Review of Non-Fluorinated Durable Water Repellent and Stain-Resistant Materials and Their Future development.

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Abstract: Materials with superhydrophobic surfaces have significant values in industrial applications for the reason that these materials usually has the abilities of self-cleaning and stain-resisting. Currently, most superhydrophobic materials are fluorinated ones because fluorinated groups contribute to decreasing the surface energy and surface tension of materials. Nevertheless, toxicity of fluorinated materials prevents them from being widely used in some industrial areas. Thus, this paper aims to have a review of methods used to fabricate non-fluorinated materials with superhydrophobic surfaces. This work introduces both the advantages and disadvantages of fluorinated materials and displays the reasons why materials can be superhydrophobic. In addition, hierarchical structures and re-entrant structures are shown in this passage and methods of making these structures are listed. Besides, this paper presents some methods to fabricate structures which contribute to superhydrophobization. Furthermore, some non-fluorinated materials are listed and their abilities of repelling water and stains are displayed, consisting of silanes, organic materials, and inorganic materials. At last, this paper illustrates current limitation of non-fluorinated materials and their future developments.

1. Introduction

1.1 Fundamentals of wettability

1.1.1 Contact angle and contact angle hysteresis
Surfaces of materials with strong repellence to both high and low surface tension liquids have a wide range of applications[1]. Two parameters can be used to characterize wettability of a surface against a liquid, which are contact angle and contact angle hysteresis[2]. The definition of contact angle is an angle formed when a liquid contacts with a solid surface. The second parameter, contact angle hysteresis, which plays a crucial role in characterizing wetting behaviors, is defined as the distinction between the advancing and the receding contact angles, which occurs because of surface roughness and surface heterogeneity[3]. It is a measure of the energy released as a liquid droplet flows along the surface of a solid. Surfaces can be categorized as superhydrophilic if \( \theta \approx 0^\circ \) (see Figure 1a), hydrophilic if \( \theta < 90^\circ \) (see Figure 1b), and hydrophobic if \( \theta > 90^\circ \) (see Figure 1c) and superhydrophilic if \( \theta > 150^\circ \) (see Figure 1d) and very low contact angle hysteresis (typically <5°) for a contacting liquid[2].
1.1.2 The Wenzel state and Cassie-Baxter state

This section will introduce two models of wetting on rough surfaces, the Wenzel state and Cassie-Baxter state. Wetting on a textured or rough surface can be very different from the wettability of liquid droplets on non-textured surfaces\[3\]. In the Wenzel state, the projection of solid surface can be penetrated completely by the liquid droplet (see Figure 2a) and its contact angle can be figured out by the Wenzel equation\[4\], given as:

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

The roughness of surface, equals to the ratio of actual surface area to its flat projected area. $\theta^*$ is the contact angle of liquid droplet on a textured surface and $\theta$ is the contact angle on a non-textured surface. When $\theta > 90^\circ$, the rough surface causes high apparent contact angle and high contact angle hysteresis. To the contrary, the rough surface leads to low apparent contact angle and high contact angle hysteresis when $\theta < 90^\circ$.

On the other hand, the liquid does not completely permeates into surface textures in the Cassie-Baxter state (see Figure 2b). It means a composite interface consists of two fractions. The contact angle is determined by the Cassie-Baxter equation\[5\], given as:

$$\cos \theta = f_1 \cos \theta_1 + f_2 \cos \theta_2$$

$f_1$ is one fractional area for one component and $f_2$ is the other one for the other component (so that $f_1 + f_2 = 1$).

A composite interface (see Figure 3) is composed of two parts, the liquid-solid interface under the droplet ($f_1 = f_{SL}, \theta_1 = \theta$) and the liquid-air interface ($f_2 = f_{LA} = 1 - f_{SL}, \cos \theta_2 = -1$). In this case, the Cassie-Baxter equation\[6\] can be given as:

$$\cos \theta^* = r_{\phi} \phi \cos \theta + \phi - 1$$

It is obvious that the Cassie-Baxter state can lead to $\theta^* > 90^\circ$ whether $\theta > 90^\circ$ or $\theta < 90^\circ$ if some of conditions are met. When the Cassie-Baxter state is formed, it can result in a very high contact angle, even for liquids with low surface tension. This is preferred state for superomniphobic surfaces when the surfaces have high apparent contact angles and low contact angle hysteresis.
Figure 2. Droplets of liquid on solid surfaces with texture. Schematic of a liquid droplet in two states, (a) the Wenzel state and (b) the Cassie–Baxter state. In these diagrams, 2D is the distance between the features and R is the radius of the feature. Note that surfaces with re-entrant texture ($\psi < 90^\circ$) can maintain a stable composite (solid–liquid–air) interface, even liquids with low surface energy, showing $\theta < 90^\circ$.\[1\]

Figure 3. Cassie-Baxter equation for the state with air-solid composite interface.\[6\]

1.1.3 Role of re-entrant texture and hierarchical scales of texture

Though the Cassie-Baxter state is preferred for designing superomniphobic surfaces for low surface tension liquids, not all situations work\[1\]. If the surface texture meets the condition, it may lead to the Cassie-Baxter state. As is shown in Figure 4, there are two types of textures. The textures shown in Figure 4a and Figure 4b are concave texture ($\psi > 90^\circ$) and convex texture ($\psi < 90^\circ$), respectively. Only when $\theta \geq \psi$ can the surface remain a stable Cassie-Baxter state\[7\]. If $\theta < \psi$, the net traction on the liquid-vapour interface is downward because the self-absorption of the liquid into the solid is facilitated by capillary force, consequently becoming a completely wetted Wenzel state\[1\]. It means that the Cassie-Baxter state cannot stay stable on textures with $\psi > 90^\circ$ (see Figure 4a) when contacting with low surface tension liquid. While when $\psi < 90^\circ$ (see Figure 4b), a Cassie-Baxter state can remain robust. This kind of texture (Figure 4b) can be referred to as re-entrant texture as well. It is necessary to create a re-entrant texture in order to design a superomniphobic surface.

Figure 4. The significant role of re-entrant texture. (a) A schematic diagram of liquid droplets on the surface with a concave texture (\(\psi > 90^\circ\)) displaying $\theta > 90^\circ$ in the Cassie-Baxter state. (b) A schematic of a lower surface tension liquid on the surfaces with a convex texture (re-entrant texture, $\psi < 90^\circ$) showing $\theta < 90^\circ$ in the Cassie-Baxter state.\[1\]
Another kind of texture possessing a hierarchical structure plays a significant role in surfaces which are repellent to low surface tension liquids. Hierarchical scale of texture is a kind of texture which contains multiple texture length scales (see Figure 5c).

The surface of the hierarchical structure includes a finer length scale texture (see Figure 5b) and a coarser length scale texture (see Figure 5b) at the bottom. The liquid contacts the surface of hierarchical texture, forming a complete Cassie-Baxter state. The droplet usually exhibits a higher apparent contact angle than the angle on the surface of a single scale texture, reasoning that air is trapped on the surface of a multilength scale structure [1].

![Figure 5. The necessity of hierarchical texture. (a) Schematics of a liquid droplet on a coarser textured surface, (b) a finer textured surface and (c) a hierarchically textured surface in Cassie-Baxter state.][1]

The contact angle hysteresis of hierarchical surfaces is lower than that of single scale of surfaces [8]. Contact angle hysteresis is associated with the energy barrier that must be overcome when the liquid droplets move along the surface of solid, so it is a characteristic of droplet movement resistance [1]. The surface of hierarchical structure has a lower solid-liquid contact area than a single texture surface, which greatly reduces the contact angle hysteresis.

In addition, theoretical analysis [9] shows that the surface of the hierarchical structure can provide more stable locations of the composite interface, thus improving the stability of Cassie-Baxter state. Recent theoretical work [10] also indicates that with the growing number of texture scales, the overall free energy is more and more inclined to the Cassie-Baxter state rather than Wenzel state. Therefore, hierarchical structured surfaces with re-entrant structures can successfully keep low surface tension liquids in the Cassie-Baxter state, making them become ideal materials for superhydrophobic surfaces.

1.2 The function of being fluorinated

The definition of the surface energy can be the excess energy of the material surface compared to the bulk [11]. It comes from the uneven distribution of molecules around the surface atoms or molecules, resulting in uneven intermolecular forces on the surface. It can be said that surface energy comes from dispersion force, orientation force and induction force.

Materials with higher surface energy than liquid such as water tend to get wet. While some solid surfaces with a lower surface energy than water do not wet out. Being fluorinated makes a surface hydrophobic, which is proved by many experiments [12]. Due to the high electronegativity of fluorines and their strong ability to capture electrons, the temporary fluctuations of the charge distribution in the molecules are small. Therefore, dispersion force is small. Surface energy is proportional to dispersion force. So the surface energy is low.

1.3 The reason of requiring un-fluorinated material

Some of the fluorinated compounds, however, are toxic. They may affect people’s physical health due to its bioaccumulation [13]. Additionally, fluorinated compounds are very expensive [14] and the process of fluorination is complicated [15], which largely limits the large-scale application in industry. In some cases, fluorinated surfaces’ stability is poor. For instance, due to the random accumulation of inorganic nanoparticles on cotton fabric, the hierarchical structure of cotton fabric is unstable. The bonding force of inorganic nanoparticles is poor [16, 17]. Many products have tried to use organic materials to change the bonding of nanoparticles to cotton fabric and bonding between nanoparticles. The organic composite coatings on cotton fabrics, however, cannot be so thin that keep the softness,
appearance, and wearing comfort of original cotton fabrics[18]. So simple, efficient, low-cost, environment-friendly methods for hydrophobic surfaces need to be developed with controllable morphology to broaden industrial applications.

2. The micro-structure and preparation methods

There are several methods which are commonly used in experiment, such as etching and lithography, layer-by-layer (LBL) assembly method, electrochemical reaction and deposition and growth on template-substrate. The advantage of etching and lithography is that the two methods are straightforward and effective. These two methods can be used to produce many kinds of micro-structures according to various purposes. There are diverse etching and lithography methods currently, such as plasma etching, laser etching, photolithography, X-ray lithography and so on. Besides, LBL self-assembly method which can be controlled by changing film thickness and chemistry in molecular level has been extensively used to produce thin film coatings. Additionally, Electrochemical reaction and deposition has been widely used to produce superhydrophobic surfaces for the reason that this method contributes to grow bumps on the flat surfaces. At last, The method called growth on template-substrate can acquire rough surfaces with patterns which is relative to the basement. Various surfaces can be produced according to different basement.

3. Alternative materials

3.1 Alternative types of materials

With low surface energy, the materials usually have a small contact angles, a condition that contributes to making this material hydrophobic even if their surface is smooth. Thus, we can also use some unfluorinated materials whose surface energy is low to produce superhydrophobic surface. Besides, some preparation methods can be also used to fabricate hierarchical structure which have a crucial effect on decreasing the apparent contact angle. Via these methods, some materials with higher surface energy can also be fabricated into superhydrophobic surface.

3.1.1. Silanes

Polydimethylsiloxane (the abbreviation is PDMS) is a well-known material which has low surface energy. Due to its low surface energy, even the flat PDMS surface is approximately hydrophobic with the water contact angle about 100°~110°. Thus, this material can be designed for superhydrophobic surfaces. For instance, Sun et al.[19] successfully produced a rough PDMS surface containing microstructure which is same as lotus leaf’s by using nano-casting method. In addition, Ma et al.[20] made a superhydrophobic membrane in the form of a nonwoven fiber mat by electrospinning a PS-PDMS block copolymer blended with PS homopolymer. The WCA of this surface is about 163°.

![Figure 6. SEM images of PDMS surface (a) produced by nano-casting method; [19](b) SEM images of PS-PDMS produced by Ma et al.[20]](image)

Generally, sliding angle (SA) is also a crucial parameter to evaluate whether a material has the ability of self-cleaning which is valuable in practical applications. Nevertheless, PDMS usually has a high SA (>90°) which restricts its industrial application in some degrees. To overcome this
disadvantage, Meihua Jin *et al.*[21] produced a surface with hierarchical structure consisting of micro-, submicro-, and nano-composite structures via one-step laser-etching method. The WCAs of them are higher than 160° and the SAs of them are lower than 5°.

They use pulse laser to fabricate microgrooves on PDMS smooth surface prepared by them. The laser pulse’s wavelength was 532nm. Figure 7(a) displays that this etched PDMS surface consists of a regular array of convexes which have a width of 25μm and a depth of 10μm. The distance between each convex is approximately 2μm. In addition, many particles [showed in Figure 7(b)] whose scales are 0.5~3.2μm are on the top surface of convexes. Thus, the particles and the convexes formed a hierarchical structure which contributing to increasing the surface roughness. Additionally, it can be seen that there randomly exist plenty of irregular nanoparticles which have a average diameter of 109nm in the further magnified SEM image of a single PDMS micro-convex [Figure 7(c)]. Figure 7(d) displays the difference in the surfaces between smooth PDMS surface and roughness one produced by laser-etching.

By calculation, the WCA of this laser-etched PDMS surface is 162° [Figure 8(a)] and the SA of this PDMS surface is lower than 5° [Figure 8(b)]. They drew curves [Figure 8(c)] to show the relationship between the width of convex and the hydrophobicity by measuring the SA and CA of PDMS surfaces with different widths of convexes. According to the curve, decreasing the width of convex contributes to increasing the superhydrophobicity and improving the ability of self-cleaning.

![Figure 7](image1.png)

![Figure 8](image2.png)
3.1.2 Organic materials

Plenty of organic materials display a high superhydrophobicity. Polyethylene (PE) is a polymer which has a symmetrical structure and no polar groups. Therefore, PE can be used to fabricate superhydrophobic surfaces. Lu et al.[22] used a method which controls the crystallization behavior of polyethylene (PE) to make a hydrophobic PE surface with high density of porosity. The WCA of this material is 173°.

Polystyrene (PS) is a polymer with benzene rings. Additionally, benzene ring which has no polar is the only group in PS. Thus, PS is also considered to be a non-polar polymer with low surface energy, a material which is fit in producing superhydrophobic surface. Lee et al.[23] obtained a three-dimesion-ally rough PS surface by producing vertically aligned PS nano-fibers. The long length nano-fibers are likely to form twisted bundles resulting to a three-dimesion-ally rough PS surface. The WCA of this surface is about 155.8 degree.

Besides the polymers listed above, there are still various kinds of polymers which can be fabricated to hydrophobic surfaces for the reason that some other groups added to polymers can also decrease the surface energy of polymers. Mengying Long et al.[24] used hierarchical aluminum (H-Al) (Figure 10) which contains structures like micro-steps and nano-platelets as the template to fabricate superhydrophobic even oleophobic surfaces. Five types of polymers concluding acrylonitrile butadiene styrene (ABS), polycarbonate (PC), polymethyl methacrylate (PMMA), polystyrene (PS), and polyurethane (PU) were made into this hierarchical structure via using H-Al as template.

In the experiment, they poured these polymer solution (ABS, PC, PMMA, PS, and PU solution) onto H-Al templates and then moved these simples into the place which is at the temperature. After sufficient evaporation of the solvent, they removed the H-Al templates by using 3M NaOH solution so that they can acquire hierarchical polymer structure; finally, they cleaned and dried these polymer out and dipped them into PDES-C2H5OH solution to obtain PDES coating on the surfaces of these polymers. The surfaces of these polymers are displayed in Figure 11.
Figure 11. FESEM images of hierarchical-ABS (H-ABS) (a), H-PC (b), H-PMMA (c), H-PS (d), and H-PU (e) surfaces under high-magnification. [24]

To test these H-polymers’ hydrophobicity, they measured the various contact angles (CAs) and sliding angles (SAs) of these surfaces by differently using water, ethylene glycol, and hexadecane at room temperature. The values of water’s surface tension, ethylene glycol’s one and hexadecane’s one are 72mN·m⁻¹, 48mN·m⁻¹, and 27mN·m⁻¹. The CAs and SAs are displayed in the Table 1 below.

| Samples | Water [deg] | Ethylene glycol [deg] | Hexadecane [deg] |
|---------|-------------|-----------------------|------------------|
|         | CA          | SA                    | CA               | SA               | CA          | SA               |
| H-PS    | 160±1       | 2±0.5                 | 153±1            | 6±0.5            | 142±1       | >90              |
| H-PMMA  | 158±1       | 4±0.5                 | 150±1            | 8±0.5            | 141±1       | >90              |
| H-PC    | 157±1       | 3±0.5                 | 150±1            | 7±0.5            | 140±1       | >90              |
| H-PU    | 157±1       | 4±0.5                 | 152±1            | 6±0.5            | 141±1       | >90              |
| H-ABS   | 155±1       | 3±0.5                 | 150±1            | 7±0.5            | 139±1       | >90              |

### 3.1.3 Inorganic materials

ZnO nanored films also have low surface energy. Feng et al.[25] used a two-step solution to produce a rough ZnO nanored film which displays superhydrophobicity. The specific feature of Zno nanored films is that this material can transform its superhydrophobicity to superhydrophilicity if it is exposed to specific UV irradiation. In addition, This material can be superhydrophobic again after staying in a dark environment for several days.

Carbon material which is in the feature of carbon nano-tubes can be superhydrophobic for the reason that surfaces in the shape of nano-tube is always in the Cassie-Baxter state when they contact liquid. Lin Feng et al.[26] succeed in producing densely packed aligned carbon nano-tubes (ACNTs) whose WCA is about 158.5°.

Nevertheless, the nanotube arrays are in poor stability and show a phenomenon of contact angle hysteresis. Thus, Z. Wang et al.[27] fabricated a hierarchical structures of carbon nano-tube arrays to increase superhydrophobic stability of carbon nanotube arrays. They used water-assisted thermal chemical vapor deposition process to make the non patterned multiwalled carbon nano-tube (MWCNT) arrays. The length and diameter of MWCNT are shown in Figure 12.(a). Firstly, they coated a thin layer of photoresist on the Si substrate. Then they used photolithography to fabricate regular cylindrical pattern arrays on the substrate. Next, they deposited catalyst consisting of Al and Fe for MWCNT growth onto both the substrate and patterns via electron-beam evaporation. Finally, the
cylindrical patterns of photoresist were removed and the Si substrate with catalyst on it was treated in the chemical vapor deposition chamber to grow MWCNT. Figure 12(b) shows the steps.

Figure 12. (a) SEM image of MWCNTs in the array. The inside figure shows a TEM image of a single MWCNT, displaying that the average diameter of tubes is about 10 nm; (b) image showing steps to grow the nano-tubes on the Si substrate selectively; (c) SEM image of the nano-tube array from a top view, displaying a regularly duplicating pattern of cylindrical voids which are 20 μm diameter; (d) SEM image of the film from a cross-sectional view. [27]

Figure 12.(c) displays that the MWCNT successfully grow on the Si substrate covered with catalyst leaving cylindrical voids’ pattern in the places which photoresist and catalyst on it were removed. Figure 12.(d) displays that voids run along the length of this array and this surface has a high aspect ratio dual-scale surface roughness. By calculation, they got the WCA of this surface is 164.6°.

3.2 Stain resisting via non-flurinated material
Stain resistance is defined as the ability to resist the contamination from solid, liquid, semi-liquid behaving particles. Typical ways to perform the satin resisting are normally imparted via coating, sealants or films of one type or another. Besides, Self-cleaning are also concern to be a part of stain resisting. Repellency properties can be achieves by lowering the free energy at the material surface. Fresh natural lotus leaf, hydrophobic three-dimensional epicuticular waxes were found on the surface creat a Cassie-Baxter condition(2.1), the air space lower the surface energy. While Wagner et al.[28] conclude that the surface contain a lot of hydrophilic groups which make it less hydrophobic. In additional, the lotus usually shows a high ability of self-cleaning. It is seldom seen that the lotus gets contamination. Thus, synthesizing a lotus-like structure with materials having low surface energy is viable to resist stains.

Figure 13. SEM images of (a) the fresh natural lotus leaf, (b) a single magnified papilla on the fresh natural lotus leaf, (c) the PDMS negative template, (d) a single magnified hole on the PDMS negative template, (e) the lotus-leaf-like super-hydrophobic PVC film, (f) a single magnified papilla on the lotus-leaf-like PVC film, (g) the microscope of smooth PVC film, and (h) water droplets on the as-prepared super-hydrophobic lotus-leaf-like PVC film. [29]
Furthermore, Low energy surface usually have evident effect of self-cleaning. (a) drops on the hydrophobic are Sphere. In cause of the contact area to the surface are minimise, lead to a lower wet area and lower the roll of angle, the sphere droplet are able to roll on the surface, bring the solid remainders to leave the surface. Comparing to the high energy surface in (b), the droplet remain normal and show a very poor ability to wash away particles. In conclusion, superhydrophobic surfaces contribute to form sphere drops which the liquids are poured on them. Thus, hydrophobic surfaces usually have a ability of self-cleaning in some degrees.

Figure 14. (a) A drop with a very high contact angle washes out contamination particles, (b) while a drop with low contact angle does not clean the surface. [30]

4. Limitations

4.1. Durability concerns
Superhydrophobic coatings have commercial availability, their weak mechanical durability, however, hampers the large-scale applications.
The mechanical durability of the surface depends on the bonding strength between the substrate and the water repellent coating. The Xia Zhang et al. have tested the mechanical durability of SiO2/polymer blocks.[31] (see Figure 16).

Figure 15. Radar diagrams of SiO2/polymer blocks, a brick and the “Never wet” hydrophobic spray (“WCA” and “WSA” are the short for water contact angles and water sliding angles. “initial” means the results have been obtained without any mechanical and chemical tests. “after abrasion” mean the angles have been measured after 2000 cm abrasion. “pH = 1” and “pH = 14” are the contact angles measured after 30 min “droplet test”. ). [31]

As is shown in Figure 16, results show that the durability of SiO2/polymer blocks is really poor. WSA and WCA declined greatly after abrasion, which means the surface was not superhydrophobic any more. Other parameters were also unsatisfactory.

4.2. Oleophobicity of non-fluorinated materials
Oil repellency is also an important factor which indicates the development potential of the coatings. But non-fluorinated alternatives fail to be oleophobicity. As can be seen in Figure 17, PA and PES were treated by different DWR-chemistry. Although the DWR-type with the best performance was selected for the experiment, only L-SFPs (R-C8F17) based on C8 had high oleophobicity, and the oil repellency decreased with the shortening of the chain length (see Figure 17 a1). Si and HC compounds have an oil level of 0 (see Figure 17).[32]
Figure 16. (a1) The side chain orientation of SFPs, (a2) the measured results of oil resistance and different wettabilities of mineral oil on (b1) the surface of the untreated PES, (b2) the surface of C8-based L-SFP, and (b3) the surface of hydrocarbon-based DWR, displaying no liquid repellence, superhydrophobicity and poor oleophobicity, respectively. [32]

5. Application
Non-fluorinated stain repelling material will have bright future. From raincoat to coating on building surface, non-flourinated stain resistance layer could be apply to parts of the stain and water repelling industry. Especially, as non-flourine containing, the material could be use on environmental and organism friendly products. For instance, Tyvek[34] and Nylon fiber have been commonly used in constructing raincoat now. In the future, a variety choice of coating could be used on Nylon fiber, such as dendrimeric durable water repellents (DWR). The addition of the dendrimeric surface structure on the fiber material can enhance the repellent effect by the hyperbranched polymeric structures. The high degree of freedom in customization on the coating and durability let Nylon fiber widely apply to daily life.

A common industrial application of superhydrophobicity in industry is fluidic drag reduction. The hydrophobic surface reduces the fluidic drag by dramatically reduce the interaction on solid/water interface and create the Cassie-Baxter state to establish an air/water new boundary condition. Wantanabe et al. [33] were among the first to report the laminar flow drag flow drag reduction phenomenon of superhydrophobic coating for Newtonian fluids. Recent intensive studies on the function from Ou et al. [35,36] have proposed that a superhydrophobic surface results in a reduction of a pressure drop of over 40% and apparent slip length exceeding 20mm.

6. Conclusion
Through the above analysis, it can be concluded that these non-fluorinated materials with low surface energy can be fabricated into superhydrophobic materials as well. PDMS is one of the most widely-used materials which are not fluorinated in producing superhydrophobic surfaces. Similar to silanes, people can improve the superhydrophobicity of organic polymers via changing the groups in their molecular structures. Thus, it is optimistic to have a further development of using silanes and polymers to fabricate superhydrophobic surfaces in the future. Among inorganic materials, carbon nanotubes can always make the contact angles in Cassie-Baxter State because of its unique aspect ratio. ZnO displays a unique feature which it can transform its hydrophobicity to hydrophilicity with outside intervenes. However, though plenty of materials talked above are superhydrophobic, few of them are oleophobic. After researching more information, it is shown that hierarchical structures and re-entrant structure contribute to improving oleophobicity for the reason talked above. Therefore, superomniphobic surfaces which have a potentially significant value in applications in daily-life and industry are expected to be produced in the future.

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