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Icephobic materials: fundamentals, performance evaluation, and applications

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Abbreviations

SLIPS	slippery liquid-infused porous surface
CA	contact angle, θ
CAH	contact angle hysteresis
APCA	apparent contact angle, θ^*
SA	sliding angle
ACA	advancing contact angle, θ_{aca}
RCA	receding contact angle, θ_{rec}
SEM	scanning electron microscope
AAO	anodic aluminum oxide
UV	ultraviolet
FE-SEM	field emission scanning electron microscopy
FAS-17	1 <i>H</i> ,1 <i>H</i> ,2 <i>H</i> ,2 <i>H</i> -perfluorodecyltrimethoxysilane
DSC	differential scanning calorimeter
MAGSS	magnetic slippery surface
SAM	self-assembled monolayers
DT	delay time
PVDF	polyvinylidene fluoride
SLWL	self-lubricating liquid water layer
DC-704	tetramethyltetraphenyl-trisiloxane
AFM	atomic force microscope
HMDSO	hexamethyldisiloxane
PDMS	polydimethylsiloxane
PU	polyurethane

Abstract:

Ice accretion may cause malfunction or serious performance degradation in outdoor facilities and structures, such as aircraft, ship, locks and dams, offshore platforms, solar panels, wind turbines, power transmission towers and lines, and sports facilities, leading to huge economic loss or even loss of human lives. Icephobic materials, typically applied in the form of coatings, have received growing attention in the last decade. This review focuses on recent research progress in water wetting state, ice nucleation, and ice adhesion from both theoretical and application perspectives. After a short introduction, static and dynamic water wetting behaviors are reviewed, with an emphasis on reducing the water adhesion at low temperatures. Ice nucleation theories have been applied to investigate how the surface texture affects the ice nucleation behavior, which in turn could be used to explain various observed icing delays. Icephobic performance tests at lab scale are then introduced, before several application examples of icephobic materials are illustrated. This review ends up with discussions of some outstanding issues and challenges faced by this research community, keeping in mind the complexity of different environment in which practical applications are taking place.

Keywords: icephobic; anti-icing; superhydrophobic; ice nucleation; ice adhesion; icing delay

1. Introduction

Undesirably icing on solid surfaces has become a rising issue to our daily lives through disturbing aircrafts flying, downing power lines, freezing the roads, obstructing the telecommunication facilities, and perturbing the flow field of wind-turbine blades, *etc.* [1-7]. As an example in aircraft, ice with a thickness around 1.2 mm adhered onto the airfoil surface will cause 25% reduction in the lift force per unit area, causing great difficulty in handling the aircraft [8-10]. As a consequence, ice accretion is a great threat to the flight safety and even gives rise to many crashes taking place in recent years. The ice accretion produces the troubles far more than this, and also brings many inconveniences to our daily lives, resulting in the enormous economic loss every year [11-17]. To prevent or to suppress the ice build-up, researchers and engineers have made a great deal of effort to understand the physicochemical mechanisms of freezing, and developed many anti/de-icing strategies over the last decades [18-20]. Some typical de-icing approaches, such as vapor heating, electro-thermally melting, and mechanical vibration, have been optimized and widely used in the above fields [21-24]. However, these active de-icing methods usually rely on continuously heating or intermittent vibration of the frozen locations with huge energy consumption, and the corresponding equipment / systems are also difficult to design and manufacture, therefore these strategies should be avoided or minimized in the future whenever possible [25,26].

An interesting alternative is through passive methods towards ice prevention, *i.e.*, to make the surface phobic to ice formation and/or adhesion. Considering a typical ice

formation and accretion process a flying aircraft encounters, a large number of supercooled microdroplets suspended in cold air will firstly wet the solid surface and rapidly freeze into ice [27-29]. Materials showing non-wetting characteristics may serve as a passive anti-icing agent to repel the supercooled droplets first, finally achieving the purpose of anti-icing and reducing the dependence on or even replacing the above-mentioned active de-icing methods [30,31]. In this case, superhydrophobic materials (contact angle (CA) $> 150^\circ$ and contact angle hysteresis (CAH) $< 10^\circ$) are naturally considered to be the ideal candidates as the icephobic materials [32,33]. In this regard, icephobicity generally refers to the ability of a solid surface to repel ice or prevent ice formation. It is worth noting that water repellence, a necessary feature for superhydrophobic materials, is not absolutely equivalent to ice repellence. The latter is reflected through an icing delay time or temperature and low ice adhesion. Since ice is formed through water freezing at low temperatures, water repellence is indeed closely related to ice repellence. However, the relationship is not as straight forward as it seems because the materials requirements for icing delay and low ice adhesion are not always the same as the ones for water repellent surfaces, sometimes contradicting requirements may occur. For example, the surface micro-nanoscale textures have been extensively studied to induce superhydrophobicity by trapping air pockets underneath the water droplet. At the same time, they may simultaneously bring many sites to promote heterogeneous ice nucleation [34-37]. Also, the ice adhesion may be greatly enhanced under the anchorage action caused by the surface microscopic textures. As a consequence, microscopically rough superhydrophobic

surfaces may not always be effective for icephobicity owing to the difference in reference environments [35-42]. Overall, the relationship between superhydrophobicity and icephobicity remains an interesting discussion point [43,44], and we will try to shed some lights on this controversial issue in this review.

Boinovich LB, *et al.* firstly summarized the icephobicity of superhydrophobic surfaces in the view of repelling supercooled water [45]. On this basis, Lv J, *et al.* further discussed the functions of air pockets entrapped by the surface textures for timely removing supercooled droplets and reducing ice adhesion [46]. Meanwhile, Kreder MJ and his colleagues considered that the slippery liquid-infused porous surface (SLIPS) can eliminate some drawbacks of textured superhydrophobic surfaces with the enhanced capacity of slipping off the ice [47]. In addition, some other reported reviews mainly focused on superhydrophobic surfaces [48-50] but with no or limited description towards anti-icing evaluation and application. Although some literatures provide a good insight to the apparent icephobicity of textured superhydrophobic surfaces based on the classical wetting models, there has been little focus on the solidification process (ice nucleation and growth) of supercooled droplets. Essentially, icing is a nucleation and growth process, therefore ice nucleation is an important aspect of icephobic materials development. This requires a good understanding of the interface states in order to retard the ice nucleation and growth [51-55]. Therefore, for a comprehensive review on icephobic materials, it is necessary to include the latest understanding on static-dynamic wetting behavior, ice nucleation, ice adhesion, and the evaluation methods before their application potentials are

discussed.

In this review, the interaction between water and solid surface is discussed first with the understanding that timely removal of water is a key perspective of icephobic materials. Following this, ice nucleation theories are applied to investigate how the surface texture affects the probability of ice nucleation, which in turn could be used to explain various observed icing delays. Next section mainly summarizes the recent research progress on the macro icephobic performances, including the icing delays, ice adhesion, and durability to resist mechanical damage. Following these discussions, the applications in potential fields are described in details so that the current challenges faced by icephobic materials development are better understood. Readers could better appreciate the complexity of different environment in which practical applications are taking place. Finally, we provide our remarks and the outlook on the future development of icephobic materials.

2. Wetting behavior and wetting minimization

2.1. Wetting theories

Wettability at static state is the result of the equilibrium of three phases (solid, liquid, and vapor) at their interfaces. A liquid droplet on the flat surface cannot completely spread and thus will form a CA (θ) with the solid surface, as shown in Fig. 1a. The CA is determined by the surface / interface free energies (or surface tensions), which is described by the Young's equation [56]:

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

where γ_{sl} , γ_{lv} , and γ_{sv} are the interface tensions in the system of solid / liquid,

liquid / vapor, and solid / vapor, respectively. Young's equation is the basis to investigate the wettability of solid surface, and it is only appropriate for an ideally flat surface [57]. In reality, the solid surface is often rough and uneven, and the actual CA of a droplet on a rough surface is different from the Young's CA. In order to better analyze the wettability of non-ideal rough surface, the apparent contact angle (APCA), θ^* is proposed to evaluate the wettability [58].

Fig. 1. Typical wetting mechanisms. (a) Young's contact mode on a flat surface. (b) Wenzel mode on a rough surface. (c) Cassie-Baxter mode on a rough surface with air trapping.

The Wenzel wetting model states that a liquid can completely fill into the rough surface structures (see Fig. 1b) [59], and there is a relationship between roughness and APCA given by the Wenzel equation [60]:

$$\cos \theta^* = r \cos \theta \quad (2)$$

where r is the roughness factor, defined as the ratio of actual solid / liquid contact area over the nominal interface contact area ($r \geq 1$). Following this equation, a series of wetting phenomena can be well explained. For the hydrophilic surface ($\theta < 90^\circ$), the

APCA gradually decreases with the increasing roughness, and the surface changes more hydrophilic. In contrast, the increasing roughness of a hydrophobic surface ($\theta > 90^\circ$) will induce a higher APCA (more hydrophobic). Therefore, Wenzel equation implies that constructing the microscopic rough structures is an effective approach to enhance the non-wettability with a higher APCA, even reaching 150° or beyond.

Wenzel equation well reveals the relationship between APCA and surface microscopic rough structures. However, there are some wetting phenomena in nature that cannot be explained by this equation, such as the rolling water droplets on lotus leaf and water droplets rapidly slipping off the ladybug's back surface [61-63]. Through careful investigation, it was found that there exists another type of composite interface of mixed solid / liquid and liquid / vapor contacts, as shown in Fig. 1c. In this case, the mathematic relationship between APCA and rough structures can be described by the Cassie-Baxter equation [64]:

$$\cos \theta^* = f_1 \cos \theta_1 + f_2 \cos \theta_2 \quad (3)$$

where θ_1 and θ_2 are the Young's CA of droplets on solid and vapor (or air), respectively, and f_1 and f_2 are the fractional contact of the solid / liquid and liquid / vapor interfaces, respectively. Since $f_1 + f_2 = 1$, and Young's CA of the droplet on air can be considered to be 180° , the Cassie-Baxter equation can be rewritten as:

$$\cos \theta^* = f_1 \cos \theta_1 + f_1 - 1 \quad (4)$$

This wetting model can well explain some superhydrophobic phenomena with the special composite contact interface. For a hydrophobic material with a certain value

of Young's CA, more air pockets trapped by the microscopic structures will lead to a smaller f_1 and higher non-wettability as reflected by a higher APCA [65-68].

Both Wenzel equation and Cassie-Baxter equation can explain the action mechanism of surface textures on enhancing the non-wettability, yet some differences exist. Wenzel wetting model considers that the contact between solid and liquid is a completely infiltrated state, and the microscopic structure with an appropriate geometric design can produce a higher APCA [69,70]. However, this wetting regime brings the unfavorable element that the droplet has a robust adhesion on the solid surface due to the enlarged actual contact between solid and liquid. For Cassie-Baxter wetting model, the actual contact area is much smaller than apparent contact area, therefore it will result in a low water adhesion with a small sliding angle (SA) or CAH [71]. Therefore, from the view of repelling water and anti-icing, icephobic materials are expected to possess the microscopic structures that conform to the requirement of Cassie-Baxter wetting regime.

2.2. Interface interaction to minimize water adhesion

Through extensive investigation on the natural and artificially prepared superhydrophobic surfaces, it has been confirmed that the key factors to cause the superhydrophobicity are chemical compositions that decide the surface free energy and the geometric structure at microscopic level that controls the surface roughness [72-76]. On a perfectly flat surface, the CA of a water droplet can only reach up to around 120° by reducing the surface free energy (the lowest surface free energy was reported to be around 6.7 mJ m^{-2} , which was attained by regularly aligned

closest-hexagonal-packed $-\text{CF}_3$ groups) [77,78]. However, a synergistic action with microscopic structures can induce APCA to reach 150° or higher, and SA (or CAH) no more than 10° [74,79-82]. For anti-icing purpose, the candidate icephobic materials should first be endowed with high APCA and the low water adhesion for excellent water repellence. This well explains many current research efforts focused on regulating the surface nanostructures (morphology and size) for anti-icing applications.

2.2.1. Effect of morphology and size of surface nanostructures

Surface nanostructure determines the wetting regime of solid / liquid contact mode and therefore plays a significant role in achieving the desired water repellence. By investigating creatures in nature, researchers have revealed the functions and action mechanisms of nanostructures on the non-wetting characteristics and have artificially mimicked these special non-wetting surfaces [53,54,83-85]. Through the observation of microscopic features of superhydrophobic lotus leaf surface [86,87], the almost-hemispherical papillae with size of 5-10 μm (height to basal radius aspect ratio of ~ 1) are randomly distributed on the surface and simultaneously decorated with branch-like protrusions with size of approximately 150 nm, as shown in Fig. 2a-c. This type of hierarchical micro-nanostructures is considered the main reason to achieve the superhydrophobicity, displaying almost complete suspension of water droplets on the surface (see Fig. 2d). Subsequently, the contact interface of solid / liquid is confirmed to be in line with the Cassie-Baxter wetting regime [88-92]. The microstructures entrap a large number of air pockets to hold up the droplets, as shown

in Fig. 2e. Meanwhile, the surface shows low droplet adhesion (as illustrated in Fig. 2f) and droplet cannot stably sit on the superhydrophobic surface when tilted at an angle $\sim 4.0^\circ$ [93].

Fig. 2. Nature-inspired nanostructures for special non-wetting states. (a) The lotus leaf surface and its microscopic features (b and c). (d) Optical image of a droplet statically sitting on the surface of lotus leaf. Reproduced with the permission from Ref. [86], copyright 2008, Wiley-VCH. (e) Schematic diagram of wetting regime of droplet on lotus leaf. (f) Artificially prepared superhydrophobic surface with high CA and low SA. Reprinted with permission of Ref. [93], copyright 2011, Elsevier Inc. (g,h) Microscopic topographies on the gecko's toes and the artificially fabricated bio-mimicked nanostructure. (i) Superhydrophobicity with high droplet adhesion on

the artificially prepared surface. Reproduced from Ref. [95] with the permission of Royal Society of Chemistry.

At the other end of droplet adhesion, gecko's toes exhibit extremely high droplet adhesion strength, and at the same time a high water CA. Fig. 2g and h show the microscopic feature of the its toes. A water droplet can be stably pinned on the surface of gecko's toes with the APCA of approximately 160° (Fig. 2i), and the droplet still adheres to the surface the place upside down. It is believed that the high CA and a high adhesive force with water are related to the microscopic surface features. Scanning electron microscope (SEM) images illustrate the microscopic morphologies of gecko's toes, as shown in bottom of Fig. 2g. Gecko's toes are covered with millions of well-aligned microscopic keratinous hairs called setae (20-70 μm in length and 3-7 μm in diameter), which further splits into hundreds of smaller nanoscale ends (100-200 nm in diameter) [94,95]. Therefore, the superhydrophobicity of gecko's toes can be well explained using the similar wetting mechanism as superhydrophobic lotus leaf surface (Cassie-Baxter contact mode) [88-90,97]. However, unlike the lotus leaf that presents a very low adhesion with water, there exists a high adhesion between water and gecko's feet. Such seemingly peculiar behavior was found to be due to the collective intermolecular (van der Waals) force between the high-density nanoscale ends (spatulae of the gecko) and water [98-101]. It is noted that to enable this so-called gecko's contact state, a large number of nanostructured contacts have to be made at molecular level of closeness. To verify the proposed mechanism, Liu K. *et al.* artificially fabricated similar microscopic nanostructure polyimide films using anodic

aluminum oxide (AAO) as a template, as shown in Fig. 2h [95]. The resultant surface possesses a high droplet adhesive force, showing the water droplet does not slid off the polyimide films when tilted at 90° or even 180° (see Fig. 2i). Hereto, it can be concluded that various wetting characteristics can be achieved by regulating the microscopic nanostructure features with different topographic features.

Following this principle, a great progress has been made in tuning water adhesion on superhydrophobic surfaces. Lai Y, *et al.* designed and prepared three kinds of superhydrophobic nanostructured (nanopore array, nanotube array, and nanovesuvianite) TiO₂ surfaces [102], and obtained different water adhesion ranging from 5 μ N to 76 μ N, as shown in Fig. 3a-c. They considered that the different water adhesion was mainly attributed to the change of solid / liquid interface action force from capillary adhesive force (for nanopore array and nanotube array) to van der Waals force (for nanovesuvianite). Meanwhile, the capillary adhesive force can be also controlled by regulating the porous nanostructure diameter, finally causing the distinction in water adhesion [103-105]. On this basis, Zhao XD, *et al.* prepared various MnO₂ nanostructures and achieved superhydrophobicity with the APCA reaching 155°, as shown in Fig. 3d-g [106]. These nanostructures induced the different water adhesion from nearly 0 μ N to 130 μ N, which was explained from the view of kinetic barrier difference resulted from the unique extent of continuity of the triple-phase contact line (insets in Fig. 3d-g). Subsequently, a large number of experimental investigations were reported to confirm and further enrich the studies on the regulation of water adhesion on superhydrophobic surfaces [98,99,107,108].

Having summarized all these reported research work, we believe that superhydrophobicity can be easily obtained under the synergistic action of micro / nanostructure and the surface chemistry. However, the water adhesion can show huge variation, which depends a lot on the nanostructure features (size, closeness in contact, open vs. closed pores, *etc.*).

Fig. 3. (a-c) Schematic illustrations of three types of superhydrophobic porous-nanostructures with water adhesive forces ranging from high to low. Reproduced with the permission of Ref. [102], copyright 2009, Wiley-VCH. (d-g) SEM images of MnO₂ mesh-like structure (d and e for large and small mesh size, respectively), tilted nanorod structure (f), and cactus-like ball structure (g). Insets show the dragging water droplets and the triple-phase contact line at the contact interface of solid / liquid. Reproduced with the permission of Ref. [106], copyright 2011, American Chemical Society.

It is worth noting that nanostructure setae appearing on gecko's toes belong to the complete open system, but they are still able to induce a high water adhesion. As analyzed above, enabling true molecular contact implies that, besides the

topographical factor, there should be additional considerations of the size and the mechanical flexibility of the nanostructures. Fig. 4 shows schematic diagrams of contact interfaces of water droplet on the nanostructures (open system) with different sizes. When the spacing distance of nanostructures gradually increases to a certain extent (~ 100 nm), the nanostructure will not be able to maintain the Cassie-Baxter mode to hold up the water droplet. Instead, complete infiltration contact of solid and liquid (*i.e.*, Wenzel wetting mode) will take place, as shown in Fig. 4a. In this case, water droplet on the surface cannot slide away due to the high adhesive force caused by the intimate contact, which reflects the wetting characteristics of a rose petal. With a decrease of the nanostructures size, the wetting mode gradually changes from the Wenzel wetting mode to Cassie-Baxter mode with a large number of air pockets trapped underneath water droplet, leading to smaller actual solid / liquid contact area with a low water adhesion (see Fig. 4b). If the spacing of nanostructure reduces to the extent of nanostructure setae on gecko's toes (as seen in Fig. 4c) a high water adhesive force will be induced within the Cassie-Baxter wetting mode [95] due to the cumulative intermolecular forces caused by a large number of nanostructured contacts, as discussed above [96].

Fig. 4. Schematic diagrams of different solid / liquid contact modes with different water adhesion. (a) Wenzel mode inducing high water adhesion (represented by the rose petal in nature). (b) Cassie-Baxter mode inducing low water adhesion (represented by the lotus leaf). (c) Cassie-Baxter mode inducing high water adhesion (represented by gecko's toes).

All these discussions on the effect of nanostructure topography and size on non-wettability (especially water adhesion) have revealed in details their underlying mechanism to control water repellence, and represent recent research advances in theory. It is clear that only keeping the non-wetting state is insufficient to achieve the robust water repellence, avoiding the gecko's state in which high-density of van der Waals nano contacts is necessary. These understandings are of great significance to guide the design of superhydrophobic nanostructures with ultralow water droplet adhesion for the purpose of achieving self-cleaning and icephobicity.

2.2.2. Ultralow water adhesion

As discussed above, ultralow water adhesion of the surface is critical for rapidly removing supercooled droplets and eventually avoiding freezing. Tian J, *et al.* [109] utilized the diffusion-limited crystal growth principle to control the tapering of ZnO

nanorods in an extremely strong alkaline reaction system. They prepared nanoneedle, nanopencil, and nanorod arrays (Fig. 5a-c) through regulating the reaction time and temperature, and the resultant surfaces exhibited different extent of anti-water adhesion ability, as shown in Fig. 5e and g. With decreasing synthesis temperature, the profiles of nanocrystals switched from nanorods (prepared at 90 °C and 80 °C) to nanopencils (at 70 °C) and nanoneedles (at 60 °C and 65 °C), accompanied by a gradual reduction in both the top diameters (from ~125 nm to 30 nm) and water adhesion. Compared with the water adhesive force (50 μ N) induced by nanorods, the nanoneedles only produced water adhesive force as low as ~3 μ N, which can be further confirmed by the optical images of aligned nanorod (left) and nanoneedle (right) films separating instantaneously from the suspended droplet (see Fig. 5e). Correspondingly, the water droplet rolling off angle exhibited the same trend, as shown in Fig. 5f-h. Shen Y, *et al.* reported a layer of TiO₂ nanowires with different length and diameter grown on a Ti substrate with different water adhesive forces [110,111]. These studies further confirm that ultralow water adhesion condition is indeed achievable, and it does not only depends on the topography of nanostructures, but also their size and surface properties.

Fig. 5. Nanostructured superhydrophobic ZnO surfaces and water adhesion. (a-c) SEM tilted views of the ZnO nanorods, nanopencils, and nanoneedles synthesized at 80 °C, 70 °C, and 60 °C for 1 h. (d) Water adhesive force as a function of reaction temperature. (e) Images showing aligned nanorod (left) and nanoneedle (right) films. Water droplet was instantaneously separated upon being dropped on to the surface. (f) Measured tilting angle of five ZnO nanostructured samples. (g) Optical images showing that the droplet can pin on to the nanorod surface when placed horizontally, but roll off when tilted at 10°. (h) The droplet instantly rolls off the nanoneedle surface at nearly 0°. Reproduced with the permission of Ref. [109], copyright 2014, Wiley-VCH.

Another strategy to obtain ultralow water adhesion is inspired by the perfect slipperiness of *Nepenthes* [112-115]. The functional surface, prepared via lubricant

infusing nanoporous structures (denoted as slippery liquid-infused porous surfaces or SLIPS), exhibits an extremely low wetting hysteresis because of the presence of a layer stable film made of low surface energy liquid [116]. The latest report from Aizenberg J's group used a layer-by-layer deposition method to prepare alternating layers of negatively charged silica nanoparticles and positively charged polyelectrolytes with a high porosity [117]. Subsequently, the nanostructures were further functionalized with fluorinated silanes and infiltrated with fluorinated oil to form a smooth, highly water-repellent coating, as illustrated in Fig. 6a. Fig. 6b shows the morphologies of surface nanostructures with different number of layers of silica nanoparticles. When the coatings were prepared with four or more deposition layers, a higher roughness was created with a stronger ability to immobilize the lubricant layer and induce the stable water repellence with lower CAH and SA, as shown in Fig. 6c and d. Even a low surface energy liquid can slide freely on the surface, as shown in Fig. 6e.

Fig. 6. (a) Schematic diagram of the layer-by-layer process to prepare nanoscale slippery, lubricant-infused porous coatings. (b) SEM images showing the surface nanostructures with different number of deposited layers. (c, d) Contact angle hysteresis of water (c) and octane (d) for the layer-by-layer silica nanoparticle coatings in dry, fluorosilanized and lubricant-infused states as a function of the number of deposited layers. (e) Images verifying the slippery performance of surface nanostructure with infiltration of lubricant (bottom image), compared with the untreated surface (top image). Reproduced with the permission of Ref. [117], copyright 2014, Wiley-VCH.

Despite the excellent properties reported in the lab, the slippery liquid-infused

porous surfaces still face great challenges for practical application. Mainly from mechanical perspective, there are two key limitations. First, the infused liquid might be drained away eventually by gravity or capillarity force. Second, the mechanical property is weak due to the formation of highly porous structures for the purpose of locking the lubricant in the surface layer. These limitations prevent SLIPS to be applied in harsh working conditions, for example, aircraft or wind turbines, where the strong airflow poses great challenge to the mechanical property and durability of the surface coatings. In addition, the infused organic oils may also be decomposed under long-term ultraviolet (UV) exposure in an outdoor environment.

2.3. Low temperature non-wettability

As discussed above, non-wettability is mainly caused by air pockets trapped by surface nanostructures, and can be well explained using Cassie-Baxter wetting model. However, when the ambient temperature decreases to below the ice freezing temperatures, the over-saturated water molecules will start to condense on the surface of a nanostructured superhydrophobic coating. This type of tiny water droplet formation effectively prevents the air pocket formation, and may lead to a change of non-wettability at low temperatures. Fu Q, *et al.* prepared a group of superhydrophobic coatings by means of sol-gel method, with varied amount of silica particles to achieve the different surface roughness, as shown in Fig. 7a-d [118]. The increasing content of silica particles causes increased surface roughness from 0.1 μm to $\sim 1.7 \mu\text{m}$ (see Fig. 7e), and the corresponding CA increases from 50° to 165° (with 20 wt% silica particles). Interestingly, the non-wettability changes with the ambient

temperature. As shown in Fig. 7f, the reduction in CA is more obvious for the sample surface with a higher CA at room temperature (e.g. the M-20 sample). The sample surface exhibits very high adhesion (water droplet cannot slide away) at low temperatures, while at room temperature the droplet can slide away easily (SA of $\sim 5^\circ$). The high adhesion at low temperatures is explained by the wetting of the air pocket surface through moisture condensation [119-122]. Thus, it is not surprising that ice adhesion strength on this coating is even higher than one on uncoated flat glass substrate because the latter has a smaller water / solid contact area [118]. Accordingly, an important consideration for the development of icephobic materials is how to maintain non-wettability at low temperatures [121,123].

Fig. 7. Superhydrophobic coatings prepared by means of sol-gel method with different content of silica particles. (a-d) SEM images showing the morphologies of superhydrophobic coatings with different amount (5, 10, 15, and 20 wt%, respectively) of silica particles. (e) Roughness of the resultant superhydrophobic coatings. (f) Water CA (solid symbol and line) and SA (open symbol only available at room temperature; water droplet cannot slide down at lower temperatures) at temperatures ranging from 25 $^\circ\text{C}$ to -10 $^\circ\text{C}$. Reproduced with the permission of Ref. [118], copyright 2014, American Chemical Society.

In order to reveal the process of non-wettability change with decreasing

temperature, the profiles of a water droplet on the superhydrophobic surface under different temperatures were recorded (see Fig. 8) by He M, *et al.* [124]. Using the modified ZnO nanorod array superhydrophobic surface, they found that at $-10\text{ }^{\circ}\text{C}$ the CA showed a decrease of approximately 8° compared with that at room temperature. This further indicates that the environmental temperature affects the wetting state. Furthermore, some other reports proposed that the surface free energy of superhydrophobic surface was also influenced at low temperatures, showing an increased surface free energy at low temperatures [125-127]. All these studies confirm that superhydrophobic surface with perfect non-wettability at room temperature is not always superhydrophobic at low temperatures, especially when below the freezing point, due to the change of pressure of trapped air pockets and surface free energy.

Fig. 8. Profile of water droplets on superhydrophobic ZnO nanorod array surfaces (with different APCA from top to bottom) at (a) room temperature, (b) $-5\text{ }^{\circ}\text{C}$, and (c) $-10\text{ }^{\circ}\text{C}$. Reprinted with the permission of Ref. [124], copyright 2011, Royal Society of Chemistry.

2.4. Dynamic water repellence

In many practical situations, supercooled droplets would dynamically hit the surface at a certain angle with a kinetic energy. Immediately after the droplet is in contact with a superhydrophobic surface, it spreads out to a maximal deformation and then retracts, before it finally bounces off the surface. The process is illustrated in Fig. 9. Contact time of the entire impact process directly reflects the extent of energy transition between water droplet and surface, which is considered to be crucial to anti-icing performance of superhydrophobic surfaces under this dynamic environment [128,129]. The contact time should be kept short enough to repel the supercooled droplet off the surface before it freezes.

Fig. 9. Bouncing process of impact droplet on the superhydrophobic surface. (a) Schematic diagram of moving process of impact droplet on the superhydrophobic surface. (b) Images recording the moving process captured via high-speed video, insets are the field emission scanning electron microscopy (FE-SEM) image of the superhydrophobic surface and the static image of a water droplet deposited on the surface. Reprinted with the permission of Ref. [128], copyright 2015, AIP publishing LLC.

Generally, the contact time has been widely investigated and analyzed according

to a simplified system with inertial-capillary nature. The impact droplet can be considered as a free oscillation system with stiffness γ and mass ρD_0^3 , and the contact time t is scaled as the inertial time scale $t_i = \sqrt{\rho D_0^3 / \gamma}$ [129,130]. The contact time is mainly divided into two parts: 20-30% of the total contact time is required to spread to the maximum deformation and the remaining time is spent in the retraction stage. It is well acceptable that the spreading stage is mainly driven by the inertia, yet the capillarity plays a dominant role during the retraction process. The retraction time of the impact droplet is highly dependent on the viscous force at the solid / liquid interface [131].

Recently, Shen Y, *et al.* has revealed the relationship between the contact time and wetting hysteresis of the solid surface [132]. They prepared six types of solid surfaces with different non-wettability on a titanium alloy (Ti6Al4V) substrate, and recorded the bouncing process and the contact time. As shown in Fig. 10, the ability of impact droplet bouncing off is closely associated with CAH rather than APCA [133]. The work done W against wetting hysteresis resistance is related to the wetting parameters as:

$$W \propto \frac{\cos \theta_R - \cos \theta_A}{1 - \cos \theta^*} \quad (5)$$

where θ^* is the APCA, and θ_A and θ_R are the advancing contact angle (ACA) and receding contact angle (RCA), respectively. The impact droplet with less kinetic energy consumed to overcome the work done will show higher ability to bounce off the surface with a shorter contact time.

Fig. 10. Correlation between contact time of impact droplet with wetting parameters (APCA and CAH) of different surfaces prepared on an Ti6Al4V alloy (labeled as HS-1, HS-2, HS-3, HS-4, HS-5, and HS-6, respectively). The impact droplets on HS-2 and HS-3 sample surfaces cannot bounce off, as shown by the blue arrows. Reprinted with the permission of Ref. [132], copyright 2015, American Chemical Society.

Many factors affect the contact time of an impact droplet on superhydrophobic surfaces. Intuitively, if the water droplet strikes a superhydrophobic surface with higher velocity, the water droplet would more rapidly bounce off with a shorter contact time. Some recent researches, by gradually increasing the impact velocity, found that the contact time remains unchanged with the impact velocity, and the contact time has a linear relationship with the radius of impact droplet, as seen in Fig. 11 [129,134,135]. When a water droplet impacts on the superhydrophobic surface at a higher velocity, the spreading diameter becomes bigger, which requires more kinetic energy to be consumed to overcome the viscous resistance during the spreading and retraction processes. Meanwhile, the viscous resistance to hinder the movement of droplet also has a certain extent of enhancement due to the change of dynamic

pressure with higher impact velocity [136]. Thus, the contact time of impact droplet on the superhydrophobic surface does not change with the impact velocity, and the ratio of spreading time or retraction time occupying the total contact time is almost constant, although increased impact velocity causes a large variety of modes of droplet deformation during the contact process.

Fig. 11. Contact time as functions of impact velocity and radius of droplet. (a) Contact time keeping unchanged with increasing impact velocity. (b) Linear relationship between contact time and radius of droplet. Data are fitted by the equation $t = 2.6\sqrt{\rho R^3 / \gamma}$ (pink dotted line), as found in Ref. [129]. Reproduced with the permission of Ref. [134], copyright 2015, Macmillan Publishers Limited.

As illustrated in Fig. 11b, the contact time has a linear relationship with the radius of impact droplet, which conforms to equation $t = 2.6\sqrt{\rho R^3 / \gamma}$ (R is the radius of original droplet, and γ is the stiffness). This phenomenon may be well explained by balancing the constantly antagonistic system of inertia force ($\rho R / t^2$) with capillarity force (γ / R^2). It also indicates that with the increase of droplet radius, the increment of capillarity force to resist the movement of droplet is higher than that of inertia force [137]. Furthermore, Shen Y. *et al.* also discussed the relationship between bouncing dynamics of impact droplets and static liquid adhesion driven by

micro/-nanostructure features [138,139]. They designed and fabricated three types of nanostructure (nanotube, nanomesh, and nanowire) superhydrophobic surfaces based on the TiO_2 nano-materials. All these resultant surfaces were endowed with lower static liquid adhesion (the sliding angles from 7.5° to 3°). However, there was a remarkable difference in the bouncing dynamics of an impact droplet on these surfaces: nanostructures with high openness (such as nanowire) is beneficial to the impact droplet bounding off the solid surface. Regarding the bouncing dynamics of impact droplets on superhydrophobic surfaces, many efforts have been devoted to reveal the correlation and action mechanisms of various factors, including non-wettability, surface temperature, kinematic parameters of impact droplet, and intrinsic properties, and so on. All these investigations aiming at reducing the contact time of impact droplet on superhydrophobic surfaces are very necessary and will certainly contribute to the ultimate design of superhydrophobic surfaces for anti-icing applications [133,140,141].

2.5. Submillimeter macrostructure enhanced dynamic water repellence

A minimum contact time (approximately 12 ms) of the impact droplet on an extremely hydrophobic surface has been theoretically proposed and experimentally verified [128-130,132,133,140-142]. However, the contact time is still longer than the significant time scale in freezing conditions. In an exciting effort, Kripa K. Varanasi and his co-workers were able to reduce the above minimum contact time to 7.8 ms by designing a ‘minus-shaped’ macroscopic ridge structure on the superhydrophobic surface to enable a non-axisymmetric retraction process of the impact water droplet,

as shown in Fig. 12a and b [143]. Research has found that the reduction of contact time induced by the macroscopic ridge structure mainly occurs during the retraction process. If a droplet impacts on the uniform superhydrophobic surface, the rim with a certain thickness h should retract axisymmetrically with the retraction velocity $V = (2\sigma / \rho h)^{1/2}$, where σ is the solid / liquid surface tension and ρ is the liquid density. With the assistance of macroscopic ridge structure, the retraction velocity is faster in the thinner regions with less mass to accelerate, leading to the spreading droplet dividing into two parts and decreasing the retraction time. Under inspiration of this work, Shen Y, *et al.* constructed some more complex ridge macrotextures (“three-forked”, “cross-shaped”, and “five-forked”, *etc.*) on the superhydrophobic surface, and through more properly altering the hydrodynamics of impact droplet, finally obtained an even lower contact time of 5.5 ms [128]. This value is further evidenced to be a limiting contact time, regardless of the droplet hydrodynamics, as shown in Fig. 12c. They suggested that the retracting process could be completely integrated into the spreading process to the maximal deformation under the assistance of the “cross-shaped” surface macrotextures, resulting in a limiting overall contact time of approximately 5.5 ms, the theoretically calculated time required for spreading out to maximal deformation. Similar work was also reported by Gauthier A. *et al* [134], which confirmed the function of submillimeter macroscopic structures reducing the contact time of an impinging droplet on superhydrophobic surfaces.

Fig. 12. Approaches to reduce the contact time of impact droplet on superhydrophobic surfaces through macrostructure design. (a-b) Images showing the impact droplet on the superhydrophobic surface with macroscopic ridge structures rapidly bouncing off (contact time of 7.8 ms) and along ridge dividing into two parts, (a) top view and (b) side view. Reprinted with permission of Ref. [143], copyright 2013, Macmillan Publishers Limited. (c) The contact time of impact droplet on the superhydrophobic surface with more complex macro-ridges. Reproduced with permission of Ref. [128], copyright 2015, AIP Publishing LLC. (d) Image illustrating that the impact droplet on the convex superhydrophobic surface can also rapidly bounce off with a 28% reduction in the contact time. Reproduced with permission of Ref. [144], copyright 2015, AIP Publishing LLC. (e) Selected snapshots showing a droplet impacting on an *Echeveria leaf* bounces off the surface at a much-shortened contact time of 11.8 ms. Reprinted with permission of Ref. [145], copyright 2015, Macmillan Publishers

Limited. (f) A water droplet impacts on the tapered surface and bounces off the surface with a pancake shape at ~ 3.4 ms, and (g) the detailed topography of the tapered surface. Reprinted with permission of Ref. [146], copyright 2014, Macmillan Publishers Limited.

Subsequently, Shen Y *et al.* further verified that droplet impacting onto convex superhydrophobic surfaces can also rapidly bounce off with a 28.5% reduction in contact time compared with that on a flat surface [144]. Onto the convex surface, the impact droplet produced a special hydrodynamic distribution with an annulus shape, as shown in Fig. 12d. This has resulted in a high retracting velocity of the external and inner rims, assisted by the inertia force and the surface energy change, respectively. Liu Y, *et al.* fabricated curved macroscopic textures (convex and concave) with the curvature of radius comparable to the droplet size [145]. As illustrated in Fig. 12e, the droplet spreads larger in the azimuthal direction than in the axial direction, and bounces off the curved surface with an elongated shape along the azimuthal direction. As a consequence, the asymmetric momentum and special mass redistribution produces a unique hydromechanics, which has led to a 40% reduction in the contact time.

In 2014, a further breakthrough in reducing the contact time was reported. The superhydrophobic surface decorated by macroscopic tapered structures could induce the impact droplet to bounce off the surface with a pancake shape, reducing the contact time by 80% comparing with the flat superhydrophobic surface (see Fig. 12f and g) [146,147]. The bouncing regime is called "pancake bouncing", which has been

widely discussed because of the remarkable reduction in contact time [148-150]. This observation also challenges the conventional understanding on droplet bouncing behavior. A widely recognized explanation for such "pancake bouncing" phenomenon is that the liquid that has penetrated into the macroscopically tapered structures can store a certain amount of capillary energy at the time of spreading to the maximum deformation. Such energy causes the droplet to bounce off more rapidly. The occurrence of "pancake bouncing" is highly dependent on geometrical features of the macroscopic tapered structures, because they directly determine the ability to store the capillary energy. All these innovative investigations provide many refreshing inspirations to design micro / macroscopic structures to reduce the contact time of an impact droplet. They also shed new light into the impact dynamics of a liquid droplet onto textured surfaces. The improved understandings have already been seen, and will continue to bring in advances in timely removal of supercooled droplets from the surface, an important consideration for icephobic materials.

3. Ice nucleation

Following the non-wettability for timely removal of supercooled droplets, another key consideration for icephobic materials is to delay the freezing process. This is governed by ice nucleation and growth, which follows the classical nucleation and crystal growth theories in materials science [151-154]. An icephobic material should have the ability to delay ice nucleation in terms of temperature (under continuous cooling) or time (under a constant temperature). In this section, we will begin first with the classical nucleation theories on homogeneous and heterogeneous

surfaces, after which nucleation behaviors on two types of icephobic coatings will be discussed.

3.1. Homogeneous ice nucleation

Upon cooling, water freezes into ice, which is a spontaneous phase transformation process accompanied by the reduction in the Gibbs free energy of the system. Under the thermodynamic driving force, ice nucleation will occur once a sufficient number of relatively long-lived hydrogen bonds spontaneously develop at the same location to form a compact nucleus. Subsequently, the nucleus alters the shape and size until reaching a stage that allows the rapid expansion, and finally causes crystallization of the entire system [152,153,155]. As shown by the molecular dynamics simulation in Fig. 13, the water freezing process after quenching (at $t = 0$ ns) from high temperature to 230 K is clearly illustrated [156]. Water molecules first spontaneously connect into many small rings at the junction of hydrogen bonds. Subsequently, the individual rings are destroyed and continuously reformed, and the entire system still displays a disordered state. However, there are some long-lived hydrogen bonds appearing occasionally and randomly at different locations. With extended time, a polyhedral structure is formed spontaneously and contains long-lived hydrogen bonds, as shown in the yellow circle region in Fig. 13b. The polyhedral structure is termed as the initial nucleus, and slowly changes its shape and size by continually adjusting the surrounding hydrogen bonds. Once the initial nucleus meets the requirement for expansion, the polyhedral structure will rapidly replace the disordered water molecules into a stable state, *i.e.*, forming ice (see Fig. 13c-e). The

first stage (*i.e.*, corresponding to Fig. 13a) consumes most time of the entire freezing process (red line in Fig. 13f). Once the nucleus forms with the polyhedral structure, the expansion occurs rapidly to form ice, which can be explained by the reduction of the total potential energy, as marked by the light-color background in Fig. 13f.

Fig. 13. Images showing the molecularly-simulated hydrogen bond network structure of pure water at a given time and the change of total potential energy during water freezing process (quenching at $t = 0$ ns from the high temperature to 230 K). (a-e) At time of 208 ns, 256 ns, 290 ns, 320 ns, and 500 ns, respectively. Therein, lines represent hydrogen bonds, and the intermolecular bonds of water participating in such hydrogen bonds. (f) The total potential energy in the trajectory for 512 water molecules. Reprinted with the permission of Ref [156], copyright 2002, Macmillan

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Molecular dynamics simulation visually exhibits the water freezing process, which has further emphasized the three essential conditions of ice nucleation, *i.e.*, supercooling, structure fluctuation, and energy fluctuation. Controlling these essential conditions is able to regulate the ice nucleation for achieving the aims of anti-icing [157]. From the simulation process, there is one vital precondition for the occurrence of ice nucleation: only the ice nuclei reaching the critical size can induce the rapid occurrence of ice nucleation, or else they will be destroyed and restore into water molecules [151,158]. On a continuum scale, the classical nucleation theory requires that the critical ice nucleus radius r_c is governed by:

$$r_c = \frac{2\gamma_{IW}}{\Delta G} \quad (6)$$

where γ_{IW} is the water / ice interfacial energy (23 mJ/m² at 253 K [159]) and ΔG is the free energy barrier of bulk ice vs bulk liquid, which conforms to the Gibbs-Helmholtz equation:

$$\Delta G = \frac{\Delta H(T_m - T)}{T_m} \quad (7)$$

Furthermore, $\Delta H = 287 \text{ MJ/m}^3$ is the water volumetric enthalpy of fusion, and $T_m = 273 \text{ K}$ is the ice melting temperature at 1 atm. Following equations (6) and (7), the critical ice nucleus radius can be calculated to be $r_c = 2.2 \text{ nm}$ for water at $-20 \text{ }^\circ\text{C}$ [160]. This critical size varies with the varying degree of supercooling. It was reported that $r_c = 1.7 \text{ nm}$ at $-25 \text{ }^\circ\text{C}$ and $r_c = 2.6 \text{ nm}$ at $-15 \text{ }^\circ\text{C}$ [161,162]. The variation was also verified with large-system molecular simulation [158].

Molecular dynamics simulation plays a key role in the study of ice nucleation, since it provides a visual process of water molecule motion and ordering process that is experimentally difficult or impossible [163]. The motion of water molecules in the system mainly depends on the Newtonian mechanics in the simulation process. Subsequently, the system configuration integral is calculated to further predict the thermodynamic quantity and the macroscopic performance. However, it should be noted that the effect of environment factors is ignored during the molecular calculation. Its potential function and numerical algorithm have the great influence on the accuracy of simulation. In order to improve the accuracy of potential function, the combination of local density functional theory, quantum chemical analysis, Ab initio molecular dynamics, and Monte Carlo method is expected to be the best method to study the potential function in the future [164,165]. Experimentally, the microscopic motion process is difficult to trace, therefore a statistical analysis is need to verify the predicted results by molecular dynamics simulation.

3.2. Heterogeneous ice nucleation on geometric surfaces

In most of the practical situations of ice formation, the above-described homogeneous nucleation does not happen. Instead, heterogeneous nucleation can be more easily induced with a lower nucleation free energy, because an existing solid surface is able to reduce the energy barrier for the ice nucleation. On the other hand, if the roughness of a solid surface is lower than the critical ice nucleus size and the surface energy is very low, ice nucleation could be delayed to be comparable to that of a homogeneous nucleation. Till to date, the size of critical ice nucleus has not been

experimentally determined, posing an uncertainty when developing nanoscale features favoring icing delay. Currently, the development of icephobic materials mainly follows two directions: superhydrophobic surface mimicking the lotus leaf structure and the slippery liquid-infused porous surface [160,166]. Both strategies will be discussed in details later in this chapter based on the classical nucleation theory to reveal the underlying icephobic mechanisms. A third emerging direction of preparing smooth, non-porous, solid surface with a low energy surface will be briefly discussed in Chapter 5 as an example of new development in this field driven by the requirement for transparent icephobic coatings for a number of practical applications.

In a heterogeneous nucleation between solid / liquid interface, the free energy barrier $\Delta G_c'$ is reduced by a geometric factor $f(\theta)$ compared with the free energy barrier ΔG_c for homogeneous ice nucleation, and the relation is well given through the classical nucleation theory:

$$\frac{\Delta G_c'}{\Delta G_c} = f(\theta) = \frac{2 - 3\cos\theta + \cos^3\theta}{4} \leq 1 \quad (8)$$

If the heterogeneous ice nucleation takes place on the perfectly flat surface, it is only related to the CA (θ), and the variation of geometric factor $f(\theta)$ with CA is shown in

Fig. 14. A completely non-wettable surface ($\theta = 180^\circ$) requires the same nucleation energy as the homogeneous case, since $f(\theta) = 1$.

Fig. 14. Geometric factor $f(\theta)$ for a heterogeneous ice nucleation as a function of contact angle θ on a flat surface.

However, this relationship is not usually applicable for an actual solid surface, where some microscopic geometrical structures are present. The effect of the surface geometric structure on the free energy barrier for heterogeneous ice nucleation can be studied through the convex and concave surfaces (as shown in Fig. 15) [167-170].

Fig. 15. Schematic diagram of heterogeneous ice nucleation on a (a) convex surface. (b) concave surface. Reproduced with the permission of Ref [169], copyright 2008, American Institute of Physics.

In this case, the critical size of ice nuclei is confirmed to be the same as that in homogeneous nucleation, and the free energy barrier for the heterogeneous ice

nucleation is given by [168]:

$$\Delta Gc' = \Delta Gc \cdot g(R, \theta) \quad (9)$$

where

$$g(R, \theta) = \frac{1}{2} \left[1 - \cos^3(\phi + \theta) - \frac{3 \cos \theta \sin^2(\phi + \theta)}{1 + \cos \phi} + \frac{(2 - 3 \cos \phi + \cos^3 \phi) \sin^3(\phi + \theta)}{\sin^3 \phi} \right] \quad (10)$$

$$\text{and } \phi = \arccot \left(\frac{\frac{R}{r_c} - \cos \theta}{\sin \theta} \right) \quad (11)$$

In the above equations, θ is the CA of ice nucleus on the spherical substrate, and ϕ is the angle between the spherical substrate and the planar substrate, as illustrated in Fig.

15. It is worth noting that Equation (9)-(11) can be applied to ice nucleation on both convex and concave surfaces ($R, \phi < 0$) [169]. Equation (10) can be replaced by another form, which allows a better view of the contribution of varying CA with a fixed value of R [168] as in:

$$g(R, \theta) = \frac{1}{2} \left[1 - \cos^3(\phi + \theta) - 3 \left(\frac{R}{r_c} \right)^2 \cos \theta (1 - \cos \phi) + \left(\frac{R}{r_c} \right)^3 (2 - 3 \cos \phi + \cos^3 \phi) \right] \quad (12)$$

Fig. 16. (a) Three-dimensional diagram showing the relationship among the 3 parameters $g(R, \theta)$, R/r_c , and θ in equation (12). (b) $g(R, \theta)$ decreases with increasing R/r_c . (c) Relationship between $g(R, \theta)$ and θ at different R/r_c . Reprinted with the permission of Ref [168], copyright 2005, American Institute of Physics.

Fig. 16 illustrates the relationship among $g(R, \theta)$, R/r_c , and θ . From Fig. 16b, $g(R, \theta)$ varies between 0 and 1, and there is a stiff reduction with increasing R/r_c when it is small. At a fixed value of R/r_c , $g(R, \theta)$ gradually increases with increasing θ (see Fig. 16c). Furthermore, it can be found that $g(R, \theta)$ gradually decreases to 0 while the value of θ tends to 0 only under the condition of $R/r_c \geq 1$. When $R/r_c < 1$,

$$g(R, 0) = 1 - 3\left(\frac{R}{r_c}\right)^2 + 2\left(\frac{R}{r_c}\right)^3. \text{ Within } R/r_c < 1, g(R, 0) \text{ approaches 1 with decreasing } R/r_c,$$

which implies the tendency to become homogeneous ice nucleation when the surface roughness is much small than the critical homogeneous nucleation size. On the other

hand, when R/r_c is greater than 5, $g(R, \theta)$ curves are very close to each other. In summary, smaller size of geometric structure and higher intrinsic CA will be beneficial to a higher free energy barrier and finally results in a lower icing temperature or longer icing delay time.

Cooper SJ, *et al.* [169] further developed these equations about curved surfaces *via* adopting θ_p , which is the angle of ice nucleus on the planar substrate as marked in Fig. 15. The free energy barrier of ice nucleation can be given in another form:

$$\Delta G_c' = \Delta G_c \cdot f(\theta_p) \quad (13)$$

where $f(\theta_p)$ is the heterogeneous ice nucleation factor with a similar role as $g(R, \theta)$ in Equation (9). As shown in Fig. 17a and b, ice nucleation on a concave surface is more easily triggered comparing with that on a convex surface, and the difference will be greater on surfaces with a smaller R .

Fig. 17. (a) The heterogeneous nucleation factor $f(\theta_p)$ and (b) initial ice nucleation

temperature with different CAs versus radius. The negative and positive values of R refer to ice nucleation on the concave and convex surfaces. Reprinted with the permission of Ref [169], copyright 2008, American Institute of Physics. (c) Ice nucleus with CA α on a step of angle η . (d) Geometry used in the evaluation of $F(\eta, \alpha)$. Reproduced with the permission of Ref [172], copyright 1964, Elsevier BV.

On this basis, Chakraverty BK, *et al.* [171] and Sholl CA, *et al.* [172] investigated the heterogeneous ice nucleation of liquid from vapor on the solid steps, as shown in Fig. 17c, and the results are applicable for ice nucleation directly from liquid [173]. In this case, the free energy barrier for ice nucleation is given by:

$$\Delta G_c' = \frac{16\pi\sigma^2}{3(\Delta G)^2} \cdot \frac{1}{4} F(\eta, \alpha) \quad (14)$$

where

$$F(\eta, \alpha) = \frac{1}{\pi} \left[\cos \alpha \sin^2 \alpha \sin \psi - \cos \alpha (3 - \cos^2 \alpha) \psi + 4 \sin^{-1} \left(\sin \frac{\psi}{2} \sin \frac{\eta}{2} \right) \right] \quad (15)$$

The meaning of symbols, such as α , η and ψ , are marked in Fig. 17d. The dependence of geometric factor $F(\eta, \alpha)$ on the values of η and α is summarized in Table 1 and Fig. 18. Furthermore, the relationship between the geometric factor $F(\eta, \alpha)$ and the angle α of steps is shown in Fig. 19. It can be clearly seen that a smaller contact angle leads to lower value of geometric factor $F(\eta, \alpha)$.

Table 1. Geometric factor versus the values of η and α . Reproduced with the permission of Ref [172], copyright 1964, Elsevier BV.

Conditions on η and α	Replace $F(\eta, \alpha)$ by	Physical situation
$0 \leq \eta \leq \pi$ $2\alpha \leq \pi$	Unstable	Fig. 17a

Fig. 18. Geometrical situations corresponding to entries in Table 1. Reprinted with the permission of Ref [172], copyright 1964, Elsevier BV.

Fig. 19. The relationship between the geometric factor $F(\eta, \alpha)$ and the step angle α in equation (15). Reprinted with the permission of Ref [172], copyright 1964, Elsevier BV.

3.3. Heterogeneous ice nucleation along three-phase contact line

Aiming at more accurately predicting ice crystallization rates, surface crystallization has been widely discussed in recent years both experimentally and theoretically. At the solid / liquid interface, the ice nucleation is governed by the conventional heterogeneous nucleation theory, with the extension into different geometric surfaces as introduced in section 3.2. These were considered to be the valid models determining the ice nucleation of supercooled droplet on solid surfaces [160,174]. However, recently further studies suggest yet another possibility, *viz.*, nucleation at the solid / liquid / vapor triple-phase contact line. The basic principle remains the same, *i.e.*, more favorable (lower) nucleation energy barrier at the 1D triple-phase contact line than the 2D solid/liquid interface, therefore this location should be more favorable for structure and energy fluctuation to induce the occurrence of ice nucleation [175]. A schematic illustration is given in Fig. 20a for homogeneous nucleation, heterogeneous nucleation at solid/liquid 2D interface, and heterogeneous nucleation along 1D triple-phase contact line.

A freezing process (as shown in Fig. 20b) was observed by Suzuki S, *et al.*, where ice nucleation occurred at the interface between solid and water, yet it initiated not from the inside of the solid/water interface but at the triple-phase contact line [176]. In order to confirm the preference of ice nucleation at triple-phase contact line, they utilized UV irradiation through a stainless photomask to achieve a small hydrophilic region (water CA of $\sim 0^\circ$) at the center of the hydrophobic coating, as shown in Fig. 20c. Subsequently, the freezing process of supercooled droplet on the

surface was recorded by a high-speed camera. Freezing still initiated at the triple-phase contact line, even when there was a more favorable 2D hydrophilic solid/liquid region at the center. There are two possible explanations for this observation: one is the excess energy of the triple-phase contact line, and the other could be due to the temperature difference between the contact line and the contact area inside. Thus, there could still be a doubt cast on the suggested preferred nucleation site at the triple phase contact line.

Fig. 20. (a) A schematic diagram of homogeneous nucleation, heterogeneous nucleation at the 2D solid/liquid interface, and heterogeneous nucleation along the 1D solid / liquid / vapor triple-phase contact line. (b) Sequential photographs of freezing behavior of a supercooled water droplet on a silicon surface treated with 1*H*,1*H*,2*H*,2*H*-perfluorodecyltrimethoxysilane (FAS-17) showing that the ice

nucleation occurs at the bottom left of the droplet (marked with a red circle). (c) Small hydrophilic region at the central part of FAS-17 coating formed by UV irradiation through a stainless photomask. Reprinted with the permission of Ref. [176], copyright 2007, Elsevier B V.

At the triple-phase contact line, the free energy of the nucleus is lowered due to the juncture of solid / liquid, solid / vapor, and liquid / vapor interfaces, all of which can counteract a certain amount of free energy [175]. On this basis, Djikaev and his co-workers considered that, besides the free energy, line tension may also contribute to such a preference for ice nucleation at the triple-phase contact line [177]. Line tension has the dimension of energy per unit length, and can be positive or negative. If the line tension of triple-phase contact line is positively large enough, it will contribute to reducing the heterogeneous ice nucleation barrier [178].

Gurganus CW, *et al.* obtained high-speed images of a supercooled droplet on a flat silicon substrate, and accurately located the ice nucleation sites on the horizontal plane [179]. As shown in Fig. 21a, the 189 freezing events displayed nearly perfect spatial uniformity in the contact region of solid/liquid, and there was no obvious preference for nucleation at the triple-phase contact line. The quantitative sorting of the icing events into equal area zones (see Fig. 21b) visually shows the uniform distribution of ice nucleation sites. A numerical simulation of ice growing process of a supercooled droplet also indicates the perfect symmetry with the ice formation from bottom to top [180]. Therefore, they considered that surface tension might not play a significant role in triggering the ice nucleation, provided there is a temperature

uniformity over the base of the supercooled droplet.

Fig. 21. Spatial uniformity of ice nucleation events revealing no preference for triple-phase contact line. (a) Locations of the 189 freezing events on the horizontal plane. (b) An equal area histogram of 10 circular bands provides a quantitative measure of spatial uniformity. Reprinted with the permission of Ref. [179], copyright 2011, American Chemical Society.

An interesting experiment was designed by Gurganus CW, *et al.* They added a catalyst in the supercooled droplet and then fast-filming the freezing process at 200 μs between frames [181]. As shown in Fig. 22a, a fiber with the same chemical composition (silica) as the substrate was placed horizontally through the supercooled water droplet. Many repetitions of this freezing process were performed to make a statistical analysis of the spatial distribution of nucleation events (see bottom in Fig. 22a). For the smooth silica fiber, it is confirmed that ice nucleation events are distributed randomly with no preference at the triple-phase contact line [180]. However, the rough fiber with nanotexture exhibited a shift in the spatial distribution of ice nucleation events to the fiber contact line, as revealed in Fig. 22b. Also, the nanotexture planted on the surface of fiber is in the length scale of ~ 10 nm, which is a

few times larger than the critical size for ice nucleation. Based on the early analysis on ice nucleation on nanoscale curved surfaces (see Fig. 16c), this type of texture would promote ice nucleation. The recorded crystallization initiation temperature as shown in Fig. 22c indicates that the ice nucleation occurring at triple-phase contact line needs less supercooling temperature ΔT . This implies that the ice nucleation rate could be varied by orders of magnitude for this particular type of nanotexture when compared with the smooth one [182].

Fig. 22. (a) Top: a schematic diagram of a fiber, serving as a heterogeneous nucleation catalyst, penetrating a water droplet on a siliconized cooled substrate. Bottom: High-speed camera images capturing the nucleation site. (b) Number of nucleation sites observed at the different places. It shows that nucleation sites shift to the contact

line for the rough fiber, as compared to the smooth fiber. (c) Nucleation events taking place at different places with the change of temperature (ΔT represents supercooling temperature). Reprinted with the permission of Ref. [181], copyright 2014, American Physical Society.

Experiment and the analysis by Fu Q, *et al.* support nucleation along the triple-phase contact line on a series of sol-gel coatings [183]. They added different weight percentage of silica nanoparticles into the coatings to vary the surface roughness. Owing to the addition of fluorocarbon in the coating, the measured apparent surface energy was quite low (see Fig. 23a), giving rise to hydrophobic and superhydrophobic surfaces depending on the surface roughness. The gradually reduced apparent surface energy corresponds to a lower freezing temperature (as shown in Fig. 23b), defined by the temperature at 50% unfrozen events in the statistical analysis of 500 icing events of a single water droplet. The statistical analysis is necessary since ice formation is a stochastic process, and the ice nucleation temperature of the same water droplet may vary substantially. In the analysis, the observed nucleation temperatures are analyzed using a probability function. When coupled with the classical nucleation theory, the nucleation rate on a particular site can be expressed as a function of temperature. The obtained information on the nucleation process is able to provide important insight into the physical mechanisms responsible for ice formation. The corresponding solid / liquid interface and the triple-phase contact line ice nucleation rates are deduced and shown in Fig. 23c and d, respectively. The nucleation rate does not comply with the observed lowest nucleation

rate for the F-16 sample if the 2D interface nucleation is assumed. However, the 1D contact line curves agree well with the observation. Therefore, this research indirectly supports the three-phase nucleation model for their sol-gel coatings.

Fig. 23. (a) The values of surface energy and roughness for a group of samples treated with fluoroalkylsilane (FAS-17). The change of roughness is mainly caused by adding different weight percentage of silica nanoparticles. (b) The fraction of unfrozen events as a function of temperature. (c,d) Plots illustrate, respectively, the 2D solid/liquid interface and the 1D three-phase contact line ice nucleation rates as a function of temperature for the samples with different roughness and surface energy. Reproduced with the permission of Ref. [183], copyright 2015, Royal Society of Chemistry.

Despite of all these advances, the issue of nucleation at the triple-phase contact line vs. the two-phase contact area is still far from settled. Possible reasons for the apparent controversy exist. Theoretical calculation is very much affected by the

assumptions made and the boundary conditions used. For example, during the calculation process, the model system consists of many rigid particles and the involved substrate is considered to be defect-free. Periodic boundary conditions are always applied for the calculation, which may bring in certain degree of error. Furthermore, there is always an uncertainty in the potential function used that describes the interactions between atoms / molecules. Sometimes, neglecting certain interactive forces is necessary to enable a better revelation of certain characteristics of interest. Experimentally, there might be difference in the conditions adopted in different reports, including the possible existence of temperature gradients across different interfaces (intentional or unintentional), the substrate materials used (with different thickness and heat conductivity), and the ambient conditions (e.g. vapor concentration, cooling rate and so on). Clearly, more research is needed to clarify this issue, and contributions from both theoretical calculation and experiment are essential. With the assistance of more advanced analytical tools and experimental techniques, we will be able to understand better how the length scale of surface texture and cooling conditions, in relation to the critical nucleation size, affects the ice nucleation. The theoretically estimated ice nucleation size should be experimentally verified with the assistance of modern techniques, such as the cryogenic transmission electron microscopy. This datum is critical since the design of icephobic coatings requires a good knowledge of its precise value. In general, the revelation of ice nucleation preference and mechanisms is of great significance to the control of ice nucleation process, which in turn helps in the design and fabrication of icephobic materials.

3.4. Ice nucleation on lubricant-infused porous surface

Based on the characteristics of ultra-slippery and chemical homogeneity, SLIPS has been widely discussed for its icephobic capacity [72,160,184-190]. Because of the infused low surface energy lubricant that poses a higher free energy barrier, SLIPS is considered a promising candidate to inhibit ice nucleation. In this section, we will mainly discuss the recent research advances on the inhibition of ice nucleation on lubricant-infused porous surface.

So far, most of the studies on ice nucleation have been based on statistical results of occurring nucleation or freezing events. Wilson PW, *et al.* used SLIPS-coated differential scanning calorimeter (DSC) aluminium pans to investigate the ice nucleation of supercooled droplet [187]. They measured the freezing temperatures with continuous circulations between melting and freezing (see Fig. 24a), and defined the temperature at 50% freezing events as the average nucleation temperature, as shown in Fig. 24b. The ice nucleation temperature of supercooled droplet on the SLIPS sample surface was -24.9°C . Following this procedure, the level of supercooling of four types of sample surfaces was obtained to reveal the ability of SLIPS in inhibiting ice nucleation. As shown in Fig. 24c, the SLIPS sample surface shows significantly increased amount of supercooling compared with the hierarchical superhydrophobic surface. Additional improvement in the uniformity was believed to have greatly reduced the number of ice nucleation sites. However, up to now, there are no relevant reports on the quantitative calculation of ice nucleation rates on the SLIPS surface. A firm confirmation on its ability to inhibit ice nucleation is necessary.

Fig. 24. Ice nucleation temperature of supercooled droplet on lubricant-infused porous surface. (a) Schematic diagram of the experimental arrangement for measuring the freezing temperature with continuous circulation between melting and freezing. Inset shows the schematic diagram of the lubricant-infused porous surface. (b) Typical survival curve of supercooled water droplet freezing on the lubricant-infused porous surface. (c) The amount of supercooling required to trigger ice nucleation for each type of sample surface (N: untreated hydrophilic surface; T: textured hydrophobic surface; H: hierarchically structured superhydrophobic surface; S: lubricant-infused porous surface). Reproducing with the permission of Ref. [187], copyright 2013, Royal Chemical Society.

Inspired by the lubricant-infused surface, Irajizad P, *et al.* reported a more

promising icephobic material with magnetic slippery surface (MAGSS), which further reduced the ice nucleation temperature, and 2-3 orders of magnitude higher icing delay time [188]. The magnetic slippery surface is schematically shown in Fig. 25a, and conceptually compared with the other icephobic surfaces (*i.e.*, superhydrophobic surface and lubricant-infused surface). They suggest that only the magnetic slippery surface can induce a real liquid / liquid interface with an ultralow interface energy, which increases the free energy barrier for ice nucleation, and finally results in a lower ice nucleation temperature. The reported ice nucleation temperature of MAGSS was -34 ± 1 °C (see Fig. 25b), while the superhydrophobic surface and lubricant-infused surface provided higher ice nucleation temperatures at -23 °C and -26 °C, respectively. For comparison, the homogeneous ice nucleation temperature was -40 °C. The reported -34 °C for the MAGSS is the closest to the homogeneous nucleation temperature, which means it has led to the highest free energy barrier among different types of tested coatings [189,190]. Correspondingly, ice nucleation delay time for MAGSS was also much longer (2-3 orders of magnitude) than other icephobic materials (see Fig. 25c). The ice nucleation delay time for MAGSS can be further enhanced with increasing the intensity of imposed magnetic field, especially after the magnetic field reaching a threshold value of 347 mT (see Fig. 25d). Finally, MAGSS has an extremely low ice adhesion strength at ~ 2 Pa, as shown in Fig. 25e. This value is approximately 5 orders of magnitude lower than those reported ice adhesion strength for superhydrophobic surface or lubricant-infused surface [191,192]. Thus, MAGSS exhibits a remarkable ability to inhibit the heterogeneous ice

nucleation due to the low interface energy, which provides a new path to develop icephobic materials. Nevertheless, a clear constraint for this technology is the difficulty to apply and maintain the magnetic field in a practical application, especially for large-area outdoor structures.

Fig. 25. Magnetic slippery surface (MAGSS) inhibiting heterogeneous ice nucleation.

(a) One water droplet on the superhydrophobic surface, on a lubricant-infused surface, and on the MAGSS. (b) Ice nucleation temperature (T_N) of MAGSS is compared with the other icephobic materials. (c) Ice nucleation delay time (τ_{av}) for MAGSS is much longer (2-3 orders of magnitude) than the other icephobic materials. (d) The

increasing magnetic field causes a longer delay time of ice nucleation. (e) Ice adhesion strength on the MAGSS also shows a 5-orders of magnitude reduction compared with the superhydrophobic surface and lubricant-infused porous surface. Reproduced with the permission of Ref. [188], copyright 2016, Macmillan Magazines Ltd.

3.5. Ice nucleation on nanostructured superhydrophobic surface

Different from the smooth liquid-infused surfaces, superhydrophobic surface makes use of micro / nanostructures to enhance the surface hydrophobicity as discussed earlier. If the non-wettability can be retained at low temperatures, such materials possess a great potential for icephobic applications. The presence of surface roughness at scales larger than the critical ice nucleation size may be considered unfavorable as far as inhibiting ice nucleation is concerned. Nonetheless, owing to a large fraction of air pockets trapped underneath a supercooled water droplet, the actual solid / liquid contact area is very small (can be as small as ~10% or less). The presence of air pockets leads to a smaller supercooling gradient, therefore a superhydrophobic surface could still exhibit a lower tendency towards ice nucleation [193-196].

Alizadeh A, *et al.* constructed a hierarchical micro-nanoscale superhydrophobic surface on a Si substrate, and recorded the transient temperature of a 4 μL water droplet during the freezing process [197]. The transient temperature profile of the water droplet freezing on the superhydrophobic surface is shown in Fig. 26a, and compared with the ones on flat hydrophobic and hydrophilic surfaces. Once the

freezing event occurs, certain amount of heat will be released to cause a sudden rise of the transient temperature. It can be clearly found that ice nucleation on the superhydrophobic surface has a much longer delay time, which is mainly attributed to the smaller local supercooling gradient caused by a large number of trapped air pockets [194,195]. Subsequently, Li K, *et al.* focused on the investigation on the effect of non-wettability on ice nucleation without consideration of surface nanostructures [198]. The statistical investigation on ensembles of independent freezing events provided the ice nucleation rate in addition to the freezing probability density. As shown in Fig. 26b, the ice nucleation rate on the hydrophilic surface is about 1 order of magnitude lower than that on the flat hydrophobic surface at the same temperature. This finding seems to contradict most other observations that a hydrophobic coating usually reports a lower nucleation rate than a hydrophilic surface. The authors believed that the viscosity of interfacial water could affect the diffusion and relaxation of water molecules near the active sites, and the difference in the viscosity was believed to be accountable for the observation.

For the micro-nanostructured superhydrophobic surface, results indicate that ice nucleation rate is determined by the actual solid / liquid contact area [199]. Fig. 26c shows that the ice nucleation rate is a function of actual solid / liquid contact area. With the assistance of Cassie-Baxter wetting model, the actual solid / liquid contact area decreases greatly and therefore leads to less probability to trigger heterogeneous ice nucleation. Overall, the nanostructured hydrophobic or superhydrophobic surface exhibits a strong ability to inhibit ice nucleation, and such ability is affected by the

size of nanostructures and the actual solid / liquid contact area [200,201].

Fig. 26. (a) Transient temperatures of a 4 μ L water droplet freezing on Si-PEG (hydrophilic), Si-F (hydrophobic), and Si-Single Texture-F (superhydrophobic) substrates, respectively. Reproduced with the permission of Ref. [197], copyright 2012, American Chemical Society. (b) Relationship between surface ice nucleation rate and temperature on the unmodified and FAS-17-modified silicon surfaces. Reprinted with the permission of Ref. [198], copyright 2012, American Chemical Society. (c) Ice nucleation rate versus the actual solid/liquid contact area. Reprinted with the permission of Ref. [197], copyright 2012, American Chemical Society.

To further clarify the effect of solid / liquid contact interface on the ice nucleation rate on superhydrophobic surfaces, Shen Y, *et al.* constructed various Ti6Al4V surfaces with different roughness and CA, and calculated the actual solid / liquid contact area using the wetting models [202]. Compared with the untreated hydrophilic surface, the micro-nanostructured superhydrophobic surface greatly

reduces the actual solid / liquid contact area from 7.136 mm^2 to 0.025 mm^2 , finally causing a high extent of reduction (~ 19 orders of magnitude) in the ice nucleation rate.

In 2016, Metya AK and his co-workers further addressed the ice nucleation behavior of a supercooled monatomic cylindrical water droplet on nanoscale textured surfaces using molecular dynamics simulations as shown in Fig. 27a [203]. In the case of the Cassie-Baxter state, the ice nucleation rate is slightly enhanced with the increase of surface contact fraction α , yet the opposing situation appears for the Wenzel state (see Fig. 27b). At a higher surface contact fraction, the heterogeneous ice nucleation is clearly observed with Cassie-Baxter state, and the initial nucleation sites are along the triple-phase contact line rather than at the solid / liquid interface, as shown in Fig. 27c. With the reduction of surface contact fraction, it is possible to produce the homogeneous ice nucleation in the case of Cassie-Baxter state (see Fig. 27d). When the surface contact fraction $\alpha = 0.089$, the highest ice nucleation rate can be obtained with heterogeneous nucleation, and this contact regime of solid / liquid conforms to the Wenzel state (as depicted in Fig. 27e). In summary, when the length of the ice crystal matches the accessible width of the surface roughness features (e.g., the width of the grooves), the ice nucleation rate is increased significantly, which is consistent with the early discussion. Similar conclusions were also made by the other research groups [201,204,205]. As explained earlier, the ice nucleation on the heterogeneous solid surface is a quite complex matter, and requires more effort to completely understand the behavior on nanostructured surfaces.

Fig. 27. (a) Top and side views of a simulation system. (b) The ice nucleation rate versus surface contact fraction (α) at 203 K. The values of the ice nucleation rate are expressed as $\log_{10}(J/J_0)$, where J_0 is the ice nucleation rate of bulk water. (c-e) Snapshots of crystallization trajectory of supercooled water on the nanostructured surfaces. The colors of light red, red, green and blue represent water molecules in cubic ice, hexagonal ice, intermediate ice and liquid water, respectively. Reproduced with the permission of Ref. [203], copyright 2016, Royal Society Chemistry.

4. Performance evaluations

Lab-based performance evaluations are important to verify any emerging technologies before actual applications can take place, and there is no exception for icephobic materials. The discovered microscopic mechanisms of inhibiting water wetting and ice nucleation should eventually lead to remarkable macro-performance in preventing or delaying ice formation, as well as easy removal of ice. Currently, most of the performance evaluations are focused on icing delay and ice adhesion strength [18-20,206-208]. Icing delay, in a broad sense, may refer to either a decrease in ice formation temperature under a continuous supercooling condition, or an extended time to freeze under a fixed temperature. We will cover both tests in this review. Furthermore, durability against mechanical and environmental damages is a key challenge to the practical application of icephobic coatings, as explained at the beginning of this review. These are crucial considerations for this passive anti-icing technology to be successful in replacing the traditional high-energy consuming active de-icing approaches [19,207,209-211]. This section will discuss these macro-performance evaluation techniques and the durability challenges.

4.1. Icing temperature

A lower ice formation temperature means less probability of ice formation or more time for water droplets to be removed before ice formation. The icing temperature is usually taken as the one at which icing begins, and can be measured by capturing the exothermic signal during the freezing process [183,212,213]. It is noted that the freezing process is rapid once ice is nucleated. An example for an automated

icing temperature measurement device is shown in Fig. 28a [183]. It consists of a Peltier electric heating and cooling unit, and a laser detecting system. A temperature sensor is embedded in a high-thermal conductivity substrate to monitor the temperature change. When an icing event occurs, the laser detector reading will experience a sharp change. Owing to the release of latent heat due to phase transformation from water to ice, there is a sudden increase in the temperature (the green line in Fig. 28b), which can be used to corroborate the ice nucleation temperature by laser detection. The advantage of this device is it can automatically carry out the cooling / heating cycle for one water droplet for hundreds of cycles and record the events for analysis [187].

Fig. 28. Measurement of icing temperature. (a) Schematic diagram of the testing device. (b) The detection of temperature variation during a freezing cycle.

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In 2016, Zhang Y, *et al.* systematically characterized the freezing temperature of water on the surfaces with water CAs from 5° to 110° (obtained by means of wet chemical processing and spin coating), and kept the same water volume and solid-liquid contact area by using a specially-made sample cell [214]. As shown in Fig. 29, they found that the freezing temperature had a better response with a reducing trend to the gradually increased surface hydrophobicity only in the case of $\sim 10 \mu\text{L}$ water. For $\sim 300 \mu\text{L}$ water, the freezing temperature is independent of surface wettability at the level of around -7°C . This reason is that the increasing volume of water leads to the weakening of surface nucleation comparing with bulk nucleation, as discussed above [215].

Fig. 29. The icing temperature as a function of contact angle. The measured freezing temperature is dependent on the droplet size. Reproduced with the permission of Ref.

[214], copyright 2016, American Chemical Society.

Water droplet size and cooling rate seem to have a great influence on the measured icing temperature. As shown in Fig. 30a, when the water droplet cap height increases beyond ~0.14 cm, the freezing temperature increases drastically. The cooling rate affects the freezing temperature: only at high enough cooling rate, a steady-state lower freezing temperature will be recorded (see Fig. 30b). With these results, it is not surprising why the reported freezing temperatures sometime may disagree [198,216,217]. For example, an FAS-coated Si surface was reported to have reduced the freezing temperature by 6.4 °C in comparison with uncoated substrate under a cooling rate of 0.5 °C/min [218]. However, at a higher cooling rate of 5 °C/min, an opposite trend was observed with the freezing temperature slightly increased by ~0.4 °C [198]. All these studies clearly suggest that evaluation of freezing temperature should take into consideration parameters like water impurity level, droplet size, cooling rate and so on.

Fig. 30. Freezing temperature versus (a) droplet radius and (b) cooling rate. Reprinted with the permission of Ref. [214], copyright 2016, American Chemical Society.

4.2. Icing delay time

Icing delay time measures the time required for the water droplet to freeze on a solid surface under a constant temperature. The icing delay is closely related to the ability of thermal transmission at the apparent contact interface of solid/liquid [207,208]. As shown in Fig. 31a-d, Guo P, *et al.* designed a hierarchical micro-nanostructured superhydrophobic surface under the inspiration of butterfly wings [219]. The resultant surface is endowed with an excellent icing delay performance, lasting for a long delay time (DT) of ~ 7220 s for ice formation (see Fig. 31e). The icing delay performance of microstructured surface (M-surface) is the

lowest due to the largest actual solid / liquid contact area (under the Wenzel wetting mode). However, the as-constructed hierarchical micro-nanostructure induces a large amount of air pockets underneath water droplets (Cassie-Baxter wetting mode) to have effectively slowed down the thermal transmission, causing a longer icing delay time [207,220].

Fig. 31. Remarkable icing delay performance of hierarchical micro-nanostructured superhydrophobic surface (labeled as MN-surface). (a) SEM images of micro-nanostructure showing that microstructure array is composed of a ratchet with the periodicity of $\sim 300 \mu\text{m}$ and the height of $\sim 80 \mu\text{m}$ (side view). (b) SEM images showing that the surface is only planted with a layer of nanohairs (labeled as N-surface). (c) The morphologies of single microstructure (labeled as M-surface). (d) The smooth surface without any structures (labeled as S-surface). (e) Freezing processes of $7 \mu\text{L}$ droplets on these sample surfaces at -10°C with icing delay time (DT) marked by pink arrow. Reprinted with the permission of Ref. [219], copyright 2012, Wiley-VCH.

Subsequently, Shen Y, *et al.* observed the freezing process of water droplets (4 μL) on the hierarchical micro-nanostructured superhydrophobic surfaces at $-10\text{ }^{\circ}\text{C}$ [221,222], as shown in Fig. 32a. They considered that a freezing process mainly consists of a precooling stage and an ice growing stage, and most of the icing delay time ($> 95\%$) is occupied by precooling. Without surprise, the droplet on the micro-nanostructured superhydrophobic surface needs a longer time to complete the precooling and ice growing processes. From the point of view of thermodynamics, the droplet on a cold surface acquires heat from air through heat conduction and thermal radiation, and loses heat to the cold substrate through heat conduction. The energy change of a droplet can be expressed as [219]:

$$\Delta Q = Q_1 - Q_2 \quad (16)$$

where ΔQ is the net heat decrease in unit time; ΔQ_1 is the heat lost to the cold solid surface, and ΔQ_2 is the heat gained from the air. Furthermore, for the reference droplet, the reduced temperature can be expressed as:

$$\Delta t = \frac{\rho_w C_p (T_0 - T_1)}{\Delta Q} \quad (17)$$

where Δt is the time required for water droplet to completely freeze; ρ_w is the water density; C_p is the specific heat capacity of water; T_0 is the starting temperature of the droplet; T_1 is the ample surface temperature. Equations (16) and (17) indicate that smaller Q_1 (or larger Q_2) leads to a smaller ΔQ , and finally results in a higher Δt . Thus, it can be well explained that a droplet sit on top of the hierarchical micro-nanostructured superhydrophobic surface takes a longer icing delay time compared with the smooth surface [221]. Fig. 32b shows schematic diagrams of a

droplet on the nanostructured and micro-nanostructured surfaces. It is obvious that the contact interface between air and liquid leads to a smaller heat loss from droplet to cold contact solid surface. The micro-nanostructures can entrap more air pockets underneath the droplet, which would lead to better thermal insulation and a smaller heat loss.

Fig. 32. (a) Optical images revealing the visual ice formation processes on smooth, nanostructured, and micro-nanostructured Ti6Al4V surfaces. (b) Schematic diagrams of the interface between freezing droplets and nanostructured and micro-nanostructured surfaces. Reproduced with the permission of Ref. [222], copyright 2015, Royal Society of Chemistry. (c-e) Top images show the morphologies of ZnO nanoparticles, nano-cones, and nano-hexagonal rods on the PVDF microsphere surface. Middle optical images show the droplets on the micro-nanostructure surfaces (at -10 °C) with the initial CAs of 122°, 162°, and 160°. The icing delay time is 7 min, 126 min, and 118 min, respectively. Bottom optical images illustrate the droplet on the surface with CAs of 95°, 162°, and 160° after

increasing the temperature from -10 °C to 10 °C. Reproduced with the permission of Ref. [223], copyright 2014, Royal Society of Chemistry.

In order to confirm the contact interface mechanism during droplet freezing period, Wang L, *et al.* analyzed the wetting interface after melting the as-formed ice based on three types of micro-nanostructured surfaces prepared by growing ZnO nanoparticles, nano-cones and nano-hexagonal rods on polyvinylidene fluoride microspheres on a flexible thin film [223]. As shown in Fig. 32c-e, the droplets are placed on the micro-nanostructured surfaces at -10 °C with the initial CAs of 122°, 162°, and 160°, respectively. The corresponding icing delay time is 7 min, 126 min, and 118 min. After re-melting, the droplets on the nano-cone and nano-hexagonal rod surfaces are recovered to the original state with the same CAs as the initial ones. This is due to the stable contact interface mechanism conforming to Cassie-Baxter wetting model. This experiment verifies the validity of the above analyses on the thermal transmission at the contact interface [222,224].

Anti-icing against condensed droplets remains a challenge to the hierarchical micro-nanostructured superhydrophobic surface, because the size of condensed droplets is too small to be held up by the micro-nanostructure in the Cassie-Baxter wetting mode. Fig. 33 shows the in-situ snapshots of a bare Mg alloy and Mg alloys coated with the micro-nanostructured superhydrophobic surface and lubricant-infused surface on a cooling stage maintained at -20 °C and under $65 \pm 5\%$ humidity. The bare Mg substrate sees frost and ice within 5 min, and is completely covered by a layer of thick ice in 10 min. The situation is slightly improved on the micro-nanostructured

superhydrophobic surface, where a small number of frost and ice nuclei are microscopically observed after 5 min, but a distinct ice layer is formed within 10 min. This indicates that the micro-nanostructured superhydrophobic surface exhibits certain but insufficient ability prevent condensed droplets from freezing. In contrast, the condensed droplets on the lubricant-infused surface can combine with each other to form a large droplet, and remain liquid after 5 min until partly freezing at 10 min [225]. The condensed droplet or partly formed ice can be easily removed by tilting the lubricant-infused surface. From the point of view of preventing ice formation from condensed moisture, the lubricant-infused surface exhibits a more robust icing delay performance than micro-nanostructured superhydrophobic surface [226-230].

Fig. 33. Snapshots of a bare Mg alloy and Mg alloys coated with micro-nanostructured superhydrophobic surface and the lubricant-infused surface on a cooling stage at $-20\text{ }^{\circ}\text{C}$ (humidity of $65 \pm 5\%$). The images were selected at the initial state, after 5 min, and after 10 min. Reproduced with the permission of Ref. [225], copyright 2017, American Chemical Society.

4.3. Ice adhesion

Ice adhesion strength is another important parameter that has been widely used to evaluate icephobic properties. It provides an indication of how easy the formed ice can be removed from the substrate. As well known, freezing is an inevitable process under the condition of sufficient supercooling, and the low ice adhesion strength, coupled with the traditional de-icing approaches, is able to reduce the energy consumption during de-icing operation [231,232]. For some moving components such as wind turbine blade or airplane wings, the force exerted on the ice might be sufficient to remove the ice itself without de-icing operation if the ice adhesion strength is low enough. Some authors suggested that an icephobic surface should possess ice adhesion strength no greater than 0.1 MPa [233,234].

Ice adhesion strength can be characterized by either a shear or tensile adhesion test. Currently, most researchers report ice adhesion strength in shear due to its relatively easy sample preparation and test setup. However, since there is no standard for ice adhesion test, each research team adopts its own testing facility. An example is shown in Fig. 34a. To perform the measurement, an ice column is firstly prepared on the sample surface. A shear force F to separate the ice column from sample surface is captured to calculate the shear strength of ice adhesion, τ , according to $\tau = F/A$, where A is the contact area of ice column with sample surface. Shen Y, *et al.* measured the shear ice adhesion strength on a superhydrophobic surface containing the hierarchical structure of sand-blasted microstructure and hydrothermally growing TiO₂ nanowires [235]. As shown in Fig. 34b, the shear ice adhesion strength (~80 kPa)

on the superhydrophobic surface is much lower than that (760 kPa) on the untreated substrate. Meuler AJ, *et al.* believed that there is a strong correlation between the shear ice adhesion strength and the parameter of $1 + \cos\theta_{\text{rec}}$ (θ_{rec} is the RCA) for liquid water [236], as shown in Fig. 34c. The validity of the predicting shear ice adhesion strength by measuring the RCA can be extended to the micro-nanostructured superhydrophobic surface under the condition of water droplet freezing in the Cassie-Baxter mode. Furthermore, Wang Y, *et al.* measured the tensile ice adhesion strength and found the same trend among these similar surfaces (see Fig. 34d) [237]. The micro-nanostructured superhydrophobic surface (Sample 4#) displayed the lowest tensile ice adhesion strength of 200 kPa, indicating that the Cassie-Baxter interface has remained during the period of water droplet freezing into ice.

Fig. 34. (a) Schematic diagram of a device to measure the ice adhesion strength in shear. It consists of a force transducer, force gauge, and a cooling plate. (b) The shear

ice adhesion strength as a function of temperature. Four types of samples are designed as (SS) Ti6Al4V substrate surface without modification; (MS) Micrometer-scale pit surface with FAS-17 modification, (NS) Nanowire structured surface with FAS-17 modification, and (MNS) Micropit-nanowire structured surface with FAS-17 modification. Reprinted with the permission of Ref. [235], copyright 2015, Royal Society of Chemistry. (c) Relationship between ice adhesion strength and wettability, revealing the shear ice adhesion highly depending on the RCA θ_{rec} . Reproduced with the permission of Ref. [236], copyright 2010, American Chemical Society. (d) Tensile ice adhesion strength (at -10 °C) on the various sample surfaces with different wettability (Sample 1#: hydrophilic, Sample 2#: hydrophobic, Sample 3#: superhydrophilic, Sample 4#: superhydrophobic). Inset showing the schematic diagram of measuring tensile ice adhesion strength. Reprinted with the permission of Ref. [237], copyright 2013, American Chemical Society.

The interfacial mechanisms for low ice adhesion strength on the micro-nanostructured superhydrophobic surfaces are clearly revealed by Nosonovsky *M. et al.* [238]. When the ice forms on the micro-nanotextured superhydrophobic surface conforming to the Cassie-Baxter mode, the trapped air pockets are changed into air voids, which act as stress concentrators to cause a remarkable reduction in ice adhesion strength under the condition of shear loading (see Fig. 35a). For the normal loading, the as-formed air voids can reduce the contact area between ice and solid surface, which results in a lower tensile ice adhesion strength, as shown in Fig. 35b. Furthermore, it is confirmed that the force to remove the ice is highly dependent on

the size of the air voids besides the RCA [232].

Fig. 35. (a) Shear loading and (b) normal loading regimes of water droplet and ice frozen droplet on the flat and texture surfaces. Reprinted with the permission of Ref. [238], copyright 2012, American Chemical Society.

Some literatures reported that the hierarchical micro-nanostructured superhydrophobic surface could not reduce the ice adhesion strength due to the destruction of the Cassie-Baxter mode under supercooled airflow condition. In this case, the surface micro-nanostructure plays a role of mechanical interlocking to enhance the ice adhesion strength on the superhydrophobic surface. As illustrated in Fig. 36a, the flat hydrophobic surface possesses a much lower adhesion strength than the micro-nanostructured superhydrophobic surface [239]. This is attributed to the special contact interface regime, where the Cassie-Baxter mode cannot be effectively maintained between ice and solid surface. The surface micro-nanostructure completely interlocks the ice to have resulted in a higher ice adhesion strength, as shown in Fig. 36a. The moisture condensation, as discussed before, may also lead to

enhanced ice adhesion on a micro-nanostructured surface for the same reason.

To further confirm the mechanism of interlocking action, Davis A, *et al.* developed three classes of superhydrophobic coatings with arithmetic mean surface roughness values of 8.7 μm (SH-8), 2.7 μm (SH-3), and 1.6 μm (SH-1) as shown in Fig. 36b [240]. Subsequently, supercooled microdroplets with a diameter of $\sim 20\ \mu\text{m}$ were sprayed onto the sample surfaces, as illustrated in Fig. 36c. The formed ice can completely penetrate into the surface microstructure (SH-8) with higher surface roughness, yet a relatively mild situation occurs on the SH-3 surface with a certain extent of air voids remained, as shown in Fig. 36d. As a consequence, the ice adhesion strength on these sample surfaces confirms the predicted trend, where the SH-3 surface with surface roughness of 2.7 μm displays the lowest ice adhesion (see Fig. 36e). The high ice adhesion strength on the SH-8 surface is mainly due to a large amount of supercooled microdroplets penetrating into the surface microstructure and producing a strong action of mechanically interlocking between ice and solid. The SH-1 surface has the lowest roughness, however, it cannot maintain the stable air voids between ice and solid surface, this a higher adhesion than the SH-3 sample.

Fig. 36. (a) Ice adhesion strength in shear on four different surfaces on silicon wafer (from superhydrophilic to superhydrophobic) with different size of nanopores, and the proposed interface model for failure under shear loading. Reproduced with the permission of Ref. [239], copyright 2012, AIP publishing. (b) SEM images corresponding to SH-8, SH-3, and SH-1 sample surfaces reflect the different surface roughness of 8.7 μm , 2.7 μm , and 1.6 μm , respectively. (c) Schematic illustration of supercooled microdroplets (diameter of $\sim 20 \mu\text{m}$) being sprayed and frozen into ice. (d) Morphologies of sample surfaces with different roughness and the corresponding cross section of ice accretion. (e) The ice fracture pressure of sample surfaces reflecting the tensile ice adhesion strength. Reproduced with the permission of Ref. [240], copyright 2014, American Chemical Society.

To address the interesting question on whether superhydrophobicity leads to icephobicity and to identify key factors underlying icephobicity, Wu X, et al. prepared 5 different types of superhydrophobic sol-gel coatings having a very similar surface roughness [241]. The ice-adhesion strength and icing temperature varied significantly among the different coatings. A conclusion from this study is that surface roughness is

inadequate to describe the necessary surface features that critically affect the anti-icing behavior of the coatings, detailed topological information is also necessary (which could not be captured by surface roughness datum). The study also points out that reducing the ice adhesion and reducing ice-nucleation temperature / rate have different requirements on surface geometry due to their different underlying mechanisms.

Based on the interface interlocking consideration, the lubricant-infused surface is a more suitable candidate because of the infused lubricant layer is flat. As shown in Fig. 37a, Chen J, *et al.* confirmed that the shear ice adhesion strength on the self-lubricating liquid water layer (SLWL) surface was far lower (approximately tenfold) than that on the micro-nanostructured superhydrophobic surface [242]. The ice adhesion strength on the SLWL surface is highly dependent on the surface contact fraction, and can be reduced to ~ 50 kPa when the surface contact fraction is 0.25 (see Fig. 37b). However, the low ice adhesion is only maintained in a mildly cold temperature range from $0\text{ }^{\circ}\text{C}$ to $-30\text{ }^{\circ}\text{C}$, as shown in Fig. 37c. Subramanyam SB, *et al.* drew a similar conclusion that the lubricant-infused surface exhibits a low ice adhesion strength, and could be tuned by the micropost density (see Fig. 37d) [243]. The microscopic images (see Fig. 38e and f) of ice after fracture indicate the brittle adhesive failure of the ice/substrate interface. The imprints on the surfaces of ice after being fractured from the lubricant-infused surfaces reflect that the ice slightly penetrates into the space of microposts, as shown in Fig. 37g. Consequently, the micropost edges act as the stress concentrators and crack initiation sites, which

explains the trend in ice adhesion strength with increasing the micropost density or surface contact fraction.

Fig. 37. (a) Shear strength of ice at -15 °C on the superhydrophilic surface, superhydrophobic surface, flat silicon surface, and the SLWL surface. (b) Plots of the measured shear ice adhesion strength on SLWL impregnated with cross-linked hygroscopic polymers as a function of surface contact fraction ϕ . (c) Shear strength of ice on the self-lubricating liquid water layer surface versus the supercooling temperature ΔT . Reprinted with the permission of Ref. [242], copyright 2013, American Chemical Society. (d) Effect of micropost density on the ice adhesion strength on lubricant-infused surfaces with silicone oil and tetramethyltetraphenyl-trisiloxane (DC704) lubricant. (e,f) SEM images of the imprints on the surfaces of ice after being fractured from the silicone oil infused surface and DC704 lubricant infused surface. (g) Schematic illustration of the ice on the DC704 lubricant-infused surface and the corresponding SEM image of cross

section (location marked by red circle may suffer stress concentration under the shear loading). Reproduced with the permission of Ref. [243], copyright 2013, American Chemical Society.

4.4. Stability against mechanical and environmental damages

An important consideration for practical applications of icephobic materials is the stability against to mechanical and environmental damages [244-246]. Depending on the applications, mechanical damages may include scratch, abrasion, sand erosion, and water jetting, etc., while coatings on outdoor structures may face the risk of degradation under UV exposure and water ingress. Over the past decade, limited literatures reported the research progress on the mechanical properties and stability of icephobic materials. Table 2 lists the mechanical properties of reported icephobic coatings. Techniques for mechanical property or performance evaluation of coatings such as hardness, elastic modulus, pencil-scratch resistance, cross-cut adhesion, and pull-off adhesion test are commonly employed in industry for other functional coatings, however, limited research could be found for icephobic coatings. A recent work on room-temperature processable fluorine-free icephobic coatings comprehensively studied the mechanical properties of the coatings according to the respective ISO or ASTM standards and provided an overall evaluation of the coatings [247]. The mechanical properties (hardness and modulus) and performance evaluation results are summarized in Table 2, and compared with some existing reports. The fluorine-free icephobic coating displays excellent pencil-scratch resistance and has achieved the highest cross-cut adhesion grade.

Table 2. Mechanical properties and performance of reported icephobic coatings.

Mechanical properties	Nanoindentation		Pencil scratch resistant	Cross-cut adhesion	PosiTTest Pull-Off adhesion test
	Hardness (MPa)	Modulus (GPa)			
ASTM / ISO standards	ISO 14577 standard		ASTM D3363 or ISO 15184 standard	ASTM D3359 standard	ISO 4624 or ASTM C1583-04 standard
Fluorine-free icephobic coating fabricated by our group [247]	69 ± 14	2.39 ± 0.66	4H	5B on epoxy substrate	$> 3.70 \pm 0.52$ MPa (Adhesion failure occurred between the adhesive and the coating surface, and the bonding strength of coating/substrate interface should be greater than this value)
Bilayer icephobic film synthesized on steel or silicon wafer via iCVD [248]	479 ± 7	19.1 ± 1.2	N/A	N/A	N/A
Aeronautical livery coating on carbon fiber reinforced polymer [249]	141 ± 9	4.84 ± 0.28	N/A	5 B on carbon fiber reinforced polymer	2.41 ± 0.04 MPa
Al ₂ O ₃ /PTFE icephobic coatings [250]	N/A	N/A	N/A	5 B of PTFE on anodized Al 6061	N/A
Icephobic superhydrophobic coating	N/A	N/A	N/A	5 B on aluminum alloys	N/A

[251]					
Hybrid copolymer film [252]	N/A	N/A	4 B	0 B on glass and Al substrate	N/A
Icephobic paint [253]	N/A	N/A	2 H	N/A	N/A
Icephobic hierarchically textured coatings [254]	N/A	N/A	N/A	5 B on aluminum surface	N/A
Ice release coatings [255]	N/A	N/A	2H–3H	5 B	N/A

Table 3. Environmental evaluation of the icephobic coatings.

	Water jetting	Eraser rubbing or tape-peeling test	Sandpaper abrasion	Sand erosion		UV irradiation
ASTM / ISO standards	ASTM G73-10 Liquid impingement erosion	N/A	N/A	Free fall of sands at certain distance	At certain pressure	ASTM D4587 / ASTM G154 or ISO 4892 standard
Fluorine-free icephobic coating fabricated by our group [247]	N/A	N/A	N/A	N/A	Maintain water repellence, and icephobicity after sand	Maintain icephobicity and good mechanical properties. Ice-adhesion strength increased

					erosion at pressure of 200kPa for 30s	by ~10% from 64.7 kPa to 71.3 kPa after 288 h UV irradiation and condensation
Self-lubricating liquid water layer (SLWL) [192]	N/A	N/A	the ice-adhesion strength on the SLWL maintained around 63 ± 11 kPa after 80 cycles of abrasion at pressure 12.5 kPa	N/A	N/A	N/A
Superhydrophobic steel surface [256]	Maintain superhydrophobicity after 100 μ l droplets falling from 30 cm,	Maintain superhydrophobicity after peeling 70 times by Scotch-600 adhesive tape	Maintain superhydrophobicity after 10000 grit sandpaper scratching for 110 cm under 16 kPa pressure	N/A	N/A	Maintain superhydrophobicity after 500W UV irradiation for 50 h at 50 °C
Superhydrophobic aluminum alloy [257]	After water jetting at 25 kPa for 10 min, roll-off angle increased but lower than 30°	N/A	After five cycles of 10000 grit sandpaper scratching at 10 kPa, the roll-off angle increased to $53 \pm 5^\circ$	Roll-off angle increased but lower than 30°	N/A	N/A

Liquid infused SiO ₂ -polyethylene composite coating [258]	Retained superhydrophobicity after 180 min of dripping with impacting velocity of 2.42 m/s	Retained superhydrophobicity after 40 times of 3M tape peeling	Presented superhydrophobicity after scratching on 200 grid sandpaper for 1080 cm at a pressure of 2.25 kPa	N/A	N/A	N/A
dual geometric architectures with anti-frost properties [259]	N/A	Sustain superhydrophobicity after 11 times of adhesive tape (Scotch-600) peeling	After scratching on 400 grit sandpaper with a loading of 50 g for 120 cm	N/A	N/A	N/A
Permanently grafted icephobic nanocomposites [260]	N/A	No ice formation after undergoing 30 eraser abrasion cycles	N/A	N/A	N/A	N/A
Durable superliquiphobic coating [261]	N/A	Water CA larger than 150° after 45 cycles of tape peeling	Water CA larger than 100° after 30 cycles of abrasion	N/A	N/A	N/A
Flame -sprayed polymer coatings [262]	N/A	N/A	N/A	N/A	Gain weight during sandblasting test at 2.5 bar	N/A

					pressure for 120 s	
Dissimilar SAMs coatings [263]	N/A	N/A	N/A	N/A	N/A	Water CA reduced dramatically after the 20th cycle
Icephobic fluoropolymer film [264]	N/A	N/A	N/A	N/A	N/A	Water CA remained constant at 155° after 120h of UV radiation and condensation
Ice release coatings [255]	N/A	N/A	N/A	N/A	N/A	The ice-adhesion strength of the topcoat increased from ~100 kPa (before the UVB exposure) to ~260 kPa after UV irradiation for 1700 h

Stable performance against rain, sand, and UV degradation in outdoor environment is another important consideration for the practical applications of icephobic materials. Correspondingly, researches tried various methods to estimate the mechanical / environmental stability of icephobic coatings, including water jetting, sand erosion, rubbing, sandpaper scratching, and UV weathering (see Table 3). Except the UV accelerating test, which most of the reported results followed the ASTM or ISO standards, other tests are all self-designed by researchers to evaluate durability of icephobic coatings and therefore not easy to compare. Wang N, *et al.* evaluated the mechanical durability of nanotextured superhydrophobic surface, prepared by H_2O_2 / acid etching and FAS-17 modification of a steel substrate, under the shear abrasion of 400 grid SiC sandpaper loaded with 500g of force, as shown in Fig. 38a [256]. Compared with the surface before abrasion, the microstructure was partially damaged by the coarse sandpaper with the surface roughness decreased from 1.323 μm to 0.256 μm , yet water droplets on the surface can still easily roll off (the CA higher than 152° and the SA is only 8°), as illustrated in Fig. 38b. Furthermore, Fig. 38c shows the trend of superhydrophobicity versus the number of tape-peeling following the procedures stated in ASTM D 3359-09. The superhydrophobicity exhibits a slight decline after tape peeling for 70 times, yet the surface is able to maintain the Cassie-Baxter mode and shows the strong repellence of water droplets.

Fig. 38. Superhydrophobicity of coatings on a treated steel substrate after abrasion. (a) Illustration of the abrasion test for the micro-nanostructured superhydrophobic surface with the 500 g weight loading on 400 grid SiC sandpaper. (b) The morphologies of micro-nanostructure and the non-wettability with CA of 152° and SA of 8° after the abrasion test. (c) CA and SA as functions of peeling times for the micro-nanostructure superhydrophobic surface. Reprinted with the permission of Ref. [256], copyright 2015, American Chemical Society. (d) The CA and roll-off angle of a superhydrophobic Al alloy (AA6061) surface as functions of test cycles of sand impacting, water jetting, and shear abrasion, respectively. (e) Static images showing droplets on the superhydrophobic the Al alloy surface after 5 cycles of the above three mechanical tests. (f) SEM images before and after mechanically testing for 5 cycles.

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Considering more rigorous application environments, Zhang Y, *et al.* performed sandpaper shear abrasion, high-pressure water jetting, and sand particles impacting on the micro-nanostructured superhydrophobic icephobic coatings on aluminium alloy substrates [257]. As shown in Fig. 38d, the superhydrophobic coatings undergoing 5 cycles of high-pressure water jetting and sand particles impacting remain superhydrophobic. However, the superhydrophobic coatings cannot effectively resist the shear abrasion by sandpaper, causing a reduction of water repellence with the SA increased to 53° (Fig. 38e). Correspondingly, the microtexture on the superhydrophobic surface after 5 cycles of mechanical tests also displays some damage, and the micro-protrusions are partly removed under the action of sandpaper shear abrasion (see Fig. 38f). These studies suggest that it might be risky to entirely rely on micro-nanostructured superhydrophobic surfaces to enable good long-term mechanical durability under harsh working conditions. A new strategy for the design of materials and surface structures is necessary.

In a recent study [247], different sized (10-20 nm and 200 nm) SiO_2 nanoparticles were employed to prepare icephobic coatings. The icephobicity and mechanical properties were compared among the coatings, and also bench-marked with a commercially available PU-based composite coating. In addition, the coating durability was also investigated by measuring the water wettability of the coatings before and after UV irradiation and sand erosion. The results, shown in Table 3 and Fig. 39, verified that the design of dual-sized nanoparticles has led to a lower degree

of porosity and a smoother surface (roughness $\sim 0.9 \mu\text{m}$) with better anti-icing properties and mechanical stability than a rougher surface (roughness $\sim 1.4 \mu\text{m}$) produced by adding single-sized nanoparticles. These prepared coatings have shown better performance than the commercial coating.

Fig. 39. (a) Ice-adhesion strength and (b) ice accumulation of the PU, S20, and S200 coatings before and after sand erosion. PU is a commercial coating with CA slightly higher than 90° , while S20 and S200 are superhydrophobic coatings with CA over 150° . Reprinted with the permission of Ref. [247].

Fig. 40. (a) Variation of ice adhesion strength and CA versus icing / de-icing cycles for plasma polymer hexamethyldiloxane on an anodized aluminum surface. (b)

atomic force microscope (AFM) images showing the morphologies before 15 icing / de-icing cycles. Reproduced with the permission of Ref. [265], copyright 2013, Elsevier BV.

Recently, the service life of icephobic materials is proposed and defined as the performance retention versus the icing / de-icing cycles [245,246]. Mobarakeh LF, *et al.* investigated the ice-adhesion strength on the superhydrophobic surface coated with polymerization of hexamethyldisiloxane (HMDSO) after different number of icing / de-icing cycles [265]. As shown in Fig. 40, the ice-adhesion strength gradually increases after several icing/de-icing cycles, and the water CA shows a declining trend. The essential reason to cause these changes of ice-adhesion strength and water CA is the mechanical damage of surface microscopic texture. After 15 cycles of icing / de-icing, the surface loses some necessary nano-structural features, resulting in a decrease in CA and increase of ice-adhesion strength. For the soft substrate, the as-prepared superhydrophobic icephobic surface can effectively resist the damage after the icing / de-icing cycles [266]. As illustrated in Fig. 41a, the superhydrophobic and icephobic polydimethylsiloxane (PDMS) pillars surface displays a stable ice adhesion strength of 26 ± 3 kPa with 20 successive icing/de-icing cycles. The micropillars remain intact after a series of icing / de-icing cycles (see insets in Fig. 41a) due to their excellent toughness and bonding strength with the substrate. In a separate study, Shen Y. *et al.* developed a high-performance superhydrophobic fluorinated silica on PDMS with an improvement in the bonding strength with substrate and good anti-icing performance [211]. The ice adhesion strength was only

26.3 kPa, and the icing time was delayed by 50 times. Also, the resultant coatings still retained high stability after 30 icing / de-icing cycles, soaking, and scouring of acid solution (pH=5.6).

Fig. 41. (a) Superhydrophobic and icephobic PDMS pillars surface displays the stable ice-adhesion strength of 26 ± 3 kPa within 20 icing / de-icing cycles. Insets showing the morphologies of the PDMS pillars before and after the icing/de-icing cycles. (b) Mechanical abrasion of three different icephobic coatings. The PDMS with interfacial slippage and lubricated PU rubbers are easily damaged and delaminated within 20 abrasion cycles, whereas the PU with interfacial slippage survives over 5000 cycles and still maintains the low ice adhesion strength. (c) Comparison of various coatings exhibits the durable icephobicity of PU with interfacial slippage. Reprinted with the permission of Ref. [234], copyright 2016, American Association for the Advancement of Science.

Although the nanotextured superhydrophobic surface is able to prevent large

water droplets from freezing and exhibits a certain degree of mechanical durability, it is less capable when dealing with condensed water droplets or the supercooled airflow as faced by aircraft. Compared with the superhydrophobic materials, the lubricant-infused surface with higher icing delay performance and lower ice-adhesion strength may face the more serious performance degradation, because the infused liquid layer can be easily depleted or damaged during icing / de-icing cycles [190,242]. Therefore, the lubricant-infused surface has to overcome this limitation in order to realize the actual applications under the harsh working conditions. Based on the "slippery" idea of lubricant-infused surface, a kind of soft icephobic coating with the interfacial slippage feature was reported by Golovin K, *et al.* The coating showed extreme durability under severe mechanical abrasion and icing/de-icing cycles [234]. As shown in Fig. 41b, the polyurethane (PU) rubbers with interfacial slippage have survived over 5000 cycles of the Taber abrasion test and still maintain a low ice-adhesion strength, whereas the PDMS with interfacial slippage and lubricated-PU are easily damaged and delaminated within 20 abrasion cycles. Additionally, after mild abrasion, the PU with interfacial slippage still possesses good icephobicity with ice-adhesion strength 2500% lower than other coatings relying on lubrication (*i.e.*, SLIPS) or low surface energy (*i.e.*, superhydrophobic materials). As illustrated in Fig. 41c, the comparison reveals the extreme durability of the PU with interfacial slippage even under more severe testing conditions of 100 icing / de-icing, thermal cycles, corrosion, and 5000 abrasion cycles. In summary, the stability of icephobic performance resisting mechanical damages is a key factor for the development of

icephobic materials from lab studies to real-world applications, and should be paid more attentions in future studies. More research is encouraged aiming at breakthrough materials and technologies towards mechanically durable and UV stable icephobic materials [267].

5. Applications

We have summarized the different aspects of icephobicity from minimizing water wetting before ice could form, to delaying ice nucleation, as well as reducing the ice adhesion. Lab-scale icephobic performance evaluations have also been covered, with a focus on the coating durability under simulated working environment. Without doubt, the ultimate goal for these fundamental researches on icephobic materials is to realize their practical applications. The current development of icephobic materials is of great significance to solving icing-related problems, with no or minimum reliance on the energy consuming active de-icing technologies as discussed in the Introduction. So far, the actual applications of icephobic materials are very limited although some reports are available at prototype level research. In this section, we will begin with examples in airplane and wind turbine to illustrate challenges faced by practical applications under harsh working conditions. Another interesting challenge (with emerging interest and importance) is how to ensure coating transparency while maintaining the icephobicity and mechanical durability. We will share our views and suggest potential solutions on this topic with growing interest.

As shown in Fig. 42a, De Pauw D. and his co-workers fabricated a

superhydrophobic coating using a spraying method on a small-scale airfoil [268], and observed the ice accretion process in a simulated aircraft icing environment. The superhydrophobicity of airfoil surface effectively induces the reduction of ice accretion, and the length of ice ridge (chord-wise) is obviously much shorter than that on the untreated Al airfoil surface (see Fig. 42b). Although decreasing temperature causes certain extent of enhancement of ice accretion, the superiority of superhydrophobic airfoil surface is still remarkable compared with untreated Al airfoil surface. Fig. 42c-f show the ice accretion on the untreated and superhydrophobic airfoil surfaces at 0 °C and -10 °C. Icing area on the superhydrophobic airfoil surface is much smaller than that on the untreated airfoil surface. Meanwhile, the ice adhering to the superhydrophobic airfoil surface could be easily removed, while the ice adhesion on the untreated airfoil surface was much higher.

Fig. 42. Superhydrophobic surface reducing the ice accretion on airfoils in a simulated aircraft icing environment. (a) Schematic diagram of the untreated and superhydrophobic airfoils placed in the test section of icing wind tunnel. (b) Ice ridge length (chord-wise) on untreated Al surface and superhydrophobic surface (labeled as SH) at temperatures ranging from 0 °C to -10 °C. (c,e) Images showing the ice accretion on the untreated airfoil surface at 0 °C and -10 °C. (d,f) Images showing the ice accretion on the superhydrophobic airfoil surface at 0 °C and -10 °C. Reproduced with the permission of Ref. [268], copyright 2017, AIAA.

Also aiming at airfoil applications, Shen Y, *et al.* confirmed the relationship between the size of nanotextures and their icephobic performance. They found the single nanostructured superhydrophobic surface (SN-surface) is more promising to

prevent aircraft icing than the hierarchical micro-nanostructured superhydrophobic surface (HN-surface) in an icing wind tunnel condition [269]. As shown in Fig. 43a and b, the profile of formed ice on the SN-surface is the thinnest, demonstrating a better ability to prevent ice accumulation from supercooled microdroplets in the wind tunnel test. It is reasonable to believe that the supercooled microdroplets with the diameter of 20-40 μm can more easily penetrate into the micrometer pores of the HN-surface (marked using red cycle in Fig. 43c), yet the SN-surface is more successful in resisting the penetration. This finding is highly useful to understand the icing mechanism in a real aircraft icing environment, and to guide rational design of the surface structures of icephobic materials for aircraft applications.

Fig. 43. Test results in an icing wind tunnel with the supercooled airflow at -10 ± 2 $^{\circ}\text{C}$. The wind speed is 25 m/s, the microdroplet diameter is 20-40 μm , the test time is 10 min, and the liquid water content is 0.3-0.4 g/m^3 . (a) Icing situations on the superhydrophobic nanostructure surface (SN-surface) (top) and superhydrophobic hierarchical micro-nanostructure (HN-surface) (bottom) reveals that the icing area on the SN-surface is smaller than HN-surface, and the ice weight difference is ~ 26 g. (b) The ice shapes (cross section) on the bare substrate, HN-surface, and SN-surface. (c)

Schematic diagrams of supercooled microdroplets freezing on sample surfaces.

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Wind turbines operating in cold regions or at high altitudes are also frequently facing icing environments [270,271]. If the ice formed on the wind turbine blades cannot be removed in time, it may cause many serious problems, such as measurement errors, power losses, overproduction, mechanical failure, and electrical failure, *etc.* [272]. Icephobic materials can prevent ice from sticking to the surface owing to their anti-adherent property, and lower ice-adhesion strength is a clear advantage as there is no or less energy consumption to remove the formed ice. Peng C, *et al.* prepared superhydrophobic PVDF coatings with porous microstructures on a wind turbine blade, which is made of glass fibre reinforced epoxy resin composites [273]. The superhydrophobic PVDF surface can effectively prevent ice accumulation in the icing environments. The increased ice weight on the uncoated hydrophilic blade surface shows linear increase within the test time, yet the amount of ice on the blade coated by the superhydrophobic PVDF materials is almost zero. Similarly, Wu X, *et al.* prepared mechanically robust superhydrophobic coatings by sol-gel method, with 10-20 nm sizes of SiO₂ nanoparticles added as reinforcement [118, 274]. The resultant surface was endowed with the CA up to 166° and low affinity to various oils.

Ice depositing on overhead transmission lines and insulators has been a major design concern in cold climate regions, and can be more challenging for regions that do not expect frequent icing condition. Liao R, *et al.* spray-coated SiO₂ nanoparticles on the surface of a glass insulator. The coating displayed robust icephobic

performance under simulated freezing conditions [275]. As illustrated in Fig. 44, only isolated ice spots were formed on the surface of superhydrophobic insulator surface after spraying supercooled water for 80 min. However, the bare insulator was completely covered by a thick layer of compact ice after 40 min testing, and the situation become worse with increasing test time [276].

Fig. 44. Images revealing the icephobic formation by spraying supercooled water onto the surface of a glass insulator under a simulated freezing condition ($-5\text{ }^{\circ}\text{C}$ and diameter of the supercooled droplets is $\sim 100\text{ }\mu\text{m}$). Ice accretion on (a-d) superhydrophobic coatings and (e-g) bare insulator surface for different test time.

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Transparency is another important factor for many applications, such as solar cells, windows, windshields of automobiles, and components that require their aesthetic appearance to remain. Some polymeric coatings are transparent, but their mechanical durability is limited. The well-reported micro-nanostructured superhydrophobic coatings are usually non-transparent, as the rough surface tends to

scatter light. Our group recently reported a bio-based transparent icephobic coating which presented low ice-adhesion strength around 50 kPa at -20°C , an icing-delay time of 165 s at -15°C , and resistance to supercooled water-dripping [277]. Fig. 45 shows supercooled water-dripping results on the coated and uncoated wooden floor plates and the wood boards. Residual ice was observed on uncoated surfaces, while no residual ice was found on the coated surfaces.

Fig. 45. Images of supercooled water dripping on coated and the uncoated (a) wooden floor and (b) the wood board (-15°C , tilt angle of 60° to the horizontal plane, continuous supercooled-water dripping lasted for 5min). Reprinted with the permission of Ref. [277], copyright 2017, Elsevier BV.

The demand for mechanically durable transparent icephobic coatings requires a completely different strategy from the well-adopted schemes using either the micro-nanostructured superhydrophobic coatings or the lubricant-infused porous structures (as discussed in chapter 3). We have recently demonstrated mechanically robust, transparent coatings that display very low affinity with ice and various low surface energy liquids (oils) [278,279]. The optimized coatings have a hardness of 270 MPa, an elastic modulus of 2.0 GPa or higher, and a relative transmittance $\sim 98\%$.

Other mechanical performances, including scratch resistance, adhesion, and sand erosion, have also been evaluated. The excellent overall performance is owing to the good dispersion of the added nano-fillers.

In summary, the readiness for practical application of icephobic coatings varies with the intended application environment. For mild working conditions without exposure to harsh mechanical and UV conditions, some of the developed coatings are readily applicable. However, icephobic coatings that are able to withstand harsh working conditions (e.g. airplane, wind turbine, solar cell), more research on prototype scale is needed to understand the damage mechanisms and how the damage could affect the icephobic performance in a practical situation (e.g. wind tunnel experiment). Based on the understandings, high-performance icephobic materials can be more effectively designed and produced. Smooth icephobic coatings with emphasis on low surface energy recently emerged as an alternative strategy when high transparency is required [108,280].

6. Conclusions and outlook

Recent development on icephobic materials has been comprehensively reviewed, covering three fundamental aspects of icephobicity: water repellence, ice nucleation, and ice adhesion. These three aspects represent a sequential lineup of defense against ice accumulation as discussed in the Introduction. To sum up, an efficient water-repellent surface helps timely removal of water droplet, so that ice formation can be prevented. Under the circumstance that quick removal of water is difficult or

impossible, a longer delay in ice formation time or a lower freezing temperature then becomes a necessary feature for icephobic materials. The last defense line is to ensure a low ice-adhesion strength when ice inevitably forms to ensure its easy removal.

In this review, we have discussed in details the mechanisms of static and dynamic water wettability, ice nucleation, and ice adhesion on a solid surface through selected examples. It is worth noting that although maintaining a microscopically rough superhydrophobic surface is essential for fast repellence of water droplets, attention should be paid on the possible change of the water contact mode at low temperatures or under pressurized high-speed water jetting conditions. A rough surface may be turned from an advantage to a disadvantage if the asperities or pores on the rough surface are filled by condensed moisture or pressurized water jet, under which ice adhesion can be even higher than a flat surface. It is generally observed that ultrafine nanostructures possess a better ability to resist such water penetration. Alternatively, a very flat low-energy surface could be chosen. In addition to the design and control of surface texture at micro-nano scales, macroscopic surface structure manipulation has been demonstrated to be effective in significantly shortening the dwell time of an impinged water droplet on surface before it bounces off. For example, it was shown that the contact time on a superhydrophobic surface can be significantly reduced with the creation of submillimeter tapered surface structures [126].

Inhibiting ice nucleation is another key performance indicator for icephobic materials. In this regard, micro-nano textured superhydrophobic and ultra-slippery (lubricant-infused) surfaces have displayed promising performance. On the textured

superhydrophobic surface, ice nucleation can be preferentially triggered at the triple-phase contact line. In this case, low surface / interface energies are essential to ensure a low icing temperature. On the other hand, the triple-phase contact line nucleation does not seem to have taken place on the ultra-slippery surface. Compared with the textured surface, it is hard to trigger ice nucleation on the lubricant-infused slippery surface due to a higher free energy barrier for nucleation. Overall, the lubricant-infused surface has displayed impressive icephobic properties. However, it suffers from certain limitations such as potential depletion of the infused liquid and mechanical damage under harsh application environments [190,242]. As a result, most researchers still look into textured superhydrophobic surfaces for their icephobic solutions, although this class of materials have their own constraints and limitations as we have discussed in this review. A much less-explored territory is smooth coatings with low surface energy, particularly the ones with good mechanical performance, but as indicated in the last chapter, focused research in this area has emerged in the last several years. Studies have indicated that it is possible to achieve a much-delayed icing time, low icing temperature, and weak ice-adhesion strength on a well-controlled hydrophobic flat surface, comparable with the ones on the nanotextured superhydrophobic surfaces. An added advantage for smooth coatings, compared with micro-nanoscale rough coatings, is that the coating can be made highly transparent since it is free of surface light scattering. Enabling transparency to icephobic coating widens the scope of application for icephobic materials.

Durable icephobic materials against mechanical damages and environmental

degradation are desirable from practical point of view. We have presented several examples claiming varying degree of success in retaining the icephobic performance after the mechanical or weathering tests. One of the outstanding issues with reported icephobic performance evaluations, including the stability against mechanical and environmental damages, is that there is a lack of universally accepted test standards, which makes it difficult to compare reported results from different groups. For example, research has shown the icing temperature is dependent on the water purity, water droplet size, way of cooling, and cooling rate. Meaningful comparison among different groups can only be made once all these conditions are consistent. Looking ahead, standardization of icephobic evaluation tests is urgently needed, and this requires joint effort between international standard organizations, the funding agencies, research institutions, and interested end users to work together.

Finally, we share our perspectives for future effort needed in the development of icephobic materials. The fundamental sciences behind static / dynamic wetting have been well understood. Future research in this aspect is probably limited to examining and explaining newly developed materials. Through the effort in the past decade, it is now well accepted that superhydrophobic surface does not automatically leads to icephobicity. Some more effort is needed to clarify the controversy between heterogeneous nucleation on 2D water / substrate interface and at the 1D water / substrate / vapor three-phase contact line. As ice nucleation is governed by the thermodynamics, minimizing the surface / interface energies will help increase the nucleation free energy barrier approaching the one for homogeneous nucleation.

In terms of realizing practical applications, more prototype testing is needed under simulated working environments, such as wind tunnel test for airfoil applications. This effort should be driven by the end users, working together with the research institutions. More durable coatings are desperately needed for airplane and wind turbine applications, and they represent arguably the most demanding working environment. As coating has a limited thickness, it may be necessary to develop easily repairable or self-healing coatings to reduce the economic loss due to the downtime.

Multi-functional icephobic coatings are expected to be in good demand in the future. We have shown examples of mechanically durable coatings, and there will be other functionality requirements based on different applications. Smart coatings that can respond to stimuli from the surrounding will be interesting, for example, a coating that releases anti-freezing agent upon surface icing [281]. In terms of materials and technology used for icephobic materials preparation, environmentally-friendly materials (e.g. bio-based precursors) and coating technologies (e.g. NoSOC - no small organic molecules - coating formulation) will certainly become popular due to the increased environmental awareness and commercial competition. Bio-derived materials have been investigated for quite a number of years for engineering applications; however, the use as icephobic coatings has only begun very recently [282,283]. We expect more work in the area of environmentally-friendly icephobic materials.

In summary, much has been learnt on icephobicity, the engineering solutions in ice prevention, and remaining challenges faced by the community. Having witnessed

the fast progress in the last decade, we are optimistic that more practical applications, especially the ones under harsh working conditions, will be realized soon with the increasing amount of effort made, as evidenced by the sharp rise in the number of relevant publications in the past decade. We hope that the summarized understandings and engineering recommendations could help researchers and engineers to design better icephobic materials for their intended applications.

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