Chapter 1

Introductory Chapter: Superhydrophobic Surfaces - Introduction and Applications

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Additional information is available at the end of the chapter

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1. Introduction

Superhydrophobicity was first observed in the nature on lotus leaf and in some other plants in which their leaves would not get wet. The main reason of this phenomenon was the unique surface structure of the lotus leaf and also presence of a low surface energy material on the surface of the leaf. In order to achieve superhydrophobic surface or coating, the surface must possess hierarchical micro- and nano-roughness and low surface energy at the same time. Hierarchical micro- and nanoscale roughness will trap air on the surface that will cause increase in water contact angle, and low surface energy will decrease the tendency of water to have bonding with the surface. So, almost all the methods to achieve superhydrophobicity consist of two steps: first to make a hierarchical surface roughness and then surface modification by a low surface energy solution of some materials like fatty acids, fluoroalkyl silanes, etc.

Atoms and molecules of liquid and solid have higher energy on the surface because there are few chemical bonds on the surface. This energy of surface atoms or surface molecules is known as the surface tension or the surface free energy. This energy is shown by γ and is equal to energy per unit area needed to build surface in constant temperature and pressure (J/m^2 or N/m). In case solid and liquid are in direct contact with each other, the surface energy will be lower in comparison to the situation in which these two are separated. The relation between surface energies and adhesion work is shown in Dupre equation.

$$W_{SL} = \gamma_{SA} + \gamma_{LA} - \gamma_{SL} \quad (1)$$

In this equation, W_{SL} is the adhesion work per unit area, γ_{SA} is the surface free energy between air and solid, γ_{LA} is the surface energy between air and liquid, and γ_{SL} is the surface free energy between liquid and solid.

When water droplet is placed on the surface of the solid, these two will reach equilibrium and water droplet makes a specific angle with the surface known as water contact angle (θ_0). The total energy can be calculated by the below equation:

$$E_{total} = \gamma_{LA}(A_{LA} + A_{SL}) - W_{SL}\, A_{SL} \tag{2}$$

In this equation, A_{LA} and A_{SL} are, respectively, liquid/air interface and liquid/solid interface. In this situation, regardless of gravitational potential energy and in constant volume and pressure in the equilibrium, dE_{total} is considered equal to zero.

$$\gamma_{LA}(d\, A_{LA} + d\, A_{SL}) - W_{SL}\, d\, A_{SL} = 0 \tag{3}$$

For a droplet with constant volume, θ_0 can be calculated by the equation below:

$$d\, A_{LA} / d\, A_{SL} = \cos\theta_0 \tag{4}$$

Then according to these equations, $\cos\theta_0$ can be calculated by the equation below known as the Young's equation:

$$\cos\theta_0 = (\gamma_{SA} - \gamma_{SL}) / \gamma_{LA} \tag{5}$$

2. Wetting models

Several wetting models have been defined to calculate contact angle on the surface. The first wetting model is Young's equation that was just mentioned. This model does not consider surface roughness of the solid surface. The Young's equation is shown below:

$$\cos\theta = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}} \tag{6}$$

In this equation, θ is contact angle and γ_{SG}, γ_{SL}, and γ_{LG} are, respectively, surface free energy of solid/gas, solid/liquid, and liquid/gas interface.

It is obvious that in most cases, the surface is not smooth; so, Young's equation is not able to calculate the contact angle properly; thus, Wenzel equation was introduced. In this equation, it is considered that the surface wetting occurs uniformly and the equation is shown below:

$$\cos\theta w = r\cos\theta \tag{7}$$

In this equation, θw is the Wenzel contact angle, θ is Young's contact angle, and r represents the surface roughness factor that is equal to ratio of real surface to apparent surface.

As mentioned before, wetting is considered to be uniform in Wenzel's equation, or in other words, it is considered that water went through all surface cavities and there is no dry part. On the other hand, there is another wetting model that considers that the wetting is not

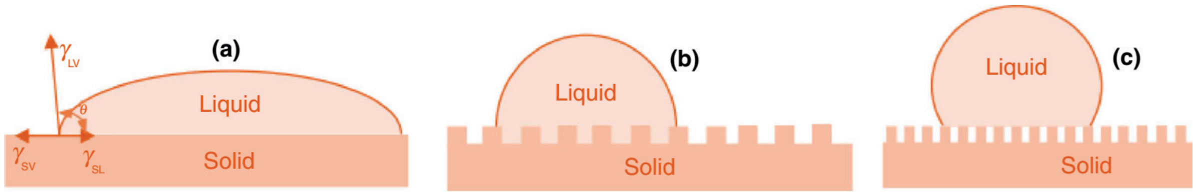

Figure 1. Schematic illustration of (a) Young's model, (b) Wenzel model, and (c) Cassie-Baxter model.

uniform and air packets do not let water to get into the surface cavities. In this case, water is in contact with solid and air packets, and water contact angle with air is equal to 180°. The model is called Cassie-Baxter and the equation is shown below:

$$cos\,\theta_{CB} = f_1 * cos\,\theta_1 + f_2 * cos\,\theta_2 \; cos\,\theta_{CB} = f_1 * cos\,\theta_0 + f_2 * \cos(\pi) \quad (8)$$

$$cos\;\theta_{CB} = f_1 * cos\theta - f_2 \quad (9)$$

$$\cos\theta_{CB} = \mathrm{f}_1 * (\cos\theta + 1) - 1 \quad (10)$$

In the above equations, θ_{CB} is the Cassie-Baxter contact angle, f_1 is the ratio of area that liquid is in contact with solid, and f_2 is that ratio of area that liquid is in contact with air packets made or trapped air inside the surface cavities. In **Figure 1**, the difference between three aforementioned wetting models is shown [1].

3. Application of surfaces with superhydrophobic properties

Superhydrophobic surfaces and coatings as mentioned have a unique behavior against water droplets. This unique behavior result into a new set of applications including self-cleaning, anti-icing, antibacterial, oil-water separation, corrosion resistance, etc. Some applications are described below.

3.1. Oil-water separation

There have been many reports of oil contaminants in sea waters and rivers due to leak of factories waste into nature and accidents like Deep Water Horizon. Removing oil contaminants from water was always challenging and expensive; so, different methods have been introduced by scientists in order to remove them. These methods are categorized into three main groups: water removing, oil removing, and smart controllable separators. The water removing filters are superhydrophilic and superoleophobic; this kind of filters works under water and when they get wet by water, the presence of the water on the surface of the filter prevents oil to pass from the filter pores. The category in oil removing method which by my personal opinion is a more efficient way because the amount of oil is always less than the amount of water; so, it is logical that we try to remove oil from water and not water from oil. To remove oil from

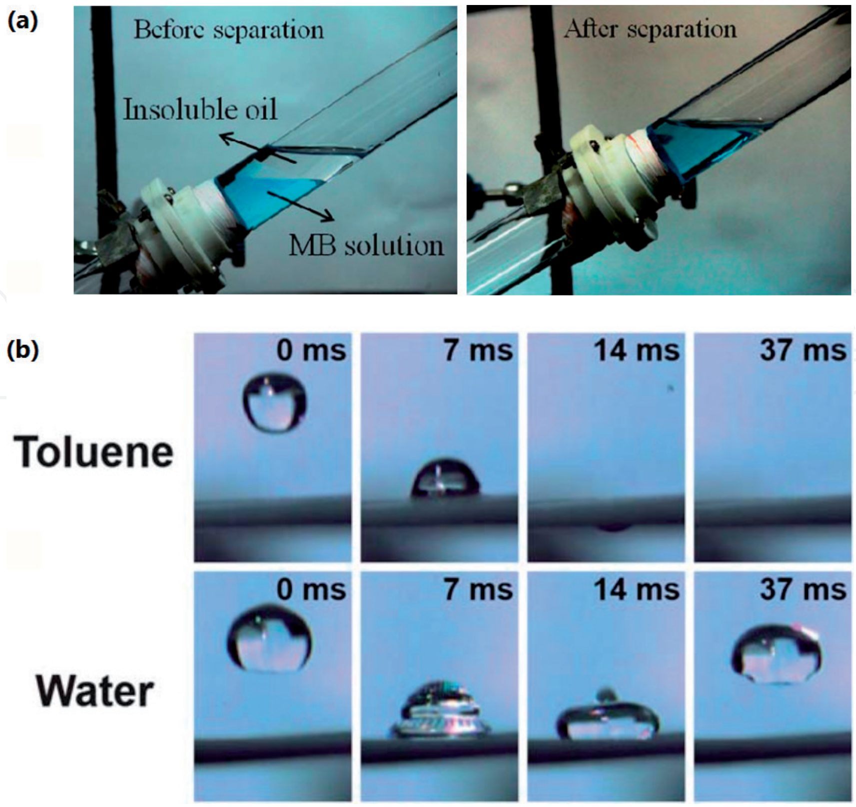

Figure 2. (a) Oil–water separation with use of TiO_2-coated superhydrophobic and superoleophilic mesh [2], (b) opposite behavior of silicone elastomer-coated mesh against water and toluene droplets [3].

water, the material should be superhydrophobic and superoleophilic. Superhydrophobic oil removing filters are the main part of the oil removing category. Gao et al. [2] used a TiO_2-coated mesh in order to separate oil from water (**Figure 2a**), and Crick et al. [3] used a silicon elastomer coating on a mesh to efficiently separate organic solvents like hexane, petroleum ether, and toluene from water. As shown in **Figure 2b**, water droplet cannot pass through the filter but toluene can easily pass through.

3.2. Corrosion resistance surfaces

There are several ways to protect a surface from corrosion. During the past two decades, scientists have been using superhydrophobic nanocomposite coatings without any toxic materials in order to protect various surfaces from corrosion. The corrosion protection capability of the superhydrophobic coatings mainly is because of the presence of air packets between surface and corrosive solution, and these packets act like a barrier and prevent from corrosive ions diffusion and protect the substrate [1].

Superhydrophobic metallic surfaces could be able to decrease the corrosion rate of metals by several orders of magnitude through imparting hydrophobization. Several reports have been published that demonstrated the enormous capability of superhydrophobic surfaces on the corrosion mitigation. The potentiodynamic polarization test revealed a significant decrease in the corrosion current density (**Figure 3**) of metallic surfaces by using a commercial hydrophobic surface modification [4].

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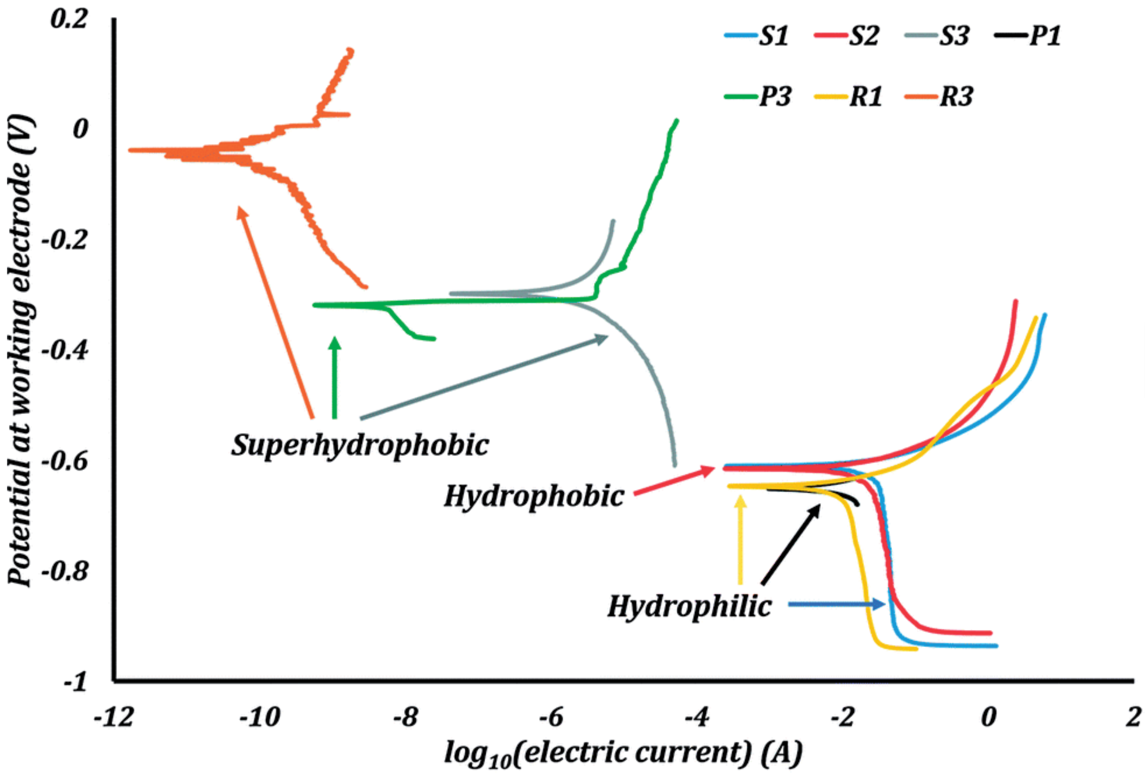

Figure 3. Potentiodynamic polarization curves of bare metallic surfaces (hydrophilic) and surface modified samples with a commercial hydrophobic material (hydrophobic) and with developed commercial hydrophobic materials (superhydrophobic) [4].

3.3. Self-cleaning properties

The lotus leaf's surface is always clean regardless of any contamination that may be present in its surrounding environment. This leaf has a unique surface structure coated with wax and shows superhydrophobic properties, and sliding angle is very low so water can easily slide on the surface of the leaf and remove any contaminants. The aforementioned properties of superhydrophobic surfaces and coatings are called self-cleaning properties. There are many superhydrophobic coatings which were synthesized with different methods and used in industries. It is worth to mention that the actual self-cleaning surface is the surface exhibiting the combined superhydrophilicity and photocatalytic behaviors to decompose the dirt. The use of the term, self-cleaning surface, is not appropriate for superhydrophobic surfaces, which are extremely dry and repel water drops. As schematically shown in **Figure 4**, these surfaces do not actually clean themselves but they wash away the dirt when the water drops roll over the surface.

3.4. Anti-icing properties

In recent years, superhydrophobic coatings have been suggested as anti-icing coatings. As mentioned before, the presence of air packets on the superhydrophobic surfaces causes the water droplets to slide easily on the surface; therefore, there will not be enough time for the droplet to freeze on the surface; consequently, this reduces the side effects of frosts on the surfaces.

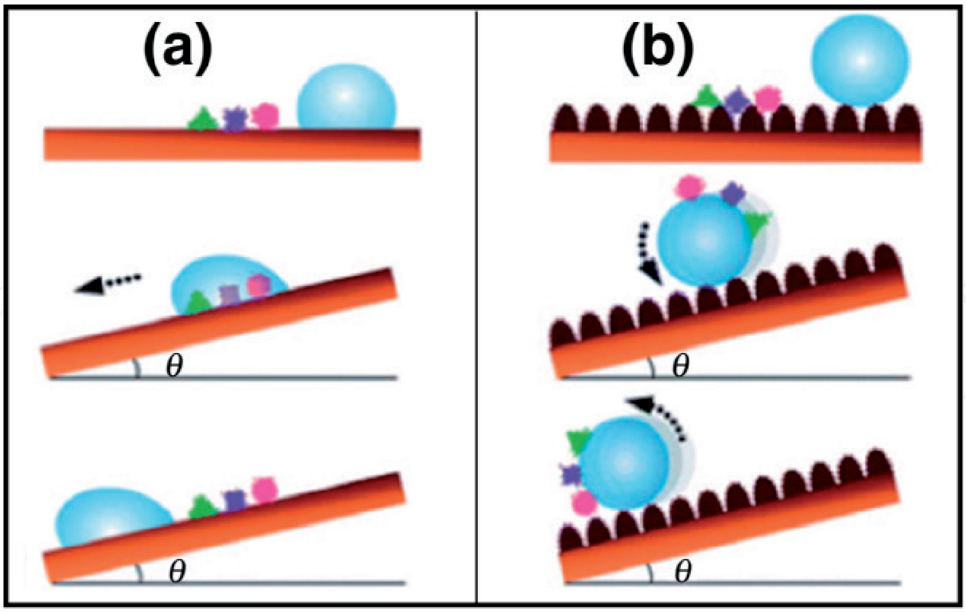

Figure 4. Schematic illustration of self-cleaning process in (a) non-hydrophobic and (b) hydrophobic surfaces.

Figure 5. Comparison of the ice formation on the uncoated and superhydrophobic-coated insulators [5].

Every year ice storms harm the equipment such as electrical transmission equipment, communication systems, aerospace facilities, highways, etc. In order to reduce this kind of damages, different methods have been developed such as local warming and preventing of ice formation by chemical activities and additives, which have some limitations in practical applications. On the other hand, the preventing of surface from ice development by superhydrophobicity phenomena could be practical in most cases without requiring special requirements and devices. One of the important applications of icephobic surfaces is using the insulators of transmission lines, which are needed to prevent the ice formation in a cold area. The experimental survey of ice formation on coated and uncoated surfaces of an insulator (**Figure 5**) under a condensing weather condition at −5°C and saturated humidity revealed that the superhydrophobic surface is completely effective in reducing ice adhesion to the surface up to 97%.

Actually scientists have some disagreements about the relations between superhydrophobicity and anti-icing properties. Some believe that these two are not related to each other; on the other hand, some insist that superhydrophobicity results to anti-icing properties. This disagreement is because there is no specific standard that can be used to evaluate ice adhesion to the surfaces; also, the method of preparing ice for each study is different from the others; so by now, it is not possible to have a definite answer to this matter. The recent studies have helped to get a better understanding about ice formation process on superhydrophobic surface but there is still much left unknown about the nucleation, growth, and adhesion to the surface which need more studies and information in this subject.

3.5. Drag reduction

Drag force is one of the major problems that a solid moving in water such as a ship or submarine faces. This force is resulted from the friction force between water and moving solid surface in the water. Inspired from shark skin, several superhydrophobic coatings were fabricated in order to reduce the drag. As mentioned before, superhydrophobic coatings have some air pockets inside their hierarchical micro- and nanoscale surface structures which will reduce the contact between solid and liquid so that the drag force will dramatically reduce. Drag reduction phenomenon by superhydrophobic surfaces was investigated in various works such as the one reported by Dong et al. [6], where they have fabricated a superhydrophobic coating on a model ship with a large and curved surface by electroless deposition of gold aggregates. The superhydrophobic model ship exhibited a remarkable drag reduction of 38.5% (**Figure 6**). On a non-coated sample, the friction is just between solid and water, but on a superhydrophobic

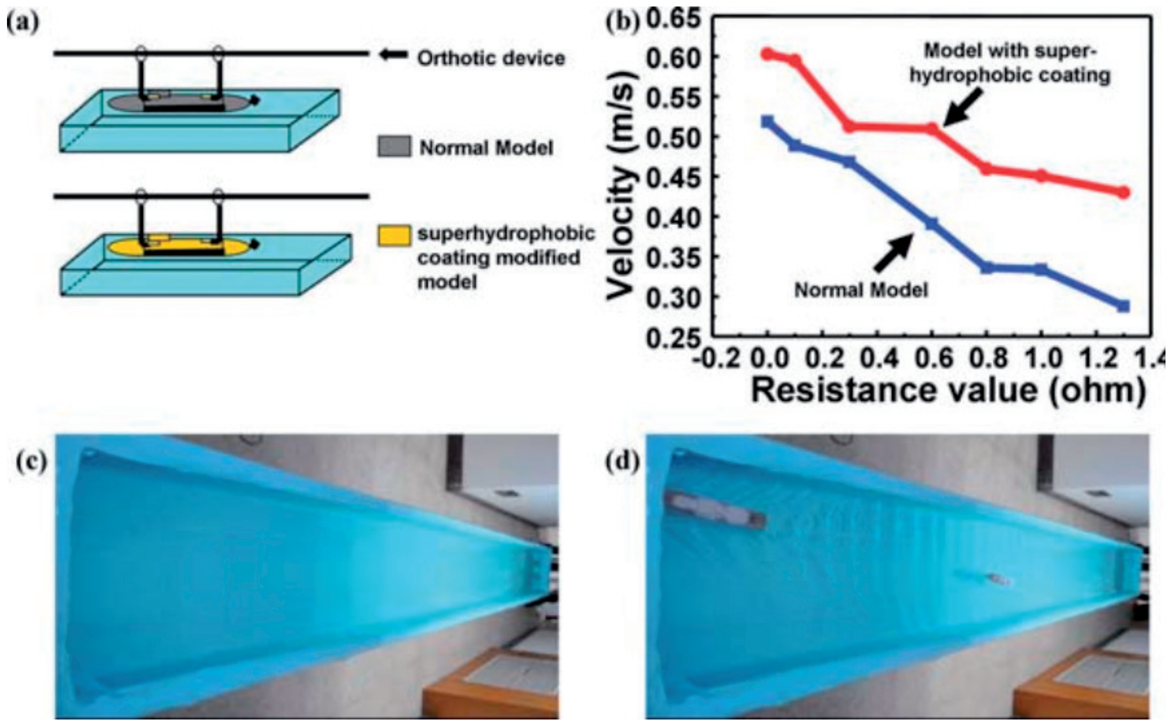

Figure 6. (a) Illustration of the device for the drag-reducing test; (b) velocity of the model ships with and without a superhydrophobic coating versus the values of the resistance in the circuit within the ship; snapshots of (c) at the beginning and (d) at the end of the drag-reducing test [6].

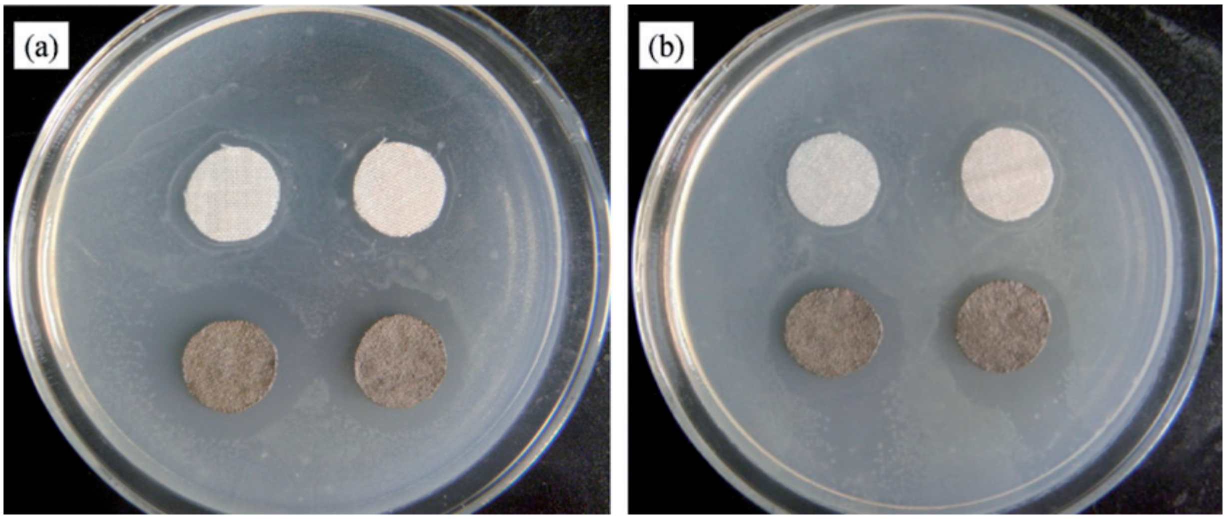

Figure 7. Antibacterial activity of (a) normal cotton (the upper two) and Ag NP modified cotton (the lower two) textiles, and (b) normal cotton (the upper two) and hydrophobized Ag NP modified cotton (the lower two) textiles [7].

surface, there are three phases, water, solid, and trapped air between these two; so, the friction will be drastically reduced in this situation which is known as the plastron effect.

3.6. Antibacterial properties

Antibacterial properties are essential in biosensors, implants, food packaging, and industrial and marine equipment. For example, one of the main reasons that cause infection in patient after surgery is bacteria that grow on implants. In order to solve this problem, antibacterial coatings that reduce the bacterial adhesion to the surface suitable are used. One research in this regard fabricated the silver nanoparticles on cotton fibers and then modified by the hexadecyltrimethoxysilane to get superhydrophobicity [7]. Antibacterial activity of the samples (inhibition zone formed on agar medium) has been determined as shown in **Figure 7**. The results showed that the normal cotton samples, exhibit no antibacterial activity, whereas the silver modified cotton surfaces killed all the bacteria under and around them showing a distinct inhibition zone with an average width of 8.78 mm around the samples.

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References

[1] Jeevahan J, Chandrasekaran M, Joseph GB, Durairaj RB, Mageshwaran G. Superhydrophobic surfaces: a review on fundamentals, applications, and challenges. Journal of Coating Technology and Research. 2018;**15**:231-250

[2] Gao C, Sun Z, Li K, Chen Y, Cao Y, Zhang S, et al. Integrated oil separation and water purification by a double-layer TiO_2-based mesh. Energy & Environmental Science. 2013;**6**: 1147-1151

[3] Crick CR, Gibbins JA, Parkin IP. Superhydrophobic polymer-coated copper-mesh; membranes for highly efficient oil–water separation. Journal of Materials Chemistry A. 2013;**1**:5943-5948

[4] Ramachandran R, Nosonovsky M. Coupling of surface energy with electric potential makes superhydrophobic surfaces corrosion resistant. Physical Chemistry Chemical Physics. 2015;**17**:24988-24997

[5] Zhu L, Xue J, Wang YY, Chen QM, Ding JF, Wang QJ. Ice-phobic coatings based on silicon-oil-infused polydimethylsiloxane. ACS Applied Materials & Interfaces. 2013;**5**:4053-4062

[6] Dong H, Cheng M, Zhang Y, Wei H, Shi F. Extraordinary drag-reducing effect of a superhydrophobic coating on a macroscopic model ship at high speed. Journal of Materials Chemistry A. 2013;**1**:5886-5891

[7] Xue C-H, Chen J, Yin W, Jia S-T, Ma J-Z. Superhydrophobic conductive textiles with antibacterial property by coating fibers with silver nanoparticles. Applied Surface Science. 2012;**258**:2468-2472