## REVIEW

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

# Effects of bio-inspired micro/nano scale structure on anti-icing properties

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Ice formation and accumulation have detrimental effects on commercial and human being's living. The ice adhesion strength decreases with the increasing surface hydrophobicity, and the superhydrophobicity of a surface can be constructed by a combination of low surface free energy and high surface roughness. Whereas, the characteristics of biological surfaces have aroused wide attention as a result of the superhydrophobicity of plants and animals derives from the synergistic effects of chemical compositions and multi-scale hierarchical structures. Therefore, inspired by bio-mimetic studies on biological surfaces, a lot of artificial bio-inspired superhydrophobic surface have been broadly designed and constructed. Here, we aim to summarize the fundamental theories of surface wettability and recent progress in the fabrication of bioinspired surfaces. The bio-inspired surfaces prepared by different facile methods not only have superhydrophobicity but also have anti-icing/icephobic properties. In the end, some challenges and problems in future study and advancement of bio-inspired superhydrophobic surfaces are proposed.

## 1. Introduction

It is generally known that the accumulation of ice on surfaces can have an adverse impact on roads, <sup>1-2</sup> aircraft, <sup>3-5</sup> boats, <sup>6</sup> power transmission lines, 7-8 and telecommunication instruments, <sup>9</sup> which could result in severe accidents, reduce efficiency in power production, and large economic losses. <sup>10-13</sup> Therefore, a large number of theories and experiments have been used to analyze the mechanism of icing and investigations on anti-icing or deicing have been widely carried out. Melting is the commonplace choice to ease ice risks, but both chemical and thermal methods are afflicted by other problems. An adequate method is employing freezing point depressants, which the crystallization temperature is much lower than water. In winter, salt and glycols (e.g. ethylene glycol (EG) and propylene glycol (PG)) are widely used to melt snow and ice on the surface of roads and aircraft.<sup>14</sup> However, this approach may cause surface corroded and groundwater polluted by the infiltration of the organic liquids. <sup>15-16</sup> Effective application of the Joule effect to make the solid surface temperature higher than the freezing point in icing conditions is anti-icing or deicing method. Particularly in the anti-icing and deicing of boats, transmission lines and telecommunication instruments, the electrothermal method is recognized to be a useful approach to inhibit ice formation or hasten ice melting.<sup>17</sup> However, the high expense for the apparatus and energy consumption has to be considered. Besides, the mechanical deicing approach is usually devoted to getting rid of ice from equipment that is freely contacted, for instance, transmission lines and power networks,

by either straightly striking to destroy ice accretion or applying the energy released by vibrations. <sup>18</sup> But this method neither safe nor efficient and mechanical force somehow causes extra stress to the electrical cables and leads to damage during the deicing process.

For the last decades, preliminary work investigated the essence of solid-liquid-vapor interactions on a solid surface, containing non-wetting and wetting circumstances. Among the many studies, free energy and roughness of the solid surface were found to be central factors for delayed ice formation and easy removal of formed ice.<sup>19</sup> Under certain conditions, water aggregation could be obviated on the low surface energy polymer coatings (such as poly- (dimethylsiloxane) (PDMS), poly-(tetrafluoroethylene) (PTFE), and polymer compound materials with nanoparticles), which cannot be wetting by water, leads to lower icing probability and ice adhesion.<sup>20-28</sup> Nevertheless, the low mechanical stability and durability of polymer coatings (PDMS and PTFE) may make it an impediment in some practical applications. For rough porous surfaces, in particular, roughness as an essential property of a surface could not present all the surface features. This is owing to even a smallish distinctness on a surface that would bring about a diverse ice-nucleation process. Lately, slippery liquid-infused porous surface (SLIPS) has been presented as a new method of water repellent materials. This method is to permeate a physically and chemically mutually exclusive lubricant on a textured solid surface to construct a smooth liquid overlay. As the water droplets are accumulated on SLIPS, a composite solidlubricant-water interface is created, and the water droplets are shed off by its own gravity at a small tilt angle. Notwithstanding, the sophisticated preparation process, high cost, and durability of SLIPS must be considered. 6, 29-36 It is crucial to avoid the lubricant loss from the solid surface structure and to explore a novel method for lubricant supplements.

The icing process is mainly induced by the quick exchange of heat at the solid-liquid interface after the supercooled water

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droplet getting in touch with solid surfaces. Hydrophobicity is an excellent character for delay the ice formation and aggregation due to a textured (roughness) surface that can remarkably reduce the heat-transfer and the free energy barrier of ice nucleation. <sup>37-39</sup> The candidate anti-icing surfaces should have ideal superhydrophobicity to firstly hinder the wetting of water droplets, and are also talented with retarding icing and lower ice adhesion strength once freezing takes place. Therefore, the main emphasis of superhydrophobic coatings has shifted to investigate the influence of surface topology/geometry on anti-icing or deicing performance. The definition of superhydrophobic surface (a surface with a water droplet contact angle ( $\vartheta_{CA}$ ) larger than 150 °and contact angle hysteresis ( $\vartheta_{CAH}$ ) (the divergence between the advancing contact angle  $(\vartheta_a)$  and receding contact angle  $(\vartheta_r)$  less than 10 °) is acceptable by researchers. <sup>40</sup>

The capability of manufactured superhydrophobic surfaces to hinder and reduce the formation of ice has been explored and studied for many years.<sup>41-45</sup> Saito et al. <sup>46</sup> were first proposed superhydrophobic materials surface with anti-icing or deicing performance by reducing ice adhesion stress. Gradually, other groups demonstrated to reduce ice adhesion or delay water droplets freezing on rough superhydrophobic surfaces, which is admitted to be good for deicing or anti-icing property.<sup>24, 40, 45, 47-51</sup> Barthlott <sup>52</sup> and Neihuis <sup>53</sup> postulated that the self-cleaning performance of lotus leaf is generated by the existence of the papilla on the microstructure and the epicuticular wax in 1997. This assumption has attracted much attention to imitating natural phenomena to construct a microstructure-based superhydrophobic surface. In 2002, Jiang et al.54 found that micro-and nanoscale hierarchical structures on the lotus leaf surface, which is nanostructures on the top of the micropapille and allowed surfaces to stav superhydrophobicity. Koch et al.55 confirmed that the significance of micro-and nanostructures in superhydrophobicity. It failed to shift away from the Wenzel state towards the Cassie state by negative Laplace pressures on microscale pillar arrays structure, but the reversible conversion between these two states (Wenzel and Cassie) has been achieved on micro/nanoscaled hierarchical structure surfaces. In recent years, various biological surfaces have obtained considerable attention, owing to their optimum morphology and surface chemistry, particularly in the excellent superhydrophobic property. <sup>56</sup> After lotus leaf, it is necessary noticing other biological surfaces, including plants <sup>54, 57-59</sup> (such as rice leaves, rose petals, and pitcher plants) and animals 60-67 (like butterfly wings, cicada wings, gecko, legs of water striders, and eyes of mosquitos). It is demanded to prompt solve how to provide surfaces with the proper surface energy and the sufficient roughness that can result in superhydrophobicity.

To figure out the micro/nanoscaled hierarchical structure surfaces on superhydrophobicity and anti-icing performance, it is meaningful to understand its fundamental theories of surface structure. Accordingly, in this review, we first elaborate on the basic mechanisms of surface wettability, which is further grouped into two sections: the mechanisms of slippery surfaces (S-surfaces) and rough surfaces (microstructured surfaces (M- surfaces). nanostructured surfaces (N-surfaces), and micro/nanoscaled hierarchical structure surfaces (MNsurfaces)). Next, some practical and promising fabrication methods of the micro/nanoscaled two-tiered structure surfaces will be introduced. Then, we will focus on the relationships between the bio-inspired superhydrophobic materials surface and anti-icing performance. In the end, we will propose a brief outlook in research into biomimetic superhydrophobic surfaces with micro/nanoscaled hierarchical structures. In general, we will primarily illustrate the following two issues: how micro/nanoscaled hierarchical structure to improve superhydrophobicity and what will this do for anti-icing or deicing.

## 2. Basic understanding of the surface structure

If the water droplet can move spontaneously on the surface without any adhesion, the solid surface can be regarded as the superhydrophobic surface. For the sake of characterizing the superhydrophobic surface quantitatively, static contact angle  $(\vartheta_{CA})$ , contact angle hysteresis  $(\vartheta_{CAH})$ , and sliding angle or roll off angle ( $\vartheta_{SA}$ ) must be measured by specialized instruments. It is generally true that the superhydrophobic surface requires a contact angle larger than 150°( $\vartheta_{CA} >$  150°), contact angle hysteresis less than  $10^{\circ}(\vartheta_{CAH} \le 10^{\circ})$ , and sliding angle less than 10°( $artheta_{\scriptscriptstyle SA}$  < 10°). Generally, much advancement has been accomplished in the design, fabrication, and application of superhydrophobic surfaces. Besides chemical composition, another crucial parameter, rough structure as well as plays a vital role in achieving superhydrophobicity. Thus, it is essential to investigate the influence of surface topology/geometry (roughness) on superhydrophobicity.



Fig. 1 Classical-wetting model of a liquid droplet on the solid surface. (a)Thomas Young model.<sup>68</sup> (b) Wenzel state.<sup>69</sup> (c) Metastable state. (d)Cassie-Baxter state.<sup>70</sup> (e) contact angle ( $\vartheta_{CA}$ ). (f) Advancing contact angle ( $\vartheta_{0}$ ) and receding contact angle ( $\vartheta_{r}$ ). When a water droplet of a certain volume on the solid surface accumulates slowly, the contact area does not increase right away as far as the contact angle reaches the  $\vartheta_{a}$  threshold. Likewise, when the volume of the water droplet is decreased, the contact area of the solid surface will decrease as far as the contact angle attains the  $\vartheta_{r}$  threshold. (g) Sliding angle or roll-off angle ( $\vartheta_{SA}$ ), which illustrates the angle of a gently sloping surface when a droplet fully rolls off the surface by gravity. (h) Shedding angle ( $\vartheta_{SHA}$ ), which refers to a water droplet with defined volume, dropped from a certain height starts to roll off or bounce off the tilted substrate.<sup>71</sup>

#### 2.1 Smooth surface

When a water droplet is in touch with a solid surface, it prefers wetting the solid surface and has a lower energy state. Therefore, a contact angle ( $\vartheta_{CA}$ ) will form between the solidliquid surfaces; the  $\vartheta_{CA}$  is taken at the triple-phase point of solidliquid-vapor. In 1805, the fundamental hypothesis of the water contact angle on a flat and smooth surface was first put forth by Thomas Young (Fig.1a). As the commonly used method to measure the wettability of the solid-liquid surfaces, the contact angle ( $\vartheta_{CA}$ ) can be explained by Young's equation <sup>68</sup>:

$$\cos\theta_Y = \frac{\gamma^{SV} - \gamma^{SL}}{\gamma^{LV}} \tag{1}$$

Where  $\vartheta_{Y}$  is static contact angle,  $\gamma^{SV}$  represents the solid-vapor surface tension (surface free energy),  $\gamma^{SL}$  represents the solidliquid surface tension, and  $\gamma^{LV}$  represents the liquid-vapor surface tension, respectively. Young's equation illustrates the relationship between the static contact angle ( $\vartheta_{CA}$ ) of a water droplet and the surface tension of three interfaces ( $\gamma^{SV}$ ,  $\gamma^{SL}$ , and  $\gamma^{LV}$ ) on an ideal slippery, homogeneous, and hard solid surface. Objectively speaking, Young's equation is only applicable for ideal smooth surfaces. But in reality, we tend to be in contact with rough and chemically heterogeneous surfaces, rather than smooth, flat, and chemically homogeneous surfaces. Accordingly, Wenzel and Cassie modified the surface wetting theories to apply for non-ideal rough surfaces.

## 2.2 Rough surface

To rectify Young's equation, there are two famous wetting models on the rough surface that have been advanced, namely the Wenzel equation and Cassie-Baxter equation. In 1936, the Wenzel equation was proposed, which mainly illustrates the relationship between surface roughness (R, geometric specific surface area/projected surface area) and contact angle ( $\vartheta$ ), as shown Eq. (2) <sup>69</sup>:

$$\cos\theta_W = R \frac{\gamma^{SV} - \gamma^{SL}}{\gamma^{LV}} = R\cos\theta_Y$$
(2)

Where *R* is the surface roughness factor (R > 1),  $\vartheta_r$  represents the static contact angle of the liquid droplet on the smooth surface of the same material, and  $\vartheta_W$  represents the contact angle on the rough surface. In terms of rough surface, the contact area is associated with the roughness factor(R), the liquid-solid contact surface is larger than the smooth surface. Also, the subsistent of the rough structure of a surface increases the wettability of the surface. However, the Wenzel model only applies to depict the contact angle in the situation that a liquid droplet is in touch with the entire solid surface and totally permeates into surface cavities or anfractuosities, as shown in Fig.1b.

Afterward, the Cassie-Baxter model was established in 1944. In this model, it is assumed that the liquid droplet is sustained on the top of asperities (textures) and the air is trapped inside the cavities or grooves of a rough surface (Fig.1d), as shown Eq. (3)<sup>70</sup>:

$$\cos\theta_C = f_s \cos\theta_s + f_a \cos\theta_a = f_s (\cos\theta_Y + 1) - 1 \tag{3}$$

Where  $f_s$  represents the apparent area fraction of the liquid droplet in touch with the solid surface,  $f_a$  represents the apparent area ratio of a liquid droplet in touch with air captured inside the cavities of rough surface ( $f_s + f_a = 1$ ),  $\vartheta_s$  is the contact angle of liquid droplet upon the solid surface, and  $\vartheta_a$  is the contact angle of liquid droplet upon the air captured inside the holes of a rough surface, respectively. Furthermore, if a spherical liquid drop in the Cassie-Baxter state is squeezed or pressed, it is more prone to shift from the Cassie-Baxter state to the Wenzel state of the solid-liquid contact state. In other words, there is a metastable or transition state between the Cassie-Baxter state and the Wenzel state, as shown in Fig.1c.

Due to the trapped air inside the cavities structure to form an "air-cushion" on superhydrophobic surface with rough structure (microstructure, nanostructure, and micronanoscaled hierarchical structure), the contact angles of rough surfaces are much larger than a smooth surface. Therefore, the surface structure of the solid material is a fundamental consideration in the study of surface wettability. However, to characterize the wettability of superhydrophobic surfaces, it is essential to measure not only the static contact angle ( $\vartheta_{CA}$ ) (Fig.1e) but also the dynamic contact angles, such as contact angle hysteresis ( $\vartheta_{CAH}=\vartheta_{\sigma}-\vartheta_{\tau}$ ) (Fig.1f), sliding angle ( $\vartheta_{SA}$ ) (Fig.1g), and shedding angle ( $\vartheta_{SHA}$ ) (Fig.1h).<sup>71</sup>It is noteworthy that the lower contact angle hysteresis ( $\vartheta_{CAH}$ ) and sliding angle ( $\vartheta_{SA}$ ) are also connected with the superhydrophobicity recognized in natural species, for example, the lotus leaf. <sup>61</sup>, <sup>72-73</sup>

Much advancement has been obtained in the design and preparation of superhydrophobic materials. Besides surface chemical compositions, the roughness of surfaces is also an essential characteristic in acquiring superhydrophobicity. In recent years, bio-inspired interfaces have attracted much attention from researchers. Various surface structures with moderate roughness and wettability that present superhydrophobicity has been investigated, for example, microstructured surface, nanostructured surface, and micro/nanoscaled two-tiered structure surface.

## 3. Micro/nanoscaled two-tiered structure surface

The microstructures of the superhydrophobic surfaces play a critical role in investigating the wetting state. The prevalent view is that lower surface energy and higher surface roughness are necessary to prepare a superhydrophobic surface. Nonetheless, most of the microstructure surfaces unable to maintain their superhydrophobicity in severe environments, for instance, in humid circumstances, prolonged immersion, and abrasion. <sup>74-76</sup> Living beings in nature had unique structures to suit the changes in the environment. Learning from nature has aroused the attention and interest of many researchers. 77-78 In terms of basic theories, chemical composition and roughness of surfaces were considered to be the most important factors for surface wettability. Superhydrophobic surfaces can remarkably reduce the actual solid-liquid contact area between the solid surface and water droplet, because of the synergistic combination of surface energy and rough structure. The biomimetic superhydrophobic surface not only possesses excellent superhydrophobicity but also the candidate of antiicing applications owing to the heat isolation and lubrication of "air-cushion".79

As we all know that the surfaces of lotus leaf can keep clean as shown in Fig.2a, due to their combined micro/nanoscaled hierarchical structure of the surface. <sup>80</sup> Later, Feng and his coworker et al. <sup>54</sup> found that the micro/nanoscaled two-tiered structure had an influence on the increased contact angle ( $\vartheta_{CA}$ )



Fig.2 Pictures of biological surfaces with water-repellent (a) Lotus leaf exhibit self-cleaning property and superhydrophobicity, owing to randomly distributed micropapillae covered by branch-like nanostructures. <sup>54</sup> (b) Water droplets only roll along the direction parallel to the rice leaf edge rather than perpendicular owing to the quasi-1D arrangement of micropapilla. <sup>83</sup> (c) Rose petal exhibit superhydrophobicity, owing to periodic array of micropapillae and nanofolds on each papillae. <sup>58</sup> (d) Butterfly wings demonstrate superhydrophobicity owing to the multiscale structure.<sup>60</sup> (e) Mosquito compound eyes exhibit anti-fogging, anti-reflection and superhydrophobicity, owing to micro-ommatidia covered by nano-nipples. <sup>66</sup> Figures reproduced from ref <sup>54</sup>, <sup>83</sup>, <sup>55</sup>, <sup>60</sup>, <sup>66</sup> with the permission of Wiley, RSC, ACS, RSC, and Wiley, respectively.

and reduce slide angle ( $\vartheta_{SA}$ ). Normally, it is uncontrolled that roll direction of water droplets in contact with most plant leaves. But water droplets on the rice leaves shown a particular characteristic, that is to say, anisotropic wetting, which refers to roll along the direction parallel to the longitudinal direction instead of the perpendicular direction. 81-83 This is mainly due to the hierarchical micropapillae arrayed in a dimensional order and nanoscale waxes on the surfaces (Fig.2b). In other words, the two-level hierarchical structure (micro-and nanoscaled) leads to the existence of this phenomenon. Furthermore, it's for sure that the hierarchical papillae and nanofolds (two-level hierarchical structure) were also present on the surfaces of rose petals (Fig.2c). 58 Similarly, the butterfly wings also have anisotropic superhydrophobicity (Fig.2d). <sup>60</sup> Butterfly wings, which are composed of ranged box-like scales with arranged microgrooves, exhibited hierarchical scales along the radical outward (RO) direction. The hierarchical structure (microscaled with well-oriented nanostripes) of the wings, which promoted to directional structure, thereby influencing the wettability of water droplets. A water droplet can readily roll away from the surfaces of butterfly wings along the radical outward (RO) direction of the pivot of the body, but the wettability of the water droplets was limited in the inverse direction. 60 Mosquitos, even if they are existing in humid environments, can also fly freely and the surfaces of eyes maintain dry and clean. Mosquito eyes take possess of hexagonal and regularly arrayed bulges micro-nanoscaled structure (two-tiered structure), therefore, they have excellent vision in the humidity and dark (Fig2e). Gao et al.<sup>66</sup> investigated and explored the microstructure and morphology of mosquito eyes for the sake of understanding the superior performance. They found that the hierarchical micro- and nanostructures (micro-ommatidia capped with nano-nipples) have contributed to the formation of "air cushion", and then led to the superhydrophobicity of mosquito eyes.

All the above living creatures are examples of micro/nanoscaled two-tiered structure, exhibiting superhydrophobicity. It is clear that the combination of elaborated morphology (hierarchical structures) and surface chemical composition that gifted remarkably non-wetting performance.<sup>84-85</sup> Inspired from living creatures with extraordinarily non-wetting performance in nature, extensive samples of water-repellent surfaces have been fabricated.

## 4. Preparation of bioinspired micro/nanoscaled two-tiered structure

It is known that fabrication of superhydrophobic materials by constructing microstructures on the surface have mainly been related to roughness and chemical composition. From the outlook of prior studies, one method is the fabrication of hierarchical (micro/nanoscaled) rough structure and then modification with low-energy materials (such as a polymer), and the other method is the construction of a hierarchical rough structure on low-energy materials directly, as the two prevalent routes for prepare superhydrophobic surface.<sup>51,86-89</sup> So far, researchers have advanced various approaches for the preparation of superhydrophobic surfaces with certain wetting stability, and durability, for example, lithography,<sup>90</sup> plasma treatment,<sup>91</sup> electrochemical,<sup>92</sup> etching,<sup>93</sup> dip-coating,<sup>94</sup> solgel,<sup>95</sup> template,<sup>96</sup> one-pot method,<sup>97</sup> vapor deposition,<sup>98</sup> spray process,<sup>99</sup> in situ growth,<sup>100</sup> and so on. Here, in this part, the methods applied to fabricate micro/nanoscaled hierarchical structure of superhydrophobic surface with mechanical stability and durability are discussed.

#### 4.1 Vapor deposition

There is chemical vapor deposition (CVD) and physical vapor deposition (PVD) two basic types of vapor deposition method, which could fabricate arranged nanostructures with certain a

a

diameter. Chemical vapor deposition was applied to deposit solid products (such as SiO<sub>2</sub>) onto substrates (such as CNTs, and cotton), which is a gas phase growth method.<sup>101-103</sup> This approach can be utilized either to construct rough surfaces through fabricating nanoparticles, nanorods, and microparticles into aligned structures or to deposit a thin coating of hydrophobic compounds on rough surfaces.<sup>103-112</sup> To be brief, this method is to obtain an anticipated deposit through the substrate in contact with one or more precursors, and the chemical reaction takes place on the surface. CVD is a traditional and useful method to construct the micro/nanoscaled two-tiered structure on a superhydrophobic surface, but it costs too much that can be generally utilized to fabricate special materials.

Guo et al.<sup>113</sup> proposed an easy and novel technique to fabricate a superhydrophobic surface with high mechanical strength and self-healing property through aerosol-assisted layer-by-layer chemical vapor deposition (AA-LbL-CVD) of epoxy resins and polydimethylsiloxane (PDMS) polymer films. It is noteworthy that the fabricated surfaces still displayed superhydrophobicity even though subsequently long term in contact with different PH solutions, UV light irradiation, knife scratching, and double-sided tape peeling. Furthermore, owing to the memory influence of the polymer films, even if the micronanoscaled hierarchical structures of superhydrophobic surfaces were devastated, the as-fabricated superhydrophobic surfaces could be recovered by heating, exhibiting thermo-triggered healing of superhydrophobicity.

A new one-step chemical vapor deposition and modification adopting tetraethylorthosilicate method (TEOS). vinyltrimethoxysilane (VTMS) as a surface modifying agent and ammonium hydroxide (NH<sub>4</sub>OH) was proposed by Rezaei et al.<sup>114</sup> They found that even though the coating deposited from pure TEOS precursor is a smooth surface, the deposition of modified silica constructs a greatly rough surface. Besides, vinyl groups of modified nanoparticles decrease the surface free energy. The synergistic effect of surface roughness and low surface energy is essential to a superhydrophobic film of the silica-coated surface. Additionally, using ammonia as a catalyzer can effectively reduce the reaction temperature, which contributes to shortening the reaction time and lower cost. Zhuang et al. <sup>115</sup> developed a simple and practical approach for preparing highly durability superhydrophobic surfaces that contributes to a bright future for aerosol-assisted chemical vapor deposition (AACVD) in their scalable and lower cost. The robust superhydrophobic surfaces with micro/nano-scale structures were fabricated as compounds of epoxy resin (EP) and polydimethylsiloxane (PDMS) by AACVD. In this process, the EP layer supplied with a firmly adhered micro/nano-scale structure onto the substrates (such as glass, copper, aluminium, and stainless steel), and PDMS as a post-treatment to decrease the surface energy. Yao et al.<sup>116</sup> first introduced a new ZnS hierarchical structure mainly consisting of nanorods arrays with branched nanosheets and nanowires developed on their upside walls (Fig.3), which was fabricated onto Au-coated silicon substrate by a chemical vapor deposition method. The prepared

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Fig.3 (a) The cross-sectional FE-SEM images of the deposited ZnS product. (b) The top view FE-SEM images of the deposited ZnS product. (c) High-magnification image showing the branched nanostructures. Figures reproduced from ref <sup>116</sup> with the permission of Elsevier.

surface exhibiting superhydrophobicity and the capacity of selfcleaning behavior.

#### 4.2 Sol-gel

Sol-gel technique is a process of using compounds with high active chemical constituents by way of solution, sol-gel, and heat treatment to convert into oxides or other composite solids, which also play a significant role in being morphology of superhydrophobic surfaces. In this process, employ a chemical solution or sol as a precursor. While considerable solvent still exists in the system during the structure construction process, a gel was created which followed in the hydrolyzes of the precursor. In addition to the surface roughness can be simply adjusted by altering the procedure of this method and the constitution of the chemical solution.117 Another obvious advantage is that many types of solid (for instance, metal, polymer, silicon wafer, textiles, and glass) can be utilized as substrates to prepare superhydrophobic surfaces by the sol-gel approach.<sup>118-122</sup> Therefore, it still was supposed to be an efficient method to fabricate the superhydrophobic surface. But the sol-gel process will cost too much time and funds, and it will also produce contaminants.

At the initial stage of the sol-gel process research, many superhydrophobic sol-gels were prepared via hydrolysis of tetraethoxysilane (TEOS) and its derivatives (for instance methyltriethoxysilane (MEOS)) under acid or alkaline conditions. Basu et al.<sup>123</sup> constructed superhydrophobic surfaces with binary micro-nano-structured, which consisted of microscale protrusions and cavities with budges of nanospheres, through integrating hydrophobically modified silica nanoparticles (HMS) in sol-gel matrixes fabricated with acid-catalyzed tetraethoxysilane (TEOS) and methyltriethoxysilane(MTEOS). They demonstrated that the combination of multi-scale rough structure and hydrophobicity of methyl groups on HMS-silica was contributed to improving the superhydrophobicity of the composite coatings and the hydrophobicity of the coatings increase with the concentration of HMS nanoparticles. Su et al.124 have fabricated a superhydrophobic film via a new sol-gel which is comprised of hydrolysis and condensation of the by-product of polymethylhydrosiloxane (PMHS) reacting with aminopropyltriethoxysilane (KH550) (Fig.4). Liang et al. <sup>125</sup> first prepared a superhydrophobic silica powder through a one-step sol-gel method compounded with polydimethylsiloxane (PDMS) (Fig.5). And then spray depositing on the glass surface, a transparent and robust composite coating with self-cleaning was obtained. Vidal et al.<sup>126</sup> has prepared a superhydrophobic surface at a high temperature (400 °C) through the sol-gel tetraethoxysilane(TEOS) approach with and

methyltriethoxysilane(MTES) as precursors, using MTES as a hydrophobic agent can effectively improve the water repellent 4.3 I of the silica films.

#### 4.3 Electrochemical



Fig.4 (a) the illustration of fabrication of by-product and cross linked polymethylsioxane of by-product with PMHS, when PMHS is excessive. The red long chain in the first and second figure stands for hydrolysate of PMHS, the blue short chain with three branches stands for hydrolyzates of KH550, the green long chain in the third figure stands for PMHS, and the purple parts mean reacting part. (b) PMHS reacting with KH550 produces by-product. (c)SEM pictures of sprayed sol-gels prepared by mass ratio KH550/PMHS corresponds to 0.25. Figures reproduced from ref <sup>124</sup> with permission of Elsevier.



Fig.5 (a) Schematic illustration for the fabrication process of superhydrophobic coating. (b) reaction mechanism for modifying silica particles. (c)schematic of preparation of PDMS/SiO<sub>2</sub> composite coatings. Figures reproduced from ref <sup>125</sup> with permission of Taylor & Francis.

Since the electrochemical method is not affected by the size and morphology of the substrate, which has greater advantages than other approaches. However, electrochemical parameters have a great impact on surface structure, which resulted in the fabricated superhydrophobic surface is not uniformed, and the used conducting solution will pollute the environment. There are electrochemical polymerization and electrochemical deposition two basic types of electrochemical methods, which are low-cost and facile approaches to construct rough surfaces.<sup>127</sup> The electrochemical polymerization approach without any hydrophobization post-treatments, which only contains a one-step method to form rough low-energy surfaces. This approach took over organic conducting polymers to lead the construction of superhydrophobic structured films on conductive wafers. Electrochemical deposition means that the current applied electric field and the electrons are redox on the poles to build a coating.128

The account of electrochemical deposition is an effective method to construct the micro and nanoscale structure, which been widely applied to fabricate bio-inspired has superhydrophobic surfaces.129-132 Since the electrodeposition method has the features of simplicity, low-cost, and commercially available, therefore, it is commonly used to coat metallic homogeneous surfaces with lasting superhydrophobicity, and has nothing to do with size and shape.<sup>133-134</sup> Furthermore, changing the electrodeposition conditions (such as electrolyte, deposition method, and time) can change the morphology and chemistry of the surface.<sup>135</sup> Qiu al.136 versatile et reported а metallic cobalt micro/nanostructure fabrication facile through а electrochemical crystal growth route. They obtained flower-like structure displayed superhydrophobicity without any modification of hydrophobic organic molecules, and since the capillary effect, the dendritic structure exhibited intrinsic superhydrophobicity. Liu et al.<sup>137</sup> presented a novel, rapid, and environment-friendly method that was applied to prepare a superhydrophobic surface by electrodepositing MB8 magnesium plate in an ethanol solution containing cerium nitrate hexahydrate (Ce (NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O) and myristic acid. The asprepared surface has consisted of cerium myristate with a hierarchical micro-nanoscaled-particles structure (Fig.6). He et al.138 fabricate a micro/nanoscaled non-wetting tin surface on the copper substrate via a simple and productive electrodeposition approach linked with annealing treatment under 180 °C for 60 min without low surface energy organics modification. The as-prepared tin surfaces are porous tremellalike architectures, exhibiting outstanding water-repellent and self-cleaning performance.





Dip coating was regarded as a simple and practical method to prepare superhydrophobic polymeric films.<sup>94</sup> Furthermore, the dip-coating treatment is applicable to prepare large-scale uniformity surface with multi-scale structure at a lower cost. Gurav et al.<sup>139</sup> prepared superhydrophobic silica coatings with self-cleaning by using a facile dip-coating treatment. Methytrichlorosilane (MTCS) as a modifying agent to modify silicon dioxide (SiO<sub>2</sub>) particles with methyl groups. Through multi-layer deposition treatment to fabricate silicon coating with water contact angle was 153 °±2° and roll-off angle was 8 °±1°. Due to the methyl-modified silica particles presented a certain surface roughness and low surface energy coatings, therefore, exhibiting superhydrophobicity, self-cleaning, and durability under a water-jet impact (as Fig.7). Cui et al. <sup>140</sup>constructed multi-scale nano/microstructures of superhydrophobic surfaces that displayed outstanding durability to the high speed scouring analysis and high stability in neutral and other organic solutions (acetone, ethyl acetate, ethanol, toluene, hydrochloric acid, and sodium hydroxide) on the epoxy paint surfaces by using dip-coating process. They first fabricated microstructures with protuberances (5-10  $\mu m$ ) on epoxy paint surface by spray coating, and then they anchored nano-SiO<sub>2</sub> (50-100 nm) onto the microstructure surface by dipcoating treatment (a nano-SiO<sub>2</sub>/ epoxy adhesive solution). In the end, the surface was further modified by aminopropyl terminated polydimethylsiloxane (ATPS) to strengthen hydrophobicity. The water contact angle of the multi-scale structure surface was 167.8 ° and the sliding angle was 7 °. Cholewinski et al. <sup>141</sup> fabricated a robust superhydrophobic hierarchical coating by using a dip-coating treatment, which anchors micron-scale polydimethylsiloxane (PDMS)functionalized silica particles with nano-scale roughness (micro/nano-silica particles) into an epoxy layer spin-coated onto a substrate (glass or stainless steel). They found that the concentration of silica particles has little effect on hydrophobicity and mechanical performance of coatings.

#### 4.5 Etching



Fig.7 (a) Diagram showing simple dip-coating process for deposition of methylmodified silica particles on glass substrate. (b) FE-SEM photo of the silica coatings prepare from three dips. (c) Variation in static water contact angle with number of dips. (d) Water droplets ( $\sim 10 \ \mu$ L) on superhydrophobic silica coating prepared after three dips. (e) Photo of self-cleaning behavior on superhydrophobic silica coating prepared after three dips. (f) Image of water-jet impact on superhydrophobic silica coating prepared after three dips. Figures reproduced from ref <sup>139</sup> with permission of Elsevier.

There are wet chemical etching, plasma treatment, and lithography (as is introduced in the following section) three types of etching method. Wet chemical etching is an accessible

approach to prepare superhydrophobic surfaces. Whereas, to achieve the needed surface roughness by wet chemical etching, which takes a lot of time.

The etching of metals in acid or alkaline solutions would be able to build the two-tiered structure (micro/nanoscaled) needed to obtain superhydrophobicity, and then subsequent surface chemical modification through low-energy materials.<sup>142</sup> This technique has been widely utilized to attain superhydrophobicity on metal substrates (steel, aluminum (AI), copper (Cu), Zinc (Zn), and so on).<sup>143-145</sup> During the etching process, a lot of high energy sites in crystalline metals are easily dislocation and devastate, which prompted the construction of micron-scale surface roughness. The superhydrophobic surfaces on polycrystalline aluminum, copper, and zinc substrates have been prepared by employing a dislocation superhydrophobic surfaces on the Zn plate via ion-assisted chemical etching was introduced by Qi et al.<sup>146</sup> They obtained hierarchical structure superhydrophobic surfaces with different morphology, high strength, and stability after treatment in solutions of nitric acid(HNO<sub>3</sub>) and different metal ions (Ag<sup>+</sup>, Cu<sup>2+</sup>, and Cr<sup>3+</sup>), moreover, their hydrophobicity modification by fluoroalkylsilane(FAS). Latthe et al. <sup>147</sup> proposed a productive method to fabricate a superhydrophobic steel surface that exhibits lasting superhydrophobicity under rigid mechanical bending. In this process, the roughness on the steel surface was constructed via etching in sulfuric acid solution (H<sub>2</sub>SO<sub>4</sub>) and its surface energy was lowered after hydrophobic silane (Methytrichlorosilane) treatment (Fig.9). Tan et al.<sup>148</sup> proposed an easy micro-etching technology to construct a micro-nano structure on the brass surface, and then modification by stearic



Fig.8 SEM Images (a) of the aluminum surface etched with a Beck's dislocation etchant for 15 s at ambient temperature. (b) the photo of water droplets (8  $\mu$ L) placed on the superhydrophobic surface fabricated by deal with A sheet(a) with fluoroalkylsilane, and the water contact angle is about 156°. (c) at low and (d) at high magnification of the copper surface etched with a modified Livingston's dislocation etchant for 24 h at ambient temperature, and the water contact angle is about 153°. (e) at low and (f) at high magnifications of the zinc surface etched with 4.0 moL • L<sup>-1</sup> HCl solution for 90 s, at ambient temperature, and the water contact angle is about 155°. Figures reproduced from ref<sup>145</sup> with permission of ACS.

etchant (such as Beck's and Livingston's dislocation etchant) and following fluorination modification (fluoroalkylsilane) (see as Fig. 8). It is demonstrated that the dislocation etchant prone to dissolves in the dislocation sites of grains, constructing greatly rough surfaces. A rapid method to prepare acid (STA) to reduce surface energy. Remarkably, the brass surface was transformed from hydrophilic to superhydrophilic

to superhydrophobic and displayed an excellent self-cleaning property.

## 4.6 Lithography

Lithography is able to form various textured surfaces with different sizes and shapes, which can achieve accurate control



Fig.9 (a) Illustration of experimental protocol for fabricating superhydrophobic steel surface. (b) FE-SEM images of E-430-SS/8h and (c) high magnification image of marked portion at Fig.(b). (d) FE-SEM images of M-430-SS/8h and (e) high magnification image of marked portion at Fig.(d). (f) optical photographs of water drop on bendable (90°) M-430-SS/8h surface at cross view and (g) front view. (h)optical photographs of water drop on bendable M-430-SS/8h surface >90° at side view and (i)top view. Figures reproduced from ref 147 with permission of RSC.

of the microstructure on the surfaces. <sup>149</sup> Wang et al. <sup>150</sup> proposed to analyze the wettability and mechanical stability of superhydrophobic surfaces from two different length scales and believed that the wettability of the surface is related to nanomaterials, while mechanical stability is related to the microstructure. Microstructure "armour" was constructed on different substrate materials (metal, ceramic, silicon, and glass) by photolithography and cold/hot pressing process, and then the armoured superhydrophobic surface with excellent mechanical stability was obtained by composite modification of superhydrophobic nanomaterials (Fig.10). Furthermore, colloidal lithography was utilized to build two or threedimensional structures, which was a common preparation technique for the production of periodic particle array (PPA) surfaces.<sup>151</sup> Li et al.<sup>152</sup> introduced a novel method for constructing hierarchically wrinkled polymer films with tunable wettability by combining top-down nanoimprint lithography and a bottom-up wrinkling technique. The obtained hierarchical imprinted nanopatterns (Fig.11). As a result of the complementary micro/nano dual-scale roughness taken on the surfaces, which are superhydrophobicity with water contact angles higher than 160 ° and sliding angle lower than 5 °. Furthermore, the wettability of the surfaces can be controlled via tune the film thickness giving great control from hydrophobic to superhydrophobic and an incredible transition from anisotropic to isotropic wetting. Generally, the advantage of lithography is that the template is easy to be prepared and can be used many times, but the disadvantage is that this method requires a flat, smooth and clean substrate to prepare more effective texture structure.

#### 4.7 Plasma treatment

Fig.11 Schematic illustration of the process for generating random wrinkles and hierarchical wrinkle/line patterns on poly (2-hydroxyethyl methacrylate) (PHEMA) films. (a) Random wrinkles via a reactive silane infusion-induced wrinkling method. (b) hierarchical wrinkle/line patterns fabricated by spontaneous wrinkling of pre-patterned PHEMA films. (c) top-view AFM image of the nanoimprinted prepattern and compression direction relative to pattern orientation. (d)schematic of ross-section of grating pattern. Figures reproduced from ref<sup>152</sup> with permission of ACS.



Plasma treatment of polymers adjustments the physicochemical characters of the polymeric surfaces, which wettability can be altering by increasing roughness or changing functional groups of the surface.<sup>153</sup> Polymer, combine with the plasma process, can construct superhydrophobic structures directly. It's a facile and useful method to fabrication of



Fig.10 Design and mechanical stability of the armoured superhydrophobic surface. Figures reproduced from ref <sup>150</sup> with permission of Springer Nature.



wrinkle patterns display regularly ordered herringbone superhydrophobic polymeric structures achieved via the geometric confinement of the structures. There are

and

surfaces

etching

plasma

hierarchical

plasma

polymerization two basic processes, which have been broadly used in the fabrication of superhydrophobic surfaces. Plasma etching is an effective method to increase the roughness of the substrates. Besides, plasma polymerization is another method to acquire a superhydrophobic polymeric surface. The surface structure is modified via the barrage of excited ions, which are produced by the plasma, to the substrate. The hydrophobic surface could be fabricated by using reactive plasma created by argon and oxygen mixture onto the polytetrafluoroethylene (PTFE).<sup>154-155</sup> And then the surface morphology turns into microstructures with various surface roughness.

Ryu et al.<sup>156</sup> reported a simple preparation method of almost ideal superhydrophobic surfaces via plasma treatment with a mixture gas of argon and oxygen. A PTFE sheet was chosen as a substrate material. After one-step plasma etching. superhydrophobic PTFE samples with a high contact angle of 178.9 °and a low sliding angle less than 1 °. Furthermore, the superhydrophobic prepared surfaces display great superhydrophobicity in the aging test, they nearly retain the original wettability, even after over-exposed to air for 80 days and the repetitive water droplet impact experiments. Wang et al. <sup>157</sup> fabricated a superhydrophobic surface that has good corrosion resistance and wears on the aluminum substrate. With anodization and low-temperature plasma to construct micro-nano-structure and then using trichlorooctadecyl-silane modified the rough surface.

It is noteworthy that applying plasma etching treatment could control the spacing, diameters, height, and related parameters for fabrication of rough structure on superhydrophobic surfaces, and the advantage of plasma treatment is that it is can be used on the whole surface. However, due to the special experimental conditions and chemicals, which results in restrictions of large-scale application. **4.8 Template** 

Learning from biological surfaces is our purpose, we can replicate the structure from living beings to fabricate superhydrophobic surface, even if relatively complex structures. The template method can directly control the sizes, shapes, and aligned microstructures, which was commonly utilized to build complicate rough surfaces with a hierarchical structure. <sup>158-159</sup> As a result of the template is easy to be prepared and be used more than once, it's an effective method to construct a rough surface. The template technique consists of three steps. First, prepare a suitable template master; second, form the replica, and lastly, take off the template. To construct the superhydrophobic surfaces with hierarchical structures, the template method was supposed to be an effective method and polydimethylsiloxane (PDMS) was an essential material to reproduce structures of templates.<sup>160</sup> However, how to achieve low-cost, large-scale application, and good performance still needs to be taken into consideration for the template method.

Lepore et al.<sup>161</sup> used lotus leaf as a pattern mask, and then fabricated artificial bioinspired polystyrene (PS) surface with hierarchical microstructure via a facile template method at ambient temperature and atmospheric pressure, and exhibited

superhydrophobicity and self-cleaning. Lv et al. <sup>162</sup> proposed a simple one-step method and efficient process for the tunable construction of hierarchically hairy particles (HHPs) on a largescale by using initiator droplets (boron fluoride ethyl ether (BFEE)) as dynamic templates, planning for imitating the papilla of the lotus leaf (Fig.12). And then obtained a robust superhydrophobic coating with superhydrophobicity, selfcleaning, and anticorrosive properties. Peng et al. 163 fabricated the microcavity-array surfaces with hierarchical structures via dip-coating polymerized n-octadecylsioxane nanosheets (PODS) onto microscale polydimethylsiloxane (PDMS) negative replicas by considering taro leaf as a template (Fig.13). It's noticed that the fine-scale roughness contributes to the metastable wetting state convert into the Cassie state on a concave surface. Therefore, the water-repellent of the microcavities surface was markedly improved by modifying with a coating of PODS. Xu et al.<sup>164</sup> investigated the porous anodized aluminum oxide membranes that were applied as the templates to construct nanostructured polystyrene (PS) surfaces through the temperature-induced capillary template wetting method. The wettability of PS with varied surface topographies at different annealing temperatures was considered (Fig.14). As a result of the construction of a composite surface existing of solid and air, the hydrophobicity of PS was dramatically improved on highaspect-ratio polystyrene nanostructures. They also found that the wetting state transition between the Wenzel and Cassie-Baxter state at a certain annealing temperature.



Fig.12 Schematic illustration of the synthesis of the HHPs. (a) The BFEE droplets stabilized by the surfactant. (b) particles formed immediately after adding monomers. and (c) HHPs obtained after polymerization for several minutes. (d) schematic diagram of the synthesis of the poly(DVB-co-VBC) HHPs. (e) one nanofiber of the poly(DVB-co-VBC) HHPs. (e) one nanofiber of the poly(DVB-co-VBC) HHP synthesized at 0.7 wt.% of DVB polymerized for 10 min followed by another polymerization of 0.7 wt.% of the VBC/DVB mixture (2:1) for another 10 min. inset image: Cl element distribution along the nanofiber. (f) FTIR spectra of (I)poly(DVB) HHPs and (II) poly(DVB-co-VBC) HHPs:1630 cm<sup>-1</sup>(C=C stretching), 1266 cm<sup>-1</sup>(C-Cl stretching). Figures reproduced from ref  $^{162}$  with permission of RSC.



Fig.13 (a) Illustration of the improved template process on a taro leaf (TEOS: tetraethyl orthosilicate). The molding process was conducted under conditions of relative humidity 33% and temperature 15 °C. (b) Optical image of taro leaf surface. (c) SEM images of negative PDMS replica obtained from the taro leaf using the traditional template method. (d) SEM images of negative PDMS replica obtained from the taro leaf using the improved template method. (e)SEM images of the PODS-coated PDMS negative replica. Insets in (c, d, and e) are CA images. Figures reproduced from ref  $^{163}$ with permission of Elsevier.



Fig.14 (a) The illustration of fabrication procedure of nanostructured PS surface. (b) SEM images of polystyrene nanorods top view obtained after annealing at 110 °C for 2 h. SEM images of polystyrene nanostructures obtained after annealing at 170 °C(c) and 190 °C (d) for 2 h.(e) Contact angles of water drops on the nanostructured polystyrene surfaces prepared at different annealing temperature. Inset images show the water drop shape on the nanostructured surface prepared at 190 °C (right image) with a contact angle of about 104 °and on the surface prepared at 190 °C (right image) with a contact angle of about 161°. Figures reproduced from ref  $^{164}$  with permission of Elsevier.

#### 4.9 Spray process

**Review** 

Spray technique is one of the facile and efficient methods to fabricate the coating with microstructures. However, the crucial issue about this technique is that to enhance the adhesion force between coating and substrate and to precisely control the surface structures. Hwang et al. <sup>165</sup> proposed a one-step simple spray-deposition strategy for preparing the superhydrophobic surface with a new statistical copolymer, which was consist of 3-[tris [(trimethylsilyl) oxy]-silyl] propyl methacrylate (SiMA) and methyl methacrylate (MMA) via free-radical polymerization under a nitrogen atmosphere (Fig.15). The obtained surface is a rough structure with a high water contact angle of 178 °and low contact angle hysteresis less than 1  $^\circ,$  which is similar to that of the lotus leaf. Li et al. 166 presented a facile method for the preparation of superhydrophobic SiO<sub>2</sub> paper that was invented via spraying hydrophobic SiO<sub>2</sub> nanoparticles suspension on paper substrate. The hydrophobic SiO<sub>2</sub> nanoparticles were fabricated through immobilizing octadecyltrichloro groups (octadecytrichlorosilane (OTS)) on SiO<sub>2</sub> nanoparticles. The asfabricated hydrophobic SiO<sub>2</sub> paper displayed super waterrepellent and highly transparent.





#### 4.10 Composite method

Up to now, a substantial amount of superhydrophobic surfaces have been fabricated by different synthetic methods and combinations of those methods (composite technique), based on consideration of surface with rough structures (microstructure, nanostructure, and micro/nanoscaled twotiered structure) and chemical compositions of low surface energy <sup>167</sup>. The fabrication strategies mentioned above can be categorized as the pre-modifying then post-roughening (such as vapor deposition and sol-gel process), and pre-texturing then post-modifying (such as electrochemical, dip-coating, etching, lithography, et al.)

Zhang et al.<sup>168</sup> fabricated the stable superhydrophobic aluminum alloy surface with dual geometric structures via a combination of the simple method of chemical etching, dipcoating, and modification of fluorosilicane. The obtained superhydrophobic surface exhibited highly durability, which was due to the dual-scale surface structure, the strong and stable bonding between SiO<sub>2</sub> particles, and fluorosilicanemodified resin (F20SP70) molecules. polvester The superhydrophobic surface also displayed great antifogging and delayed icing performances, compared to hydrophobic and hydrophilic Al surfaces. Choi et al.<sup>169</sup> introduced a hybrid method that combined sol-gel-based nanoimprint lithography with hydrothermal growth to fabricated various TiO<sub>2</sub> structures (micro, nano, and hierarchical structures). Although various TiO<sub>2</sub> structures exhibited superhydrophobicity, since air pockets trapped inside the hierarchical structure minimized the contact area between liquids and solids, therefore, hierarchical structures possess more stable and robust superhydrophobic performances than other structures for water evaporation (Fig.16). Pozzato et al.<sup>170</sup> fabricated superhydrophobic silicon surfaces via a combination of nanoimprint lithography and wet chemical etching. A positive photoresist was employed that well resists buffered hydrofluoric acid etching and allows removal of the residual resist layer in imprinted zones by UV-ozone treatment. They found that advancing contact angles of water droplets on the superhydrophobic surfaces well agree with the Cassie model. Chen et al.<sup>171</sup> constructed robust hierarchically wrinkled nanoporous polytetrafluoroethene (PTFE) surfaces that show superhydrophobic performances via a combination of PTFE micellization and spontaneous surface wrinkling on a commercially available thermo-retractable polystyrene (PS) sheet. The wrinkled patterns could closely bind the nanoporous

PTFE layer via enhanced adhesion from their carved surface and viscous liquid surfactants, making these surfaces mechanically robust and offering potentially extendable substitutes with self-cleaning, antifouling, and drag-reducing properties.

superhydrophobic surfaces were of actual significance for antiicing due to deposited water droplets can be easily removed without freezing and accumulating on the solid substrate by its gravity, when the substrate is slightly tilted.



Fig.16 (a) Schematic illustration of the fabrication process of  $TiO_2$  hierarchical structures along with sol-gel-based nanoimprint lithography and hydrothermal. SEM micrographs of  $TiO_2$  (b)microstructure, (c)nanostructure, (d)hierarchical structure. (e) SEM micrographs of  $TiO_2$  nanostructure with growth times of 4 h. (f) SEM micrographs of hierarchical structure with growth time of 4 h. Figures reproduced from ref<sup>169</sup> with permission of RSC.

Generally, with the development of technology, there will be a growing number of fabrications that are facile and convenient for constructing a rough structure on the material surface. During the past few years, researchers have constructed rough structures on different substrates, such as graphene, cotton fabric, polyester fabric, silicon rubber, aluminum, stainless steel, and so on.<sup>172</sup> As we all know, practical applications are directly subject to performances. The superhydrophobic surfaces have endowed excellent property on self-cleaning, anti-fogging, antiicing, oil-water separation, and anti-corrosion. However, undesired ice formation and aggregation has brought safety problems and huge economic loss to our lives, therefore, in the next part, the anti-icing property of superhydrophobic surface with rough structure will be delivered.

## 5. Anti-icing

Inspired from nature living to fabricate superhydrophobic surfaces, which have micro-nano structure with air trapped inside surface structures. <sup>173</sup> The superhydrophobic surfaces have large water contact angle ( $\vartheta_{CA}$ ) and small contact angle hysteresis ( $\vartheta_{\textit{CAH}}$  ), which made deposit water droplet remains at a nonwetting Cassie-Baxter state and small contact area with the solid surface. More than anything, as a result of trapped air in the surface textures, the interaction between water droplets and the solid surfaces is reduced, the energy barrier of eliminating water droplets from a superhydrophobic surface is minimized, and the water droplet slides readily on superhydrophobic surfaces when the surface is lightly tilted.<sup>174</sup> Therefore, the bio-inspired surfaces can significantly lower the actual solid-liquid contact area, reducing the thermal exchange efficiencies, and accelerating bounce off after water droplets falling or impacting on surface, which is greatly beneficial to hinder and reduce icing. Tourkine et al. 50 first indicated that

The ice formation and accumulation of water droplets on a solid surface mainly include the impact and freezing process. The droplet impacting on a solid surface usually has the spreading, retraction, oscillation, splash, rebound, or adhesion stage. As regard to impacting water droplets, superhydrophobic surfaces with well-constructed surface structures have been developed to avoid freezing, since water droplets were able to bounce off the superhydrophobic surfaces before ice nucleation occurs even in a severe environment.175 The fluid property, impact velocity, droplet size, and surface characteristics (morphology and chemical composition) can influence the impacting process, and the freezing process of water droplets on a cold surface could be affected by the droplet volume, pressure, and surface characteristics. Maitra et al.<sup>176</sup> studied and analyzed the mechanisms of droplets rebound or impalement of textured (wrinkled) surfaces with great droplet impalement resistance (water-repellent) performances down to subzero. The impacting behaviors were represented by Weber number (W<sub>e</sub>) defined as follow equation:

$$W_e = \frac{\rho_1 V^2 D_0}{\gamma} \tag{4}$$

Where the  $\rho_1$  represents the density of the liquid, V and D<sub>0</sub> is the droplet impacting velocity and droplet diameter,  $\gamma$  is its surface tension, respectively. The partial infiltration had an appreciable effect on the droplet receding dynamics and the contact time on the substrates at cold temperatures with closely related to an increase in the liquid viscosity. By using the morphology dependent W<sub>ec</sub> can accurately predict the transition from drop rebound to impalement. It's noteworthy that the hierarchical structured superhydrophobic surface has much higher W<sub>ec</sub> than micro- or nanostructured superhydrophobic surfaces, and W<sub>ec</sub> is a critical value of Weber number, beyond which impacting water droplets could not thoroughly bounce off. Furthermore, owing to the hierarchical superhydrophobic surface with minimum texture spacing between the asperities (both at the microscales and nanoscales), therefore, it's great impalement resistance (water-repellent) in surfaces with the same solid fraction.

In addition, the remarkable thing is that way in which a water droplet of the radius (R), as its impact with a superhydrophobic surface depends primarily on its impacting velocity (V). Richard et al. <sup>177</sup> investigated the contact time of water droplet (t) impacting the solid surface by using high-speed photography, and changing the impacting velocity (V) and water droplet radius (R) to draw out the rebound behavior of water droplets vertically impinging on a superhydrophobic surface. The contact time could be described by Eq. (5):

$$t \approx \sqrt{\frac{\rho R_0^3}{\gamma}}$$
(5)

Which could comprehend directly through a combination of balancing inertia (of the order  $\rho R^3/t^2$ ), and capillarity ( $\gamma/R^2$ ). According to Eq. (5), it was clearly shown that contact time (*t*) is only connected with the initial radius of a water droplet (R<sub>0</sub>) and liquid-vapor surface tension ( $\gamma$ ), and has nothing to do with the impinging velocity in a broad range from 20 cm·s<sup>-1</sup> to 230 cm·s<sup>-1</sup>. Mishchenko et al.<sup>51</sup> proposed a new mechanism stressing the significance of dynamic wetting behavior, which is prompted to rebound of impinging water droplets from a cooled (-20 °C to - 35 °C) superhydrophobic surface before ice nucleation occurs. There is a transition temperature, ice aggregated less than this temperature could be completely detached, while water droplets froze within a time lower than  $t_c$  ( $t_c$ =2.65t).

The nucleation and growth of ice have been a heated area of research over the past years.<sup>178-180</sup> On the basis of classical nucleation theory, the relationship between free energy barrier ( $\Delta G$ ) and nucleation rate (J) can be defined as Eq. (6) and Eq. (7), respectively, for heterogeneous ice nucleation from the vapor phase relies on interfacial energies, the radius of curvature, and lattice mismatch.<sup>181-183</sup>

$$\Delta G = \frac{\pi \sigma_{IV} r^{*2}}{3} (2 - 3m + m^3)$$

$$J = J_0 \exp\left(-\frac{\Delta G}{RT}\right)$$
(6)
(7)

Where  $\Delta G$  and J for a flat inconsistent interface,  $\sigma_{IV}$  represents the ice-vapor surface energy,  $r^*$  represents the critical radius, and the parameter m is the ratio of the interfacial energies as:

$$m = \frac{\sigma_{SV} - \sigma_{SI}}{\sigma_{IV}}$$
(8)

Where  $\sigma_{SV}$  is the solid-vapor interfacial energy and  $\sigma_{SI}$  is the solid-ice interfacial energy, respectively. Note that the critical radius  $r^*$  could be connected with other thermodynamic quantities given by:

$$\ln \frac{P}{P_{\infty}} = \frac{2\sigma_{IV}}{n_I k T r^*} \tag{9}$$

Where *P* represents the ambient vapor pressure,  $P_{\infty}$  represents the saturated vapor pressure on a flat ice surface at temperature *T*, n<sub>1</sub> represents the number of molecules per unit

volume of ice, *k* represents the Boltzmann constant, and  $J_0$  represents a kinetic constant. According to Eq. (6) and Eq. (7), it is clearly shown that surfaces with spatially uniform intrinsic interfacial energies will be characterized by spatially uniform nucleation energy barrier ( $\Delta G$ ) and rate (J), therefore, lend to nonpreferential frost nucleation when favorable super saturation conditions are obtained. Varanasi et al.<sup>184</sup> operated real-time frost nucleation and growth investigates on superhydrophobic surfaces fabricated by a typical photolithography process and coated with trichlorosilane in an environmental scanning electron microscope (ESEM). They found that frost nucleation and water condensation appears indiscriminately within superhydrophobic textures without any particular spatial preference.<sup>184</sup>

When considering the ice layer removed from the solid surfaces requires overcoming the ice adhesion strength ( $\tau_{ice}$ ) parallel to the superhydrophobic surfaces. Usually, the antiicing or de-icing efficiency of superhydrophobic surfaces has been assessed by measuring force (*F*), contact area (*A*) of ice, and ice adhesion strength defined as the following equation<sup>48, 186</sup>:

$$\tau_{ice} = \frac{F}{A} \tag{10}$$

Where F represents the shear force for removing the ice from a solid substrate, A is the apparent contact area between the ice and the solid surfaces. In addition, the anti-icing property or icephobic is widely applied to characterize surfaces for which  $\tau_{ice}$  $\leq$  100 kPa,<sup>187-188</sup> compared with structural materials (for instance aluminum, copper, and steel), for which  $\tau_{ice} > 1000$ kPa.<sup>189</sup> Though the study of adhesion is generally explained with regard to ice adhesion ( $\tau_{ice}$ ), it is the intensity that is widely applied to characterize failure.<sup>10</sup> It is well known that the adhesion is investigated according to surface energy, 45, 184 lubrication<sup>6,185,190</sup>, and interfacial cavitation.<sup>191</sup> There are two conflicting viewpoints for stress, toughness, and delamination could be elucidated through the cohesive zone models of fracture.<sup>192-193</sup> Among them, the simple analysis models could be applied to show that the shear strength of the interface  $(\hat{\tau})$ , regulates delamination when the length of the interface is comparatively small, therefore,  $\tau_{ice} = \hat{\tau}$ .

What is clear is that ice adhesion strength ( $\tau_{ice}$ ) can be adjusted by changing the chemical and physical properties of the materials that ice adheres to. Kendall and Chaudhury <sup>194-195</sup> further elucidated the adhesion mechanics, the critical shear stress ( $\tau_{ice}$ ) required to remove ice from a surface coating of a certain material could be described by Eq. (11). According to Eq.11, lower work of adhesion between ice and the material ( $W_{adh}$ ), lower shear modulus of the material ( $\mu$ ), and higher film thickness (t) lead to lower ice adhesion strength ( $\tau_{ice}$ ). <sup>196</sup>

$$\tau_{ice} \propto \sqrt{\frac{W_{adh}\mu}{t}} \tag{11}$$

Due to the soft materials possesses low shear modules are favorable for ultra-low ice adhesion strength ( $\tau_{ice}$ <10 kPa), so the soft materials are the up-to-date class of icephobic materials. <sup>197-200</sup> Beemer et al. <sup>201</sup> prepared low ice adhesion

PDMS gels ( $\tau_{ice}\approx$ 5 kPa) via hydrosilylation of vinyl-terminated PDMS with hydride-terminated PDMS as shown in Fig.17 (a). They elaborated on the mechanism of ice separation from PDMS gels by using separation pulses and Eq.11. They also found that the root mean square (RMS) roughness of the surface of PDMS gels (soft material) increased from 0.05  $\mu$ m±0.01  $\mu$ m to 3.52  $\mu$ m±0.2  $\mu$ m after abrasion and the ice adhesion slight increased with surface roughness. It should be noted, however, that the surfaces with liquid lubricants have negligible shear modulus ( $\mu$ ≈0) and result in a cohesive failure of liquid lubricant during the process of ice separation from a thin film as shown in Fig.17b. low-interfacial toughness materials ( $\Gamma < 1 \text{ J/m}^2$ ) applied for which the force needed to remove adhered ice from large areas is both low and has nothing to do with the interfacial area. They also indicated that coatings made of low interfacial toughness materials (such as polydimethylsiloxane, polystyrene, and polypropylene et al.) allow ice to be separated easily from large areas ( $\sim 1 \text{ m}^2$ ) only through self-weight. Guo et al.<sup>203</sup> investigated the robust icephobic/anti-icing performance that is constructed on a micro/nanostructured surface (MN-surface) imitated by the MN feature on butterfly wings. They demonstrated that the MN-surface is a robust anti-icing/ icephobic performance which is much better than that of



Fig.17 (a) Schematic of the fabrication of PDMS gels (soft material). (b)Schematic illustrating the cohesive and adhesive during the process of the ice separation from soft material. Figures reproduced from ref<sup>201</sup> with permission of RSC.

Instead, interfacial toughness  $\Gamma$  regulates separation when the length of the interface is comparatively large. The studies display that the critical bonded length at which a transition is, between the two models of failure appears, and described by the following equation <sup>202</sup>:

$$L_c = \sqrt{\frac{2E_{ice}\Gamma h}{\hat{t}^2}}$$
(12)

Where  $E_{ice}$  represents the modules of ice (~8.5 GPa) of the thickness (*h*). Most importantly, when the length interfaces (*L*) larger than the critical bonded length ( $L_c$ ), the force required to separate the ice is steady, whatever how large the interface may be. Most recently, Golovin et al.<sup>202</sup> fabricated coatings with

nanostructured surfaces (N-surfaces) and far better than microstructured surfaces (M-surfaces) and smooth surfaces without any structure(S-surface). And a great antiicing/icephobic property is attained on MN-surfaces, lasting for a long delay time of  $\sim$ 7000 s for ice-formed. As a result of the synergistic action of the micro/nano scale structure and chemical composition on the solid material surface, the water droplet is indeed suspended in a Cassie-Baxter state, at which the formed ice has lower ice adhesion ( $\tau_{\rm ice}$ ) and remove the ice easily. Furthermore, the bio-inspired superhydrophobic surface reduces the actual solid-liquid contact area to lower thermal transfer efficiency, which is greatly beneficial to the delay icing and improve anti-icing property. Some representative biological

surfaces with a micro/nano scale hierarchical structure for antiicing performance investigations are listed in Table 1.

#### Table 1 Anti-icing performance of typical biological interfaces Biological Methods Materials Functions Anti-icing property Refs interfaces Lotus leaf Soft lithography ZnO nanoparticles, PDMS Superhydrophobicity, After 100 icing-melting cycles, the 204 and dip coating self-cleaning icing delay time of the droplet freezing on the surface is not less than 152±3 min and the icing delay time of the surface was longer than 150 min even after 100 bending test times. Rose Chemical etching Hydrochloric acid, nitric Superhydrophobicity, A large film could be observed on 205 petal acid, hydrogen peroxide, UV-durability, corrosion the original steel, whereas on ice 1H,1H,2H,2Hresistance film, or even very small freezing Perfluorodecyltriethoxysil spots, could hardly be found on the ane(FAS-17) superhydrophobic surface. Butterfly Crystal growth and ZnO nanohairs Lasting for a long delay time of $\sim$ 203, Superhydrophobicity, wing dip-coating 7000 s for ice formation, $\vartheta_{CA}$ =150 self-cleaning, anti-87 °,ϑ<sub>ACA</sub>=150.2 °,ϑ<sub>RCA</sub>=141.1 °. frosting, anti-fogging, directional adhesion Petal Chemical etching, $H_2O_{2}$ Superhydrophobicity The superhydrophobic surface with 206 shaped lithography fluoroalkylsilane(FAS-17) petal shaped nanostructures process, and planted on array micro-patterns electrochemical generated a tremendous anti-icing etching potential greatly preventing the icing accumulation at -10 °C under the condition of icing wind tunnel, and exhibiting a lower ice adhesion strength compared with a market mature production of the sol-gel superhydrophobic coating. ϑ<sub>CA</sub>=164.31 °,ϑ<sub>SA</sub>≈0 °. Coral-like Chemical etching CuCl<sub>2</sub>·2H<sub>2</sub>O Superhydrophobicity The water droplet remained 207 and hot-water unfrozen on the coral-like treatment superhydrophobic surface at -6 °C for over 110 min and 71% of the surface was free of ice when exposed in "glaze ice" for 30 min.

## 6. Conclusions

Even though bio-inspired technology and superhydrophobicity are both recently advanced perceptions, they have already grown into crucial to a great deal of research and will probably significant to people's lives. The combination of them has contributed to the construction of multifunctional superhydrophobic surfaces, which play essential roles in many practical applications. However, as a result of the fragility of micro/nanoscaled two-tiered structures, the crucial challenges for bioinspired surfaces are to increase the robustness, durability, and thermal stability. In this review, we mainly have given a summary of the fundamental theories of the surface structure and recent proceeds in the construct of a range of different superhydrophobic surfaces with hierarchical structures applying an extensive variety of materials and fabrication methodologies. The anti-icing/icephobic property of superhydrophobic surfaces also has been discussed. Even if enormous accomplishments have been realized in this field during the past few years, it must figure out that there remain many challenges and problems require to be resolved for further research. First of all, a variety of methods of constructions for superhydrophobic surfaces has been developed. However, the majority of fabrications couldn't fulfill essential requirements in industries' practical applications.

Secondly, more theoretical analyses in view of original findings should be proposed to creating the superhydrophobic system, which is useful for investigating the fabrications and applications of superhydrophobic surfaces. Last but not least, the anti-icing/icephobic property of superhydrophobic surfaces has grown into a prevailing and heated research direction on account of its promising in practical applications. In addition, low cost, facile preparation methods, and environmentalfriendly raw materials should be given priority to constructing superhydrophobic surfaces, besides, the micro/nanoscaled hierarchical structures as well as should be further investigated.

On account of the aforementioned challenges and problems, it is essential to construct a robust and stable superhydrophobic surface with a hierarchical structure. From the view of practical applications, superhydrophobic films are wished to have great mechanical anti-icing/icephobic, good stability. and transparency, which can be applied in a severe environment. Furthermore, the large-scale and application of fabricating superhydrophobic films have always been taken note of. All in all, it is our firm conviction that the brilliant future of superhydrophobic surfaces with bioinspired micro/nanoscaled two-tiered structures will be witnessed and great improvements and practical applications will have come true through the efforts of the researchers.

## **Conflicts of interest**

There are no conflicts to declare.

## Acknowledgements

This work was financially supported by Research funds of the Maritime Safety Administration of the People's Republic of China (2012\_27), Fundamental Research Funds for the Central Universities (3132019305) and European Union project H2020 - MSCA - RISE 778104.

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