyl methacrylate - ethylene methacrylate) surface (smooth BMA - EDMA) to reduce the adhesion of Pseudomonas aeruginosa. Under the same conditions, environmental pseudomonas aeruginosa pa49 strains only covered about 1.8% of the sliding surface and did not cover glass is suppressed by about 55% coverage [33].

There is a report, which provides strong evidence for the anti-fouling property of the superhydrophobic surface. By chemical etching and surface caused by radical atomic polymerization (SI - ATRP), methyl acrylate grafted fluorine polymer, the preparation of superhydrophobic antifouling polyethene terephthalate polyester (PET) fabric. By adjusting the polymerization time to control surface hydrophobicity, researchers reported on polymerization after eight hours of contact, Angle is close to 160 °, with the excellent antifouling performance [34].

5.3 Physical strategies

5.3. 1Physical theory

Tuning the physical properties of the surface should be a different design approach to limit solid or liquid fouling. Especially the Youngs Modulus (E). Particularly, when a rigid material adhered to an elastic surface, the strength of its adhesive bond is proportional to both the work of adhesion and the Elastic Modulus (E) of the surface material should be meeting this relation, which has been illustrated below.

$$\sigma \propto \sqrt{W_a \cdot \frac{E}{t}}$$

Where σ is the strength of the adhesive bond. Meanwhile, W_a is the work of adhesion, E is the Elastic Modulus (Youngs Modulus), and t is the film thickness.
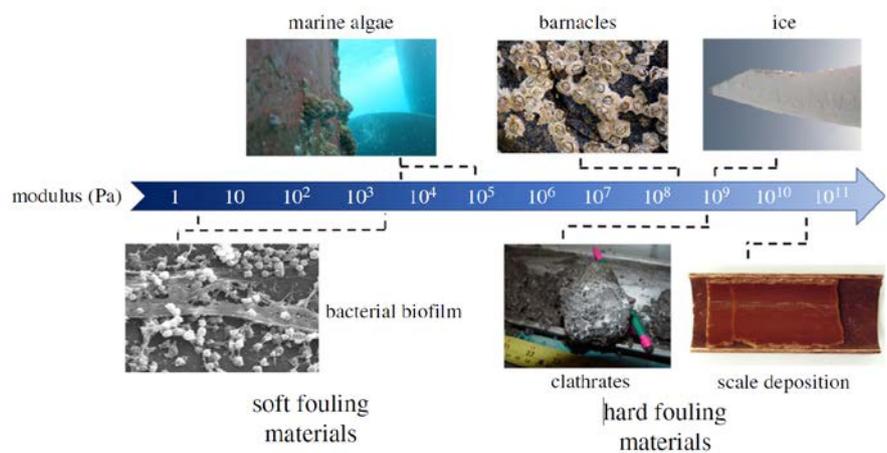

Fig. 8 Fouling material types at each modulus

5.3.2 Antifouling topography

There are two types of antifouling topography. One is the lotus effect, and another is shark-skin patterns. The microscopic structure of the surface of a shark-skin has been shown in Figure 9 below.
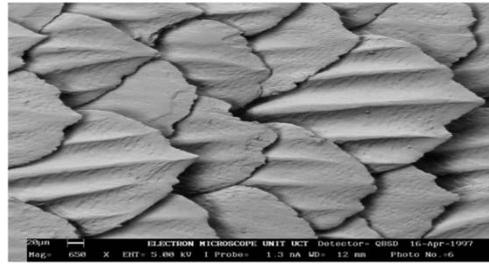

Fig. 9 Shark skin surface topography

Meanwhile, the microscopic structure of the surface of a lotus has been illustrated in Figure 10 and 11 below.
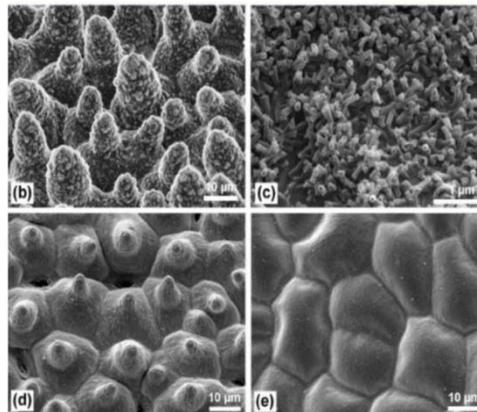

Fig. 10 Lotus leaf surface

Fig. 11 Lotus leaf surface topographies

Where (a) is the lotus leaf, it is upper showed remarkable water repellency.

(b) is an upper leaf surface image prepared by the "glycerine replacement" method, taken by scanning electron microscopy (SEM). This shows a layered surface structure composed of mastoid processes, wax clusters and wax tubules.

Picture (c) is a small wax tube in the upper side of the leaf. (d) upper leaf surface after drying at a critical point (CP). The wax tubules dissolve, and the pores are noticeable 15° inclination. (e) under the leaf surface (CP drying) were convex cells without stomata [20].

The differences between those two types of antifouling topography have been described by Table 1.

Table 1 The difference between the lotus topography and the shark-skin topography

Micropatterning of surfaces	Principle/Mechanism	Advantages	Disadvantages
Lotus effect	Super-hydrophobic self-cleaning ability to prevent water meter surface adhesion	The effect of dull, waxy surfaces is enhanced by the physical texture	Limited technology, high cost and weak universality
Shark-skin patterns	Chemical antifouling agents adhere to the surface of cells	The surface is physically modified to enhance the effect of chemical antifouling agent	Poor general cut jin Yong yu used for sports surface.

5.4 Coating

5.4.1 Intro to coating

Due to the different materials' chemical and physical stability, some firms using a thin plating on the object for protection. The different plating methods can be classified into four categories: chemical coatings, self-polishing coatings, temperature, pressure-responsive coatings, and pH-responsive coatings.

5.4.2 Chemical coatings

The application of the marine superhydrophobic coating is a type of chemical coatings, which differs from other superhydrophobic coatings. Generally, marine coatings are films made of polymer or metal materials (usually less than 500 μm thick), which are mainly used to protect and modify exposed surfaces of structural materials used in the marine environment [35]. Besides, the coating formed by the coating can prevent structural materials from being corroded by the environment. This kind of coating is generally formed by inorganic compounds suspended in liquid solutions of polymers and volatile organic solvents, but in some exceptional cases, it can also be formed in inorganic solvents such as water. Coatings can also be made of solid plastics and metals. In both processes, the dry powder adheres to the ship's surface, which is then heated to melt and re-cooled to form a solid film. Another method is to use a particular spray gun to spray dry powder, melt it into molten plastic and spray. The molten plastic cools to form a film on the surface. Solid metal can be obtained by immersing an object in a molten metal bath or spraying the molten metal on the surface to be protected. Metallic coatings usually use aluminium or zinc and are then electrochemically treated to turn them into alumina or zinc oxide. The marine antifouling coating is a kind of special marine coating, which can effectively prevent the marine organisms and microorganisms from adhering to the surface of the ship and also can prevent the inorganic salt ions in the seawater from corroding the internal structure of the ship.

5.4.3 Self-polishing coatings

Self-polishing antifouling paint is a kind of paint which can keep the bioactive interface between the coating and water and make the coating wear smoothly. Therefore, the coating not only provides a protective film for the ship to prevent the growth of the ocean but also minimizes the resistance of the ship to move forward in the ocean. The paint is similar to sharkskin. For example, non-silicone biocide-free antifouling solutions. The bactericide free self-polishing coating is a kind of coating which uses the same chemistry and technology as TBT and Wuxi copper-based self-polishing coating. In the non-toxic SPCs, the biocides combined with copolymers are replaced by non-toxic compounds. Like that of TBT and copper-based SPC coatings, the hydrolysis process separates the substituent side groups from the polymer main chain and then becomes soluble. Methacrylate and several specially designed epoxy resins are used to prepare self-polishing coatings without biological toxicity. Its purpose is to create an active polished surface, so that the adhesion of dirt on its surface becomes unstable, to achieve the purpose of self-cleaning [36].

5.5 Natural products as antifoulants

The function of rough layered surfaces is to create cavitation. The water drop is located at the top of the trapped air, which dramatically reduces the contact between the solid surface and the liquid surface. The contact angle of its surface is close to 180 ° so that the water drop forms a nearly perfect sphere on its surface and easily rolls on the surface. The most typical example of this surface is the lotus leaf. Scanning probe microscopy shows that the leaves are covered with 1-5 μm protrusions, which are called papillae. The surface structure below the top layer of waxy crystal means that raindrops and any surface dirt will roll down easily. Another example from biology is the rose petal, which has been shown in Figure 12.

Similar to the surface microstructure of lotus leaf, rose petal also has a layer of hydrophobic wax layer, and the epidermis is covered with the hierarchical structure surface formed by manifold and cone-shaped nipple. Nevertheless, different from the surface of the lotus leaf is the size of these structures (the diameter of a rose petal is 16 μ m, while that of the lotus leaf is 11 μ m) [37].

Fig. 12 Electron micrographs of the surface of rose petals

6. Design of bio-inspired surface for medical biofouling resistance

6.1 Strategies for designing anti-fouling biomedical surfaces

Biofouling is one of the main challenges in the development of biomedical equipment. Biofouling means that the surface is contaminated by microbes such as bacteria, fungi, and viruses. When biofouling occurs in common medical applications, it increases the risks of inflection, biosensor failure, and implant rejection. Common medical applications include biosensors, medical implants, surgical devices, and prosthetic devices. Moreover, the foreign body's reaction to the artificial material often leads to the formation of biofouling, which limits the clinical service lifetime of the equipment. These problems are the factors that lead to the development of surfaces with effective antifouling properties [38].

Strategies for designing medical antifouling materials can be summarized into three broad categories: inhibiting protein adsorption, killing bacteria and microorganisms, and self-cleaning [39].

Bacteria and microorganisms are the direct reason for the biofouling formation. Bacterial films are usually formed as a result of bacterial colonization. Once the right environment is established, the bacteria can attach to the surface and multiply into small colonies that formed biofilms. This is the reason for designing a surface to kill bacteria [38].

The inhibition of protein adsorption can also effectively reduce the formation of biofouling. This is because biofouling is based on the adsorbed protein on the surface, which act as platforms on which bacteria attach. Besides, protein fouling is another major problem in the development of many biomedical devices, especially which contact with blood. Thrombus formation is sometimes caused by fibrin and platelets in the flowing blood that adheres to the surface of these artificial materials. This eventually leads to fatal complications and equipment failures [39].

The third strategy is to design self-cleaning surfaces that enable the microbes not to stick to the surfaces. Many examples of this performance have been developed in nature [39].

6.2 Design for protein resistance surface

6.2.1 Coating that prevents protein fouling

The PEG-based coating is a commonly used method to given protein resistance for the surface. PEG can be attached to the surfaces by several techniques, such as chemical and physical adsorptions, block or graft copolymerization and direct covalent attachment. Comparing these techniques, covalent attachment and physical adsorption of PEG chains usually have a limitation in reducing the adsorption of proteins below a certain bound. This is due to space problems that limit the density of adsorbed polymer chains [40].

Studies have shown that the PEG chain is compressed when proteins approach the substrate, resulting in the rejection of the protein. During the compression, water molecules from the hydrated polymer chain are removed. This leads to the thermodynamically unfavorable osmotic penalties, which may cause the repulsion by the elastic and permeable stresses. The chain length of PEG and the surface density can influence the magnitude of the repulsive force. The longer chain length can generate larger protein resistance. A variety of antifouling surface generated techniques is developed to tether PEG on different substrates for achieving a higher protein resistance [39] [40].

However, in the presence of oxygen, PEG has a tendency to spontaneously oxidize and form aldehydes and ethers. This can result in lower protein resistance to the surface. Self-assembled monolayers (SAMs) presenting ethylene oxide groups are considered to be the alternative molecules for high protein resistance. Mixed SAMs can generate highly protein-resistant surfaces. Based on the researches, surfaces with SAMs of alkane thiolates with only two ethylene oxide groups show a noticeable protein resistance. This means that it is possible to add more chains per unit surface area when using SAMs. Therefore, the more effective surface coverage can be obtained by a shorter chain length [40].

Although SAMs have so far been characterized by high surface coverage and ease of manufacture, their vulnerability, and the lock of robustness need to be considered. PEGs attached to the substrates are robust, but they do not reduce the protein adsorption as effectively as SAMs [40].

6.2.2 Use of Biological molecules

Biological molecules are considered to be used for antifouling because they are natural biomolecules with less toxicity, higher efficiency, and greater specificity than many synthetic compounds. Peptide and peptoid modified surfaces are developed for the protein resistance surfaces.

Peptide-based material is chosen for designing anti-fouling surfaces due to their excellent resistance to proteins such as fibrinogen, fibronectin and so on. Amino acids, peptides, and other natural biological molecules are also used to develop innovative antifouling materials because they are structurally recombined under physiological conditions to prevent biofouling.

Peptoid-based material, which is an unnatural biomimetic polymer, and peptide-based material can regulate the surface structure and the ability of antifouling. Because of the sequence specificity of peptides, many known antifouling functions can be combined using single backbone chemistry at precisely known locations. Such sequence-specific libraries can be designed for optimal performance. The short functional peptide domains have a strong adsorption ability to various surfaces, while the oligomers of peptides are resistant to the contamination of proteins and cells. Peptide and peptoid modified surfaces show great resistance to protein adsorption [39].

6.2.3 Chemical modification of surfaces

Generally, following this approach to design a biofouling surface, the silicones or fluorinated polymers will be selected because those two types of material are among the lowest surface energy materials. Beyond those that were mentioned above. Surface chemistries which interact specifically with a fouling material vary more widely. For example, the zwitterionic polymer surfaces designed to repel biofilms and proteins and the conductive films for the repulsion of dirt and dust. Therefore, the use of superhydrophobic surfaces to avoid contamination of some soluble electrolytes, organic acids, or bacteria also makes sense in principle and engineering applications [17].

Table 2 The relevant examples of chemical modification [17]

Chemical	Principle/Mechanism	Advantages	Disadvantages

modification			
Hydrophilic polymers	The potent combination of water cannot be replaced by protein, thereby inhibiting protein adsorption.	GRAS (generally recognized as safe) substance polyethene glycol (PEG) approved by the Federal Drug Administration (FDA)	Due to oxidation damage and low surface density, the material cannot be used for a long time.
Immobilization of PEG	The use of anchor mussel - mimicking the linker.	Compared with the free polyethene glycol, it is not easy to hydrolyze and naturally degrade	Restricted to apply to the surface of the anchor pile function of availability
Zwitterionic polymers	Through the formation of "super-hydrophilic" high protein resistance	The antifouling characteristics can be survived in a long time and unique ability of ligand immobilization.	Low commercial availability
Hydrophobic polymers	The adsorption of proteins requiring polar surfaces is highly inhibitory.	Steady commercial availability and wide range	Some hydrophobic polymers have specific toxicity

6.3 Design for antibacterial surface

6.3.1 Nitric oxide-releasing materials

Microbicidal coatings can be useful in killing the bacteria approaching the surfaces. Nitric oxide-releasing coating is one of the microbicidal coatings in use [39].

Nitric oxide (NO) is a naturally generated bactericide that is produced by the body's immune system in response to bacterial infections. NO is a powerful oxidant that can destroy bacterial cell membrane, spread into cells and damage DNA and proteins within the cells. Because nitric oxide is naturally released in the body by the endothelial cells and other sources, and have a short half-life time in the body, the NO-release coating is thought to enhance the biocompatibility of biological implants. As a suitable material for the manufacture of biomedical devices with high antifouling capacity, Nitric oxide-released materials are used to reduce the antithrombotic properties of intravascular oxygen sensors, vascular grafts, and antibacterial coatings [39] [40].

Although NO-released materials have many advantages, its limitations also need to be considered. The high reactivity and short half-lifetime of NO make it difficult to apply to many biomedical applications because it requires proper storage and transport. Moreover, nitrite oxide has no effect on certain types of colonies and even stimulates the formation of biofilm in some cases [39].

6.3.2 Silver-Releasing Coatings

Unlike the nitric oxide, silver nanoparticles are not naturally produced. Silver and silver nanoparticles are widely known as strong bactericides. Also, the low toxicity of silver is another benefit of being an antibacterial material in the development of biomedical antifouling surfaces. Silver and its compounds are widely used in many medical applications, such as burn treatment, wound dressing, and medical apparatus [40].

Antibacterial silver ions or nanoparticles grow or are embedded in polyelectrolyte multilayer films, polyamides, and other polymers as well as hydrogels to form antibacterial films [40]. The rate and time of silver ion release influence the antimicrobial effect of the silver source and can be adjusted by changing the shape, size and surface coating of the added silver. For silver nanoparticles with a certain mass, the total surface area increases with the decrease in particle diameter and the ion release rate increases accordingly. The available surface area and ion release rate will be reduced if particles become unstable in solution or aggregate when bound to the matrix. Different facets of non-spherical silver nanoparticles with different shapes dissolve at different rates, resulting in the ion release rate of a particular shape. The absorption of different molecules onto the surface of the nanoparticles by the surface coating regulates the dissolution rate.

However, silver-resistant strains are emerging because of the widespread use of silver [40].

6.4 Design for self-cleaning surface

6.4.1Bio-inspired self-cleaning surface

The most widely known natural surface for its self-cleaning properties is the lotus leaf. The lotus leaf is superhydrophobic, which means when the water drops fall on the surface of the lotus leaf, the dirt can be carried away as the water drops roll down. The superhydrophobic surface and the photoactivated self-cleaning surface have similar characteristics, but the superhydrophobic surface can only prevent the pollutants from adhering to the surface instead of degrading the foulant. The preparation of superhydrophobic surfaces requires the combination of low surface energy material and high roughness surface. Silica nanoparticles are commonly used in the design and manufacture of superhydrophobic surfaces [39].

Another nature self-cleaning surface comes from the fast-moving shark skin. Based on the analysis of the microscopic morphology, parameters that need to be considered during the surface design are given. For developing a high fouling resistance surface, the fractal dimension and the mean values of roughness need to be small, while the anisotropy value and the skewness of roughness should be high. Surface characteristic and morphology characteristics are important features of biomedical antifouling surfaces. However, the surface patterning requires complex manufacturing techniques and harsh synthetic conditions, which limits the type and geometry of the substrate that can be coated [39].

6.4.2 Self-cleaning coating (Protein-degrading films)

(1) Photoactivated self-cleaning films

Self-cleaning coatings need to be considered for developing the protein-degrading films. The photoactivated self-cleaning film can be mainly focused on because it can decompose the foulants in the presence of ultraviolet or visible radiation. This is because the reactive oxygen species (ROS) produce in this condition can break down the foulant. The electrons can change from the ground singlet state to the excited singlet state when ultraviolet or visible light is applied to the photosensitizer [40].

There are two types of reaction pathways that can produce ROS. In the type one pathway, superoxide ion may be produced and these electrons can be in the ground state. In the type two pathway, electrons are facilitated into the excited singlet state because the energy is transferred to oxygen. These produced highly reactive substances (hydroxyl radicals, singlet oxygen, and superoxide ion) can be used to degrade a variety of foulant. Titanium dioxide is the most commonly used photoactive material, which can break down various types of foulant and keep itself clean under ultraviolet and visible light [40].

(2) Protease-Based Antifouling Films

Protein-degrading films can be developed by adding proteases to the surface coating. Covalent attachment or sol-gel entrapment methods need to be used to prepare the anti-protein coatings by immobilized hydrolytic enzymes into a poly (PDMS) matrix. The hydrolytic enzymes can be α-chymotrypsin (α-CT) and pronase. These formulations of enzyme-PDMS can be directly cast into thin biocatalytic films or combined with oil-based coatings [40].

When the enzyme is α-CT, using the sol-gel method for preparing the antifouling coatings can have a higher film activity than using the covalent attachment. This is due to the partial denaturation of α -CT, which is caused by the formation of covalent bonds between PDMS and enzymes during polymerization. In contrast, the covalent attachment method gives a higher film activity than the sol-gel method when using pronase as the enzyme [40].

Antifouling coatings prepared by covalent attachment with both enzymes containing PDMS significantly inhibit the adsorption in proteins on the surface. The decrease in the adsorption amount of protein on the protease-containing film is due to the increase of conformational entropy. This is caused by the protein molecules' degradation, which reduces the Gibbs free energy of the adsorbed peptide fragments [40].

7. Limitation and future development

7.1 Prospect of bionic antifouling coating on ship surface

With the improvement of marine environmental protection awareness, Environmentally Friendly Antifouling Coatings came into being. The organosilicon antifouling coating has been widely developed and used at present because it can inhibit biological pollution by physical means and does not pollute the marine environment.

However, there are many defects in organosilicon antifouling coatings due to the structural characteristics of organosilicon materials, which need to be improved. This paper introduces the research progress of polymer-modified silicone coating, and micro nanopowder modified silicone coating and silicone biomimetic composite antifouling coating system. It is pointed out that fluorosilicate modified silicone can not only ensure the low surface energy characteristics of silicone coating but also improve the mechanical properties of the coating. Polyurethane modified silicone and acrylic modified silicone use polyurethane and acrylic resin to improve the adhesion of silicone antifouling coating and substrate. The most crucial feature of micro-powder modified organosilicon is that it can be modified simultaneously with resin, to achieve double effect antifouling effect. In response to the development of biomimetic technology, silicone biomimetic composite antifouling coating is constructed to achieve the long-lasting antifouling effect by simulating the biological characteristics of marine organisms. At last, it is pointed out that organosilicon antifouling coatings will develop towards the direction of multiple modifications and composite antifouling in the future.

7.2 Prospect of bionic antifouling coating on civil engineering

Because the microorganism in soil and the ammonium ion and sulfuric acid ion in groundwater have strong corrosiveness to the reinforced concrete foundation, the service life of the concrete foundation is limited, which affects the service life of the whole building. the mechanical strength of the traditional superhydrophobic coating is low. therefore, it cannot be used as the water-resisting layer of the house foundation. however, the appearance of superhydrophobic materials with high wear resistance makes the application of bionic superhydrophobic materials in civil engineering possible.

References

[1] M. E. C. James A. Callow (2011). Trends in the development of environmentally friendly fouling-resistant marine coatings. Nature Communications, vol. 2, no. 1, pp. 244-245.

[2] M. P. Schultz, J. A. Bendick, E. R. Holm and W. M. Hertel (2011). Economic impact of biofouling on a naval surface ship. Biofouling, vol. 27, no. 1, pp. 87-98

[3] G. D. Bixler and B. Bhushan (2012). Biofouling: lessons from nature," Philosophical Transactions of the Royal Society A, vol. 370, no. 1967, pp. 2381-2417.

[4] Dove, G. Devaud, X. Wang, M. Crowder, A. Lawitzke and C. Haley (2011). 2011Mitigation of lunar dust adhesion by surface modification. Planetary and Space Science, vol. 59, no. 14, pp. 1784-1790.

[5] P. A. Schweitzer (2010). Fundamentals of corrosion – Mechanisms, Causes and Preventative Methods. Boca Raton, CRC Press, Fla, pp. 430.-431.

[6] E. &. T. D. Gellert (1999). Seawater immersion ageing of glass-fibre reinforced polymer laminates for marine applications. Composites Part A: Applied Science and Manufacturing, vol. 30, no. 11, pp. 1259-1265.

[7] S. M. Olsen, L. T. Pedersen, M. H. Laursen, S. Kiil and K. Dam-Johansen (2007). Enzyme-based antifouling coatings: a review. Biofouling, vol. 23, no. 5, pp. 369-383.

[8] S. Walmsley (2006). Tributyltin pollution on a global scale. An overview of relevant and recent research: impacts and issues. WWF UK, Godalming, Surrey.

[9] B. Antizar-Ladislao (2008).Environmental levels, toxicity and human exposure to tributyltin (TBT)-contaminated marine environment. A review. Nvironment International, vol. 34, no. 2, pp. 292-308.

[10] N. H. Budak, E. Aykin, A. C. Seydim, A. K. Greene (2014). Functional Properties of Vinegar," Journal of Food Science, vol. 79, no. 5, pp. R757-R764.

[11] C.-Y. &. J. A. Hui (2013). Surface tension, surface energy, and chemical potential due to their difference. Langmuir : the ACS Journal of Surfaces and Colloids, vol. 29, no. 36, pp. 11310-11316.

[12] Schwartz (2002). Chapter II Surface tension and surface energy," in Textile Science and Technology, vol. 13, pp. 57-91.

[13] S. Banerjee (2008). Simple derivation of Young, Wenzel and Cassie-Baxter equations and its interpretations. arXiv.org.

[14] K. Seo, M. Kim and D. H. Kim (2015). Re-derivation of Young's Equation, Wenzel Equation, and Cassie-Baxter Equation Based on Energy Minimization. in Surface Energy, M. Aliofkhazraei, Ed.

[15] C. M. Kirschner and A. B. Brennan (2012). Bio-Inspired Antifouling Strategies. Annual Review of Materials Research, vol. 42, pp. 211-229.

[16] Z. Li and Z. Guo (2019). Bioinspired surfaces with wettability for antifouling application. Nanoscale, vol.11, no. 47, pp. 22636-22663.

[17] B. Bhushan (2012). Encyclopedia of Nanotechnology, Dordrecht Springer Netherland.

[18] W. Barthlott, C. Neinhuis (1997).Purity of the sacred lotus, or escape from contamination in biological surfaces. Planta, vol. 202, no. 1, pp. 1-8.

[19] H. J. Ensikat, P. Ditsche-Kuru, C. Neinhuis (2011). Superhydrophobicity in perfection: the outstanding properties of the lotus leaf," Beilstein Journal of Nanotechnology, vol. 2, pp. 152-161.

[20] M. Nosonovsky and B. Bhushan (2012). Lotus Versus Rose: Biomimetic Surface Effects. Green Energy and Technology, vol. 49, pp. 25-40.

[21] S. Wang, K. Liu, X. Yao and L. Jiang (2015). Bioinspired Surfaces with Superwettability: New Insight on Theory, Design, and Applications," Chemical Reviews, vol. 115, no. 16, pp. 8230-8293.

[22] Roslizar, S. Dottermusch, F. Vullers, M. Kavalenka, M. Guttmann, et al (2019). Self-cleaning performance of superhydrophobic hot-embossed fluoropolymer films for photovoltaic modules. Solar Energy Materials and Solar Cells, vol. 189, pp. 188-196.

[23] Bhushan, M. Nosonovsky (2010). The rose petal effect and the modes of superhydrophobicity," Philosophical Transactions of the Royal Society A, vol. 368, no. 1929, pp. 4713-4728.

[24] L. Feng, Y. Zhang, J. Xi, Y. Zhu (2008). Petal Effect: A Superhydrophobic State with High Adhesive Force. Langmuir, vol. 24, no. 8, pp. 4114-4119.

[25] J. Long, P. Fan, D. Gong, D. Jiang (2015). Superhydrophobic Surfaces Fabricated by Femtosecond Laser with Tunable Water Adhesion: From Lotus Leaf to Rose Petal. ACS applied materials & interfaces, vol. 7, no. 18, pp. 9858-9865.

[26] C. G. Bernhard and W. H. Miller (1963). A corneal nipple pattern in insect compound eyes. Acta Physiologica Scandinavica, vol. 56, no. 3-4, pp. 385-386, November 1963.

[27] P. Perez Goodwyn, Y. Maezono, N. Hosoda, et al (2009). Waterproof and translucent wings at the same time: problems and solutions in butterflies. Naturwissenschaften, vol. 96, no. 7, pp. 781-787.

[28] Kesel, R. Liedert (2007). Learning from nature: Non-toxic biofouling control by shark skin effect. Comparative Biochemistry and Physiology A-Molecular & Integrative Physiolog, vol. 146, no. 4, pp. S130-S130.

[29] M. Liu, S. Wang, Z. Wei, Y. Song (2009). Bioinspired Design of a Superoleophobic and Low Adhesive Water/Solid Interface. Advanced Materials, vol. 21, no. 6, pp. 665-669.

[30] Z. Dong, M. F. Schumann, M. J. Hokkanen, et al (2018). Superoleophobic Slippery Lubricant-Infused Surfaces: Combining Two Extremes in the Same Surface. Advanced Material, vol. 30, no. 45, pp.12-13.

[31] B. J. Privett, J. Youn, S. A. Hong, J. Lee, J. Han (2011). Antibacterial fluorinated silica colloid superhydrophobic surfaces. Langmuir: the ACS journal of surfaces and colloids, vol. 27, no. 15, pp. 9597-9601.

[32] J. Li, T. Kleintschek, A. Rieder, Y. Cheng (2013). Hydrophobic liquid-infused porous polymer surfaces for antibacterial applications. ACS applied materials & interfaces, vol. 5, no. 14, pp. 6704-6711.

[33] C.-H. Xue, X.-J. Guo, J.-Z. Ma (2015). Fabrication of robust and antifouling superhydrophobic surfaces via surface-initiated atom transfer radical polymerization," ACS applied materials & interfaces, vol. 7, no. 15, pp. 8251-8259.

[34] H. a, S. b (2001). Marine Coatings," in Encyclopedia of Materials: Science and Technology (Second Edition), 2001, pp. 5174-5185.

[35] C. Hellio and D. Yebra (2009). Advances In Marine Antifouling Coatings And Technologies | Sciencedirect, Elsevier Ltd. pp. 1-764.

[36] T. Darmanin, F. Guittard (2015). Superhydrophobic and superoleophobic properties in nature. Materials Today, vol. 18, no. 5, pp. 273-285.

[37] D. C. Leslie, A. Waterhouse, J. B. Berthet, T. M. Valentin (2014). A bioinspired omniphobic surface coating on medical devices prevents thrombosis and biofouling. Nature Biotechnology, vol. 32, no. 11, pp. 1134-1140.

[38] V. B. Damodaran, N. S. Murthy (2016). Bio-inspired strategies for designing antifouling biomaterials. Biomaterials Research, vol. 20, pp.18-19.

[39] Banerjee, R. C. Pangule, R. S. Kane (2011). Antifouling Coatings: Recent Developments in the Design of Surfaces That Prevent Fouling by Proteins, Bacteria, and Marine Organisms. Advanced Materials, vol. 23, no. 6, pp. 690-718.