A Review on Ultrafast Laser Enabled Excellent Superhydrophobic Anti-Icing Performances

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Abstract: Fabricating and developing superhydrophobic anti-icing surfaces have been a research hotspot for eliminating undesired icing issues. Among various fabricating strategies, ultrafast laser micro-nano fabrication is regarded as a greatly promising technique owing to its advantages of high geometric accuracy, highly flexible microstructure or dimension availability, no contact, and no material limitation. A number of diverse micro-nanostructured superhydrophobic surfaces have been developed by ultrafast lasers and demonstrated extraordinary anti-icing properties. They are collectively known as ultrafast laser-fabricated superhydrophobic anti-icing surfaces (ULSASs). In this article, we reviewed the recent advances in ULSASs from micro-nano structure fabricating to anti-icing performances and to potential applications. The surface wettability and mechanisms of ultrafast laser micro-nano fabrication are first introduced, showing the strong ability of ultrafast laser for fabricating superhydrophobic surfaces. Then the deepened understanding of the relationship between superhydrophobicity and icephobicity is discussed in detail, including Cassie–Baxter stability, surface durability and environmental adaptability. Eventually, the passive anti-icing technique, the passive/active combined anti-icing technique and their practical applications are presented together with current challenges and future prospects.

Keywords: ultrafast laser; superhydrophobic; anti-icing

1. Introduction

Icing phenomena have brought tremendous troubles in many fields such as telecommunication, transportation, energy, etc. [1–4]. Especially in aviation applications, the formed and accumulated ice on airplanes greatly damages aerodynamic properties [5–7]. It has been shown that mm-thick ice on airfoils will result in about 30% loss of lift force per unit area, eventually causing catastrophic accidents [8,9]. In recent years, many crashes related to icing have taken place. To eliminate ice formation and build-up, some conventional anti/deicing technologies such as electrothermal, pneumatic, and ultrasonic deicing have been developed and widely used [10–12]. This notwithstanding, such active deicing strategies tend to be extremely wasteful of energy, are of low-efficiency, and not environmentally friendly [13]. These drawbacks overwhelmingly restrict their applications in situations such as for diminutive airplanes from drones to warcraft and some industrial applications from pipelines to power lines [14,15]. Therefore, novel anti/deicing technologies are in urgent need of researching and developing to meet the application demands.

Inspired by the water repellency of the lotus in nature, superhydrophobic surfaces (SHSs) have been one of the most promising candidates for achieving passive anti/deicing [16,17]. With extremely high contact angles of >150° and low sliding angles of <10°, SHSs can significantly reduce the solid-liquid contact area to repel external water droplets in time.
Inspired by the water repellency of the lotus in nature, superhydrophobic surfaces (SHSs) have been developed in recent years. Among these, papers about superhydrophobic anti-icing account for about one-quarter of all publications, showing their dominant role. However, with the deepening of research, it is found that superhydrophobic surfaces cannot always eliminate icing issues and have greater ice adhesion strengths than smooth pristine surfaces in some cases [25,26]. With regard to mechanisms, superhydrophobicity is mainly attributed to a large number of trapped air pockets among micro-nanostructures, where a triple-phase solid-liquid-gas interface will be constructed. However, the air pockets are very fragile. Once they are broken, greater ice adhesion will be generated owing to the mechanical locking between ice and micro-nanostructures. In this case, the micro-nanostructures also provide more ice nucleation sites to promote the icing process [27–29]. These negative results have given rise to a number of debates on whether SHSs are advantageous for anti-icing applications. Kreder et al. compared different types of anti-icing surfaces, including superhydrophobic surfaces, slippery surfaces, and hydrated surfaces. They emphasized the decisive role of surface structures on anti-icing properties [30]. To further understand the relationship between superhydrophobicity and icephobicity and explore the optimized superhydrophobic anti-icing surfaces, fabricating and easily controlling micro-nanostructures is of great significance.

![Figure 1. Number of published articles per year indexed by Web of Science. The keywords for searching are “anti-icing” and “superhydrophobic anti-icing”](image)

To date, many state-of-the-art strategies have been developed to fabricate micro-nanostructures, including chemical etching, machining, 3D printing, sol–gel methods, laser processing, and others [31–35]. Among these, ultrafast laser micro-nano fabricating, as a novel top-down processing strategy, shows the superior advantages of nm-accuracy, contact-free, and highly programmable processing without material dependence. This method is not only easy for fabricating surface micro-nanostructures but also greatly promising for practical applications [36–39] (Table 1). Meanwhile, compared to other conventional lasers with continuous wave and short pulses, ultrafast lasers have an ultrashort pulse width from several tens of femtoseconds to tens of picoseconds, which is equivalent to or shorter than the heat conduction time of an electron lattice. Hence, a smaller
heat-affected zone and higher processing quality could be realized [40,41]. Generally, the surface structures formed by ultrafast laser irradiation can be divided into two types: laser-ablated structures (arrayed microstructures) and laser-induced structures (random and/or periodic nanostructures) [42,43]. The former’s geometry is mainly determined by the ablation process with intense laser energy interaction with materials and can be closely controlled by user-defined structure shapes. The most typical representative of the latter, the laser-induced periodic surface structure (LIPPS), is formed by linearly polarized laser radiation with fluences slightly above the ablation threshold [44]. By varying laser processing conditions such as wavelength, pulse duration, power density, incidence angle, scanning speed, and processing environments, the morphologies of LIPPS could also be closely controlled. Adopting the above two structures, microscale and nanoscale structures on surfaces could be easily and tunably fabricated with ultrafast lasers. In the meantime, during laser ablation, the plasma plume contains abundant energetic species, which reunite and rapidly deposit on microstructures to form nanostructures, thus constituting the hierarchical micro-nanostructures [45–47]. The fabrication of various micro/nanostructures enabled by ultrafast lasers has paved a solid pathway to preparing SHSs. Although most materials such as metals and ceramics are intrinsically hydrophilic so that the superhydrophilic interfaces are produced after laser processing, the superhydrophobicity can be easily achieved by surface chemical modification, including vapor deposition, solution immersing, spinning coating, and so on [48–50]. Many reports and advances have been produced in fabricating SHSs and controlling their superhydrophobic states by ultrafast lasers [51,52]. Compared to the SHSs fabricated by other methods, laser-fabricated superhydrophobic surfaces have shown tremendous advantages in durability, stability, and repeatability as well as high tunability [53–56]. Many reviews have summarized laser-fabricated superhydrophobic surfaces in various application scenarios [40,42,57]. Specifically, research articles about ultrafast laser-fabricated superhydrophobic anti-icing surfaces (ULSASs) have sprung up in recent years [58–61], as shown in Figure 2. However, to our best knowledge, related reviews and perspectives are rarely reported. In response to the special issue “Superhydrophobic and Icephobic Coatings”, it is of significance and value to summarize recent progress in ULSASs and to propose current challenges and future prospects.

Table 1. Comparison of common micro-nanofabrication techniques in terms of fabrication rate, accuracy, structural tunability, applicable materials, and large-scale fabricating.

<table>
<thead>
<tr>
<th>Methods</th>
<th>Accuracy</th>
<th>Structural Tunability</th>
<th>Applicable Materials</th>
<th>Large-Scale Fabricating</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultrafast laser process</td>
<td>nm</td>
<td>√</td>
<td>Any materials</td>
<td>√</td>
<td>[62–64]</td>
</tr>
<tr>
<td>Chemical treatment</td>
<td>nm</td>
<td>×</td>
<td>Metals</td>
<td>√</td>
<td>[65–67]</td>
</tr>
<tr>
<td>Photolithography</td>
<td>nm</td>
<td>√</td>
<td>Silicon</td>
<td>×</td>
<td>[68,69]</td>
</tr>
<tr>
<td>Template methods</td>
<td>nm</td>
<td>√</td>
<td>Polymer, metal</td>
<td>√</td>
<td>[70–72]</td>
</tr>
<tr>
<td>Machining</td>
<td>μm</td>
<td>√</td>
<td>Any materials</td>
<td>√</td>
<td>[73,74]</td>
</tr>
<tr>
<td>3D printing *</td>
<td>μm</td>
<td>×</td>
<td>Polymer, metal, ceramics</td>
<td>×</td>
<td>[35,75]</td>
</tr>
<tr>
<td>Sol–gel methods</td>
<td>nm</td>
<td>×</td>
<td>Polymer</td>
<td>√</td>
<td>[76,77]</td>
</tr>
</tbody>
</table>

* Here, we take two-photon lithography (TPL) as the representative of 3D printing.

In this review, we focus on ultrafast laser enabled superhydrophobic anti-icing performances and draw examples from surface fabrication, anti-icing mechanisms, and advances and applications, as shown in Figure 3. The fundamental wettability and ultrafast laser micro-nano fabricating examples are discussed first, elucidating the structural diversity and tunability of ultrafast laser fabricating. Adopting ultrafast laser-fabricated SHSs, some novel and interesting phenomena involving icing and melting processes are discussed with a deepened understanding of the relationship between superhydrophobicity and icephobicity. We clarify that superhydrophobicity is one necessary but insufficient condition of icephobicity and present three common failure factors of superhydrophobic anti-icing surfaces, including Cassie–Baxter stability, surface durability, and environmental adaptivity.
The next section introduces the recent progress of ULSASs in the three aspects of passive anti-icing, passive/active combined anti-icing, and their practical outdoor applications in detail. Combining the storylines from fabrication to mechanisms and then to applications, we present current challenges in moving ULSASs toward practical applications. Finally, we give a conclusion and provide prospects for the future development of ULSASs.

Figure 2. Ultrafast laser-fabricated superhydrophobic anti-icing surfaces: fabrication, mechanism understanding and surface development. Reproduced with permission from [78], copyright (2022) Springer; reproduced with permission from [79], copyright (2022) Nature Publishing Group; reproduced with permission from [80], copyright (2020) American Chemical Society; reproduced with permission from [81], copyright (2023) American Chemical Society; reproduced with permission from [6], copyright (2023) American Chemical Society; reproduced with permission from [82], copyright (2022) Elsevier.
Figure 3. Flow chart describing the arrangement and order of each part in this review.

2. Ultrafast Laser-Fabricating Micro-Nanostructured Superhydrophobic Surfaces

2.1. Wettability and Superhydrophobicity

Surface wettability represents the ability of liquids to spread on surfaces. When the spreading reaches the equilibrium, droplets statically rest on surfaces and form an angle, namely, contact angle $\theta$ (CA). From thermodynamics, CA is the characterization of three-phase interfacial free energies. Back in 1805, the relationship between them has been well described by Young’s equation [83], as shown in Figure 4a:

$$\cos \theta = \frac{\gamma_{sv} - \gamma_{ls}}{\gamma_{lv}}$$

(1)

where $\gamma_{sv}$, $\gamma_{ls}$ and $\gamma_{lv}$ denote the interface tensions of solid-vapor, liquid-solid, and liquid-vapor, respectively. Although Young’s equation establishes the qualitative relationship
between interfacial energies and wettability, it is not appropriate for describing rough surfaces in the real world. Wenzel et al. introduced the roughness factor \( r \) and took the apparent contact angle \( \theta^* \) to characterize surface wettability \[84\], as shown in the following equation:

\[
\cos \theta^* = r \cdot \left( \frac{\gamma_{sv} - \gamma_{ls}}{\gamma_{lv}} \right) = r \cdot \cos \theta
\]

where the roughness factor \( r \) is the ratio of the actual solid-liquid contact area to the nominal contact area. However, the model is limited to the occasion that liquids completely penetrate micro-nano valleys and cannot explain some common wetting phenomena in nature such as the rolling droplets on lotuses. Cassie and Baxter further introduced the contact fractions of liquid-solid \( f_{ls} \) and liquid-vapor \( f_{lv} \) to describe the mixed triple-phase interfaces \[85\]. Considering \( f_{ls} + f_{lv} = 1 \), the Cassie–Baxter equation is expressed by:

\[
\cos \theta^* = f_{ls} \cdot \cos \theta - 1 + f_{ls}
\]

Generally, droplets on superhydrophobic surfaces show a large CA and low adhesion strength. Contact angle hysteresis is one of the most common evaluation standards of droplet adhesion. The maximum and minimum static CAs are defined as the advancing angle \( \theta_{adv} \) and receding angle \( \theta_{rec} \), respectively. The difference between \( \theta_{adv} \) and \( \theta_{rec} \) is the contact angle hysteresis (CAH), as shown in Figure 4a. Smaller CAHs mean smaller adhesion forces exist between interfaces so that droplets can move on surfaces more easily. In this case, surfaces have better liquid-repellency \[86,87\]. In nature, superhydrophobic phenomena exist widely. For example, luxuriant micropapillae covered by low-surface-energy epicuticular wax endow lotuses with excellent superhydrophobic and anti-fouling properties \[88\] (Figure 4(d1,d2)), and needle-shaped micro-nano setae combined with wax make water striders walk on rivers freely \[89\] (Figure 4(e1,e2)). Meanwhile, diverse micro-nanostructure arrangements also bring about many unique superhydrophobic properties, such as the high droplet adhesion on rose petals enabled by single-tier microstructures (Figure 4(f1,f2)) \[90\], directional adhesion on rice leaves \[88\] and butterflies enabled by directional microgrooves \[91\] (Figure 4(g1,g2,h1,h2)), and the anti-fogging properties on mosquito eyes enabled by elaborate nanonipples \[92\] (Figure 4(i1,i2)).

### 2.2. Ultrafast Laser Micro-Nano Fabricating

As discussed above, ultrafast lasers have many incomparable advantages in micro-nanofabrication. These advantages are not only ascribed to the convenience and programmability of processing methods but also attributed to the complicated light-matter interactions \[39,93\]. Generally, ultrafast lasers are defined as lasers with ultrashort pulse duration from several tens of femtoseconds to tens of picoseconds \[94\]. Figure 5a shows the timescales and intensity of the main phenomena during and after irradiating a solid with a femtosecond laser. The light-matter interacting processes could be divided mainly into three types: electronic excitation, nonequilibrium phase transformation, and morphology formation \[95\], as illustrated in Figure 5a. Overall, in most cases, electronic excitation occurs during the laser pulse (fs—ps), and nonequilibrium phase transformations take place on the picosecond timescale (about ps—100 ps). The timescale of morphology formation reaches up to nanoseconds (about ns—100 ns). There also exist some differences when processing different materials. For semiconductors or dielectrics, the irradiated laser on the one hand can prompt the generation of high-concentration free electrons across the bandgap, which might further induce non-thermal melting. Meanwhile, on the other hand, the laser also provides the excited electrons with more energy, triggering the switching to the plasma state or producing a coulomb explosion. When reaching the electron lattice equilibration, rapid heating at a rate of >\(10^{14}\) K/s occurs to further lead to homogeneous melting or the formation of a supercritical fluid \[96\]. Many new surface morphologies or metastable phases are produced in extreme environments. After the temperature decreases below material melting points, the melts start to solidify or resolidify to form surface micro-nanostructures. For metals, laser-induced electron heating dominates, resulting in
localized high-temperature melting. However, the high thermal conductivities of metals can additionally result in a high supercooling state, where some unexpected structures or defects will be constructed, such as some amorphous structures or nanocrystals [97,98].

Figure 4. Three classical wetting states and the superhydrophobic phenomena in nature. (a–c) Schematics of the three states: (a) Young’s equation; (b) Wenzel equation; (c) Cassie–Baxter equation. (d–i) Creatures with superhydrophobicity: (d1,d2) lotus leaves (reproduced with permission from [88]. Copyright (2007) Elsevier); (e1,e2) water striders (reproduced with permission from [89]. Copyright (2007) American Chemical Society); (f1,f2) rose petals (reproduced with permission from [90]. Copyright (2008) American Chemical Society); (g1,g2) rice leaves (reproduced with permission from [88]. Copyright (2007) Elsevier); (h1,h2) butterflies (reproduced with permission from [91]. Copyright (2018) American Chemical Society); (i1,i2) mosquito eyes (reproduced with permission from [92]. Copyright (2007) John Wiley and Sons).

Following the interaction mechanisms between ultrafast lasers and matter, numerous diverse micro-nanostructures can be easily fabricated and can be further tuned by varying
laser processing parameters or adjusting processing environments. Some common laser parameters include laser wavelengths, pulse duration, pulse repetition frequency, pulse input number, laser fluence, and so on [39, 99]. Here, we take two important parameters (laser pulse duration and pulse input number) as examples to introduce their effects on micro-nanostructures. Generally, different laser pulse durations result in different heat affected zones, eventually affecting the processing quality. As shown in Figure 5b, with the shortening of pulse duration from $10^{-9}$ to $10^{-15}$, the processing quality gradually improves as a result of the smaller heat-affected zone [94]. This phenomenon is mainly attributed to the pulse durations of ultrafast laser (picosecond and femtosecond laser) being shorter than the electron-lattice relaxation time (~$10^{-12}$ s). Hence, less heat is transferred, causing a smaller thermal effect. For the pulse input number, the micro-nanostructure sizes and morphologies are directly influenced. Figure 5c exhibits the evolution of micro-nanostructures with the pulse input number. It is found that the particles can be flexibly controlled not only in the wide range of nanoscale, sub-microscale, fine-microscale, microscale, and coarse-microscale but also with various structural sizes, including heights and intervals [100].
Besides the fundamental laser parameters, processing environments also play a significant role in structural morphologies and chemical elements. For example, we once adopted a femtosecond laser to process Ag samples in air and Argon atmosphere [103]. It was found that more nanoparticle clusters and less oxide were generated in Argon. In the meantime, by ablating NiFe in the NH$_3$ atmosphere, we also fabricated more abundant nanoclusters than in the air [104]. These discoveries confirm that the processing atmosphere has a great influence on micro-nanostructure morphologies.

Based on diverse processing parameters and environments, ultrafast laser-fabricated micro-nanostructures could be easily tuned to further realize the fine control for superhydrophobic states. Long et al. achieved the superhydrophobic state tunability from the Wenzel state to the CB state by simply changing the laser scanning speeds on the copper material [51]. The superhydrophobic state evolution was ascribed to the changes in microstructure sizes and nanostructure amounts, where lower scanning speeds could induce deeper microstructures and more abundant nanostructures to contribute to the CB state. Yin et al. discovered the controllable wettability on Polyimide film via femtosecond laser thermal accumulation engineering [105]. By regulating local thermal accumulation effects, different micro-nanostructures were induced, realizing the wettability changes from superhydrophobicity (~3.6$^\circ$) to superhydrophobicity (~151.6$^\circ$). Zheng et al. adopted a femtosecond laser to fabricate a temperature-response ceramic surface with switchable wettability [106]. Superhydrophobic and superhydrophilic interfaces were reversibly and repeatedly transitioned after alternate heating treatments. It was confirmed that laser-induced micro-nanostructures contributed to the removal and re-absorption of organic compounds, thus resulting in the wettability transition.

3. Anti-Icing Mechanisms of SHSs

Adopting diverse and tunable micro-nanostructures fabricated by ultrafast lasers, a large number of applications have been explored [48,107,108]. Among that, ULSASs have been extensively researched in recent years. Many new phenomena have been discovered to deepen the understanding of superhydrophobic anti-icing properties. In this section, we combine recent reports and our understanding to explain the relationship between superhydrophobicity and icephobicity and give the analysis of common failure factors of superhydrophobic anti-icing surfaces.

3.1. Relationship between Superhydrophobicity and Icephobicity

In terms of the interfacial states between droplets and micro-nanostructures, droplets on superhydrophobic surfaces mainly exhibit two states: Cassie-Baxter (CB) and Wenzel. Although droplets in both states have CAs exceeding 150$^\circ$, their icephobicity performs differently [5]. Icephobicity works only when droplets are supported by air pockets to retain the CB state. However, once air pockets are broken, droplets will rapidly penetrate into the valleys and be stuck by surrounding micro-nanostructures. In this case, the SHSs not only lose their icephobicity but also bring about more icing danger such as easy-icing and ice difficult-removal [109]. Chen et al. reported that the Wenzel ice on SHSs even showed over four times higher ice adhesion strengths than on hydrophilic surfaces [25]. Hence, superhydrophobicity is not equal to icephobicity but is one necessary but not insufficient condition.

To ensure the icephobicity of superhydrophobic surfaces, droplets should retain the CB state but not the Wenzel state. Nonetheless, much research indicates droplets tend to passively transit from the CB state to the Wenzel state under external disturbances [79,110,111], such as freezing, vibration, external pressure, and so on. Affected by the energy barrier between the Wenzel state and the CB state, the spontaneously reversible transition was once regarded as impossible. Many experts have systematically investigated the icing and melting processes on different micro-nanostructured superhydrophobic surfaces [79]. Although some found ultralow ice adhesion strengths for mL-scale ice columns, the transition from the CB state to the Wenzel state still inevitably occurred when the droplet size
diminished to the μL-scale. Figure 6 shows the icing and melting processes of droplets on laser-fabricated superhydrophobic surfaces. Compared to other SHSs, it was discovered that droplets on laser-fabricated SHSs possessed a significantly delayed icing ability, which contributed to more bubbles dissolving in supercooled droplets and further dissolving out in ice droplets. During melting processes, these bubbles could spontaneously and rapidly impact downwards under the Marangoni effect, leading to the recovery of the CB state. The dewetting transitions were closely related to surface structures, which further affected the superhydrophobicity, the delayed icing time, and the liquid retraction resistance forces. Although it was confirmed that laser-induced micro-nanostructures could well ensure the robustness of dewetting transitions, the room-temperature superhydrophobicity was still overwhelmingly different from the low-temperature icephobicity owing to complex interfacial interactions at low temperatures [112]. To ensure the anti-icing properties of SHSs, extraordinary superhydrophobicity is undoubtedly one of the most significant conditions, but there are still many other factors that need to be guaranteed. As follows, three main failure factors of superhydrophobic anti-icing surfaces are discussed.

![Figure 6. Icing and melting processes on the superhydrophobic surfaces fabricated by ultrafast laser (reproduced with permission from [79], copyright (2022) Nature Publishing Group).](image)

3.2. Failure Factors of Superhydrophobic Anti-Icing Surfaces

3.2.1. Cassie–Baxter Stability

The CB stability represents the ability of SHSs to withstand the impalement of air pockets by droplets [113,114]. In room-temperature environments, the CB stability is evaluated by the Laplace pressure of droplets, namely, \( P = 2\gamma/R_d \), where \( \gamma \) is the liquid surface tension and \( R_d \) is the radius of droplets. Higher CB stability means that SHSs can withstand higher Laplace pressure to retain the CB state of droplets. The critical Laplace pressure \( P_C \) is generally determined by two criteria [80,115]: (i) the critical Laplace pressure for the CA at the moment of droplet transitioning from the superhydrophobic state to the hydrophobic state \( (P_{CCA}) \); and (ii) the critical Laplace pressure for the contact diameter at the moment of the triple-phase line stops retracting \( (P_{CCD}) \). In terms of the two criteria, \( P_C \) is expressed by:

\[
\begin{align*}
P_C &= P_{CCA}, \text{if } P_{CCA} < P_{CCD} \\
&= P_{CCD}, \text{if } P_{CCA} > P_{CCD}
\end{align*}
\]
Many researches have confirmed that some finely designed ultrafast laser-fabricated SHSs show superior CB stability at room temperature owing to highly controllable and robust micro-nanostructures [115–117]. It is widely accepted that SHSs with higher $P_C$ could show better anti-icing properties. Pan et al. combined ultrafast laser ablation and chemical oxidation to fabricate two types of three-tier micro-nanostructures: the microcone-microflower-nanosheet (MNSF) and the microcone-microflower-nanograss (MNGF) [80]. The two surfaces showed ultrahigh room-temperature CB stability with the highest critical Laplace pressure of ~1450 Pa among all the published reports (Figure 7a,b). However, although the two surfaces showed similar CB stability at room temperature, there still existed significant differences in their anti-icing properties. For example, the ice adhesion strength on MNGF was only 1.7 kPa while that on the MNSF reached 16.9 kPa (Figure 7c). The results indicated that room-temperature $P_C$ was not appropriate for evaluating the low-temperature Cassie–Baxter stability. Focusing on this problem, related calculation models based on icing phenomena were recently established to evaluate the low-temperature CB stability of SHSs with air pocket pressure (Figure 8a,b) [118]. It was found that both microstructure morphologies and temperatures had a great influence on the air pocket pressure. Among these, the open-cell microstructures had higher air pocket pressure at low temperatures than the semi-open or closed microstructures, thus showing higher CB stability. As demonstrated in Figure 8c,d, the anti-icing properties corresponded well to the air pocket stability induced by microstructures, where the SHSs with more open-cell structures showed better and robust anti-icing properties. Hence, to avoid the failure of superhydrophobic anti-icing surfaces, open-cell structures should be adopted to maintain the low-temperature CB stability.

**Figure 7.** Morphologies (a), CB stability (b) and ice adhesion strengths (c) of laser-fabricated superhydrophobic surfaces. MNGF denotes the surface with microcone-microflower-nanosheet structures while MNSF denotes the surface with microcone-microflower-nanograss structures. The SEM images in (a) are from the MNGF surfaces. (Reproduced with permission from [80]. Copyright (2020) American Chemical Society.)
3.2.2. Surface Durability

Surface durability plays a key role in long-term practical applications. Among these, micro-nanostructures and low-surface-energy coatings are two crucial factors. For micro-nanostructures, it is well-known that the structures on SHSs are generally fragile and can be abraded easily when subjected to external shear forces [119]. To improve structural durability, much research has conducted [120,121]. In the best-known study, Wang et al. used armor-like microstructures combined with nanoparticles to realize ultrahigh superhydrophobic durability [87]. However, based on the above analysis, the introduction of armor-like microstructures would result in a decrease in air pocket pressure at low temperatures, eventually causing the failure of anti-icing properties. Hence, the closed-cell structures are not icephobic-durable (Figure 9a). Both room-temperature durability and icephobic durability need to be met for long-term anti-icing applications. Designing the micro-nanostructures to make this comprise is of significance.
For low-surface-energy coatings, durability is related only to intrinsically hydrophilic materials, such as metals, ceramics, etc. The most common coating substance is fluorosilanes, which can be facilely coated on micro-nanostructures by the methods of vapor deposition or solution immersing [123]. Although excellent superhydrophobicity could be achieved with the methods, the durability of such coatings is usually poor owing to the single molecular layer thickness of the coated fluorosilanes by bonding with hydroxyl groups [82]. Nishino et al. measured the surface roughness of the coating on glass [122], where n-Perfluoroearcosane (C_{20}F_{42}, one of the low-surface-energy substances) was vapor deposited. They found that the vapor-deposited layer was single crystal-like with a maximum roughness of only 8 Å (Figure 9b). Under external abrasion, the coatings can be easily peeled off to expose the inner hydrophilic sites, eventually leading to the failure of anti-icing properties. Therefore, research on chemical synthesis and coating materials still needs to be made in developing novel durable low-surface-energy coatings.

3.2.3. Environmental Adaptivity

Numerous complex and unexpected disturbances exist in practical application environments, including high-speed droplet impact, dust accretion, strong wind, etc. [124]. In this case, superhydrophobic anti-icing surfaces fail more easily compared to static laboratory environments. We take the common dynamic impact as an example to elucidate the influences of environments on anti-icing properties. Figure 10a,b show the comparison of four typical dynamic tests: water jet impacting, solid particle impacting, supercooled droplet impinging, and icing wind tunnel tests [81]. It can be observed that there are tremendous differences for different test conditions. For icing wind tunnel tests (a widely adopted method to simulate real aviation environments), the droplet sizes and impacting velocities are generally in the range of ~20–100 μm and ~10–100 m/s. The dynamic pressures in icing wind tunnel tests reach up to over 1 Mpa, which is more than an order of magnitude higher than those in other tests. Under continuous, high-speed, high-pressure and tiny droplet impact, superhydrophobic anti-icing surfaces tend to fail extremely easily.

**Figure 9.** Two key factors influencing surface durability. (a) Surface structure types (Reproduced with permission from [118]. Copyright (2023) Royal Society of Chemistry.) (b) Low-surface-energy coatings (Reproduced with permission from [122]. Copyright (1999) American Chemical Society.)
Figure 10c shows the icing processes of the superhydrophobic anti-icing surfaces fabricated by the DLIP. The surfaces, which could easily repel supercooled droplets (−5 °C; diameter: ~2 mm; impact speed: 3.4 m/s) at the substate temperature of −25 °C, not only failed in 0.5 min in the icing wind tunnel tests but also even resulted in more ice accretion than pristine smooth surfaces. We ascribed the phenomenon to the preferentially bottom freezing when supercooled tiny droplets contacted surfaces. Within several milliseconds, the ice embryo nucleated and generated a strong adhesion to the substrate instead of rebounding (Figure 10d). Meanwhile, subsequent high-pressure droplets continuously impacted the surfaces to further increase the ice adhesion and lead to ice accretion.

Figure 10. Influence of environmental disturbances on anti-icing performances. (a) Summarization of the relationships between the size of the droplets/particles and the impacting velocity from the four dynamic experiments: water-jet impacting, solid-particle impacting, supercooled-droplet impinging, and icing wind tunnel tests. (b) Dynamic impact pressure when the droplets/particles contact the target surfaces. (c) Image sequences of the icing processes on SHSs in icing wind tunnel tests. (d) Schematic diagrams showing the physical processes at dynamic impacting (Reproduced with permission from [81]. Copyright (2023) American Chemical Society.) (e) Comparison of structural sizes with droplet sizes. (f) Interfacial shear stress versus freezing fraction (Reproduced with permission from [125]. Copyright (2020) John Wiley and Sons.)

To ensure that superhydrophobic anti-icing surfaces have qualified environmental adaptivity, Vercillo et al. explored the design rules of ULSASs by testing various micro-nanostructures in icing wind tunnel conditions [125]. Two dominant but opposite factors
were summarized: stress concentrations and surface contact area. They found that although micro-nanostructures with small sizes had a smaller solid-liquid contact area, the structures also induced lower stress concentration. For those with larger sizes, higher stress concentration but a larger contact area was produced. It was concluded that the laser-fabricated structures should be with a spatial period of one order of magnitude smaller than the mean volume diameter (MVD) and with abundant nanostructures (Figure 10e). They also confirmed that the ice types, i.e., freezing fraction, had a strong influence on anti-icing properties, where droplets could freeze faster at higher freezing fractions and were also more difficult to remove (Figure 10f).

4. Advances and Challenges of ULSASs

Based on the above understanding, we summarize recent advances of ULSASs and proposed corresponding challenges in this section. Two typical types of SHS anti-icing technologies are discussed, including passive superhydrophobic anti-icing surfaces and passive/active combined superhydrophobic anti-icing surfaces. For ease of understanding, the challenges are presented by following their respective progress. Finally, current attempts and explores of ULSASs in their practical applications are introduced and discussed.

4.1. Passive Superhydrophobic Anti-Icing Surfaces

4.1.1. Delayed Icing/Frosting

Five stages are divided into the whole icing processes: supercooling, nucleating, recalescing, freezing, and solid cooling [79,126]. The delayed icing time generally denotes the duration time of the first three stages, which start in the original cooling from room temperatures and end in the occurrence of recalescence. Among these stages, avoiding ice embryo nucleation is the key to delaying icing [127].

Nucleation processes are divided into two types: homogeneous nucleation and heterogeneous nucleation [128]. The former generally takes place in environments without any disturbance and is completed by structure fluctuation and energy fluctuation. However, in practical environments, heterogeneous nucleation generally takes the dominant [129]. The nucleation rate of liquids can be expressed by:

$$R(T) = R_{\text{bulk}}(T)V + R_{\text{lv}}(T)S_{\text{lv}} + R_{\text{ls}}(T)S_{\text{ls}}$$  \hspace{1cm} (5)

where $R(T)$, $R_{\text{bulk}}(T)$, $R_{\text{lv}}(T)$ and $R_{\text{ls}}(T)$ are the nucleation rates of the total, the bulk, the liquid-vapor interface, and the liquid-solid interface, respectively; $S_{\text{lv}}$ and $S_{\text{ls}}$ are the contact areas of the liquid-vapor interface and the liquid-solid interface, respectively; $V$ is the liquid volume, and $T$ is the surface temperature. Compared to $R_{\text{ls}}(T)$, the value of $R_{\text{lv}}(T)$ is very small. Hence the total nucleation rate $R(T)$ is mainly dependent of $R_{\text{ls}}(T)$ and $S_{\text{ls}}$ [5]. Among them, $R_{\text{ls}}(T)$ is determined by the heterogeneous nucleation energy barrier, which is expressed by:

$$\Delta G_{\text{het}} = \frac{16\pi\gamma_{\text{lv}}^2}{3 \Delta G_{\text{V}}^0} \left(2 + \cos\theta\right)\left(1 - \cos\theta\right)^2$$  \hspace{1cm} (6)

where $\Delta G_{\text{het}}$ is the energy barrier of heterogeneous nucleation; $\gamma_{\text{lv}}$ is the liquid-vapor interface energy; $\Delta G_{\text{V}}$ is the Gibbs free energy per unit volume; and $\theta$ is the contact angle of the ice embryo on a surface. The value of $\Delta G_{\text{het}}$ is proportional to the contact angles, where higher contact angles could induce a higher heterogeneous nucleation energy barrier, further slowing down the nucleation rate. However, as discussed above, superhydrophobic delayed icing properties work only when the CB state is retained. Once droplets transit to the Wenzel state, the significantly increased solid-liquid contact area will greatly accelerate the icing proceedings. Hence, maintaining the CB stability at low temperatures is of great importance. Many researches reveal that it is mainly affected by surface wettability and micro-nanostructure morphologies [11,30]. Undoubtedly, wettability is the key factor that influences delayed icing properties. However, the above analysis confirms
that the micro-nanostructure topologies play a more important role in low-temperature air pocket stability [118]. To explore the optimal ULSASs, numerous state-of-the-art micro-nanostructures have been developed. Pan et al. combined femtosecond laser ablation and chemical etching to fabricate the triple-scale micro-nanostructures on copper and aluminum alloy materials [130], where the open microcone arrays were covered by densely distributed submicroflowers and nanograss (Figure 11a). It was found that the triple-scale micro-nanostructures showed a significantly longer delayed icing time of 52 min 39 s, longer than on smooth surfaces (8 min 15 s) and double-scale structured SHSs (34 min 38 s). Ge et al. fabricated a hybrid micro-nanostructure with square pillars integrated Siberian–Cocklebur-like microstructures on PTFE by controlling femtosecond laser parameters [131], as shown in Figure 11b. They found that the surfaces not only had excellent superhydrophobicity but also exhibited significantly enhanced delayed icing time. Xing et al. adopted a picosecond laser to fabricate the cauliflower-like protrusions with nanostructures on the open micro-gratings [132], as shown in Figure 11c. They revealed that the laser-processed multi-tier micro-nanostructures moderated the heat loss to delay the icing process. Summarizing recently reported data on ULSASs [61,129,131,133–136], Figure 12 shows the delayed icing times versus different droplet volumes and materials. Compared to organic and inorganic ULSASs, most metallic surfaces have better delayed icing properties. This is attributed to the differences of the formed micro-nanostructures on different materials owing to different light-matter interaction mechanisms (discussed in Section 2.2). Some chemical component changes during ablating also account for the differences.

![Image](image-url)  
**Figure 11.** Delayed icing properties of ULSASs. (a) Image sequence of icing processes on the pristine copper surface, the double-scale structured ULSAS, and triple-scale structured ULSASs (reproduced...
Figure 12. Delayed icing times on ULSASs versus different droplet volumes and materials. The test temperature of all data was $-10 \, ^\circ\text{C}$. Data were from the references [61,129,131,133–136].

In contrast to droplet freezing, frosting is a more complicated process, involving more phase transformations [137–139]. Generally, two types of frosting modes are included: desublimation frosting and condensation frosting [140]. Desublimation frosting involves the gas-solid phase change and occurs mostly when the surface temperature is lower than the triple point of water. In condensation frosting, vapor first condenses onto surfaces, and then condensates freeze to form frosts when surface temperatures decrease below the icing point [4]. On hydrophobic surfaces, the required supersaturation degree for desublimation frosting is an order of magnitude larger than on hydrophilic surfaces [137]. Therefore, in practical applications, the delayed frosting on SHSs generally represents the delayed condensation frosting. Numerous studies have been made on understanding the mechanisms of condensation frosting on SHSs and developing related anti-frosting surfaces [24,68,141,142]. The most remarkable is the discovery of droplet jumping on SHSs induced by the decreased Laplace pressure and droplet coalescence [21,24]. Taking advantage of the spontaneous droplet jumping, condensates could be swept off the surfaces in time before freezing. However, some remaining droplets can still freeze to inevitably form frosts. To diminish the frosting ratio, two strategies have been mainly developed: (i) designing and optimizing micro-nanostructures to inhibit the growth of frost layers; (ii) designing the chemical components of surfaces to enhance droplet jumping. For ULSASs, the first strategy is adopted more frequently. By adjusting the microstructure sizes and morphologies, the frost growing extent and spreading directions could be well con-
controlled. Many experts have investigated frosting behaviors on ULSASs. He et al. adjusted laser fluence and pulse repetition frequency to fabricate different micro-nanostructures and investigated the relationship between surface morphologies and anti-frosting properties [143]. They found the smaller tip area and the larger nanostructures were preferred for delaying frosting. Long et al. fabricated 3D conical microtextures covered with nanowires on copper materials [144]. In condensation environments, the fine structures could contribute to the departure of condensate droplets, thus realizing the dropwise condensation and delaying frosting. Although much effort has been expended on developing diverse laser-induced micro-nanostructures for anti-frosting, which type of structures performed better was still unclear. In 2023, we classified all micro-nanostructures into two types: open-cell and closed-cell structures [118]. By comparing the condensation frosting processes on the two structures, it was found that more small condensate droplets emerged on the closed-cell structures since the microframes provided more nucleation sites (Figure 13). The delayed frosting time decreased as the area ratio of closed structures increased, indicating open structures performed better than closed structures. This conclusion could greatly guide the structural design of ULSASs for better anti-frosting properties.

![Figure 12. Delayed icing times on ULSASs versus different droplet volumes and materials. The test temperature of all data was −10 °C. Data were from the references [61,129,131,133–136].](image)

**Figure 12.** Delayed icing times on ULSASs versus different droplet volumes and materials. The test temperature of all data was −10 °C. Data were from the references [61,129,131,133–136].

![Figure 13. Delayed frosting phenomena on the ULSASs with different microstructures. 
(a,b) The frosting processes on the closed-cell microstructures and open-cell microstructures. (c) Schematics describing the differences of condensates nucleating and growing on different microstructures. (d) The densities and diameters of condensate droplets on the ULSASs with different microstructures. (e) Delayed frosting times versus different microstructures. (reproduced with permission from [118]. Copyright (2023) Royal Society of Chemistry).](image)

**Figure 13.** Delayed frosting phenomena on the ULSASs with different microstructures. (a,b) The frosting processes on the closed-cell microstructures and open-cell microstructures. (c) Schematics describing the differences of condensates nucleating and growing on different microstructures. (d) The densities and diameters of condensate droplets on the ULSASs with different microstructures. (e) Delayed frosting times versus different microstructures. (reproduced with permission from [118]. Copyright (2023) Royal Society of Chemistry).

Although much progress has been made in delaying icing/frosting of ULSASs, the icing/frosting cannot still be completely avoided. Especially in some extremely low-temperature and high-humidity environments, numerous droplets initiate and adhere to the micro-nano valleys, and then rapidly freeze [145,146]. How to inhibit the icing/frosting
4.1.2. Ultralow Ice Adhesion Strengths

Besides delaying ice embryo nucleation, lowering ice adhesion strengths is also one of the most important properties of ULSASs [147]. In some severe icing environments (e.g., ice wind tunnel conditions), freezing processes inevitably occur on SHSs [81]. How to lower ice adhesion strengths is the key for avoiding ice accretion.

Centrifuge adhesion tests and push-off adhesion tests are the two most common methods [148,149]. The former determines the adhesion strengths by measuring the maximum shear forces or pulling forces at the moment of ice shedding during the centrifugal rotating while the latter records the maximum shear forces of the ice column detachment by the horizontal pushing. Although the reported ice adhesion strengths in literature cannot be compared accurately owing to the differences in test methods, it is widely regarded that the surfaces with ice adhesion strengths below 100 kPa are icephobic surfaces, and the ice adhesion strength of 20 kPa is the benchmark for passive anti-icing surfaces, where ice could be removed by wind blow or slight vibration [30,150]. To date, many ULSASs have been designed and fabricated with ultralow ice adhesion strengths [37,125,151–153]. Milles et al. tested the ice adhesion strengths of different ULSASs under various icing conditions and found that the cross-like DLIP pattern with the size of 2.6 µm showed the lowest ice adhesion strengths of 6~10 kPa [154]. As shown in Figure 14a, the accumulated ice layer on laser-structured surfaces could be easily removed by vibration. Considering that the solidification of environmental-related mixed liquids always took place in practical applications, we adopted a femtosecond laser to fabricate the superomniphobic surface showing excellent repellent ability for multiple liquids from deionized water to mixed solutions and then to organic liquids [78]. Figure 14b shows the ice adhesion strengths of different liquids on the designed surfaces. It was found that our fabricated surfaces had ultralow ice adhesion strengths for various liquids. Even after multiple deicing cycles, the ice adhesion strengths could be maintained below 20 kPa. However, some challenges still exist [11,30], such as poor icephobic durability (discussed in the next section), the poor environmental adaptivity, and the difficulty of large-scale fabrication. These issues greatly limit ULSASs for practical applications.
damage, which decreased the ice-solid contact area and further led to the lower ice adhesion strengths. The lowest ice adhesion strength on the prepared surfaces reached 12.2 kPa and could maintain 17.3 kPa even after 60 deicing cycles. To date, it is the lowest ice adhesion strength after so many deicing cycles among all reported ULSASs[156].

Figure 14. Low ice adhesion on the ULSASs. (a) Images of the ice easy-removal of ULSAS with vibration. Ice was formed and accumulated in the icing wind tunnel condition (reproduced with permission from [154]. Copyright (2021) MDPI). (b) Low ice adhesion of ULSASs for different liquids (reproduced with permission from [78]. Copyright (2022) Springer).

4.1.3. Durable Icephobicity

Icephobic durability directly determines the lifespan of ULSASs in practical applications. Based on the discussion in Section 3.2.2, to enhance the icephobic durability, both the micro-nanostructure durability and the coating durability need to be enhanced.

On SHSs, microstructures work as the robust skeleton while nanostructures endow surfaces with better superhydrophobicity[155]. Although the closed microstructures could
greatly enhance the room-temperature superhydrophobic durability, the open microstructures exhibit higher icephobic durability at low temperatures [118]. Hence, maintaining the open structures and further introducing more durable nanostructures become a good strategy for improving the micro-nanostructure durability. Chen et al. utilized ultrafast laser ablation and chemical oxidation to fabricate the micro-nano-nanowire triple-scale structures, where the Cu(OH)$_2$ nanowires with an average length of 6–8 µm and a width of 50 nm in situ grew on the microcones (Figure 15a). After continuous deicing tests, it was found that the surface icephobicity was progressively enhanced with an increase in deicing cycles, showing a unique property that the surfaces could become more and more icephobic after wear. The phenomenon was mainly ascribed to the side nanowires and the flat microcones constructing the moderate top roughness after the top nanowires were damaged, which decreased the ice-solid contact area and further led to the lower ice adhesion strengths. The lowest ice adhesion strength on the prepared surfaces reached 12.2 kPa and could maintain 17.3 kPa even after 60 deicing cycles. To date, it is the lowest ice adhesion strength after so many deicing cycles among all reported ULSASs [156].

Figure 15. Enhanced icephobic durability. (a) Enhanced micro-nanostructure durability by fabricating the micro-nano-nanowire triple-scale structures (reproduced with permission from [156]. Copyright (2022) American Chemical Society). (b) Enhanced low-surface-energy coating durability by using the method of PDMS spin coating (reproduced with permission from [82]. Copyright (2022) Elsevier).
To provide more durable low-surface-energy coatings, many durable coating materials have been developed and tested [157–159]. Among these, PDMS materials show great application potential owing to strong bonding strength and an easy preparation process. Many durable superhydrophobic surfaces have been fabricated by the PDMS spin coating method instead of the vapor deposition of fluorosilanes [157,160,161]. Based on these properties, Chen et al. fabricated a cauliflower-like micro-nanostructure combined with PDMS coatings by taking advantage of ultrafast laser ablation and wet chemical reactions [82]. As shown in Figure 15b, the prepared surfaces exhibited excellent superhydrophobicity and highly effective photothermal properties. Adopting FIB and EDS techniques to analyze the cross-sectional elements, it was found that the PDMS solutions could cover and bond the cauliflower-like structures well, forming an integrated structure. The infiltrated depth of PDMS in micro-nanostructures could reach the µm-scale, which meant that the low-surface-energy coating could still be preserved to maintain the qualified superhydrophobicity after structure damage. With the robust coatings and abundant micro-nanostructures, surface icephobicity could be well maintained after 25 abrasion cycles or 1.5-hour water impact or 500 tape peeling cycles.

Overall, the improvement of micro-nanostructures and low-surface-energy coatings contributes well to the enhancement of icephobic durability. However, most of the reported surfaces are far away from real industrial applications. Further developing durable icephobic surfaces to meet various demands is still needed.

4.2. Passive/Active Combined Superhydrophobic Anti-Icing Surfaces

In some severe application scenarios, the single passive anti-icing of SHSs is still limited to eliminating ice formation and accretion. Combining with other active anti-icing technologies to achieve passive/active combined anti-icing could overcome the disadvantages [162–165]. Among various hybrid anti-icing methods, electrothermal/superhydrophobic and photothermal/superhydrophobic anti-icing surfaces have been developed most widely. Here we introduce the main advances in the two methods.

4.2.1. Electrothermal/Superhydrophobic Anti-Icing Surfaces

In terms of different heating methods, electrothermal/superhydrophobic anti-icing surfaces are divided into two main types [166,167]: one is achieved by directly installing heating elements under SHSs; the other is enabled by electricity power input to transform from electricity to heat. The former has no requirement for the electrical conductivity of SHSs while the latter requires surfaces with good conductivity and electro-to-heat conversion performances. Alamri et al. used an ultrafast laser to fabricate the hierarchical micro-nanostructures on the NACA 0012 airfoil [151]. After chemical treatment, the surfaces showed strong water repellence with a contact angle of 163° ± 6° and a roll-off angle of 8° ± 6°. Combining the SHSs and their bottom-heating elements (Figure 16a), the electrothermal/superhydrophobic deicing tests were conducted in the icing wind tunnel environment (TAS (true air speed) = 65 m s⁻¹; SAT (static air temperature) = −10 °C/−20 °C; LWC (liquid water content) = 0.2 g m⁻³ and AoA (angle of attack) = 3°). Figure 16b shows the plot of the required deicing time as a function of heating power density. The power density and time of deicing on the reference surfaces were significantly higher than on the laser-fabricated SHSs. For the SATs of −10 °C and −20 °C, the deicing power densities on the reference surfaces reached up to ~2.1 and ~2.5 W cm⁻², respectively, while those on the SHSs decreased to ~0.5 and ~1.1 W cm⁻², respectively. Sun et al. also compared the electrothermal/superhydrophobic deicing properties of pristine surfaces and laser-fabricated SHSs in the icing wind tunnel conditions (TAS = 0–200 m/s; SAT = −35 °C; LWC = 0.2–3.9 g m⁻³) [168]. They found that although external heating could avoid icing on the heating zone of the pristine surface, the runback ice would be accreted more severely at the tailing edge of airfoils. In contrast to the icing phenomena on pristine surfaces, the liquid water could quickly roll away from the laser-fabricated SHSs to prevent the runback icing (Figure 16c).
For the second electrothermal deicing technology, some new phases with electrothermal properties are usually added to substrates to reinforce the thermal conductivity and electro-to-heat conversion ability. The common electrothermal materials include carbon-based materials (e.g., graphene, carbon nanotube, etc.), Ag-based materials, and some conducting polymers [169]. Xue et al. mixed multi-walled carbon nanotubes (MWCNT) and N-methylpyrrolidone solutions to prepare the MWCNT/PEI nanocomposite film [170]. An ultrafast laser was adopted to fabricate the micro-nanostructures, realizing the superhydrophobicity with a contact angle of 156.6°. Under 12 V, the three-dimensional conductive network constructed by MWCNT could rapidly rise the temperature to 109°C within 370 s. With excellent electrothermal and superhydrophobic properties, ice on the surfaces could completely melt in 170 s (Figure 16d).

Figure 16. Electrothermal/superhydrophobic combined anti-icing surfaces. (a) Schematics showing the NACA0012 support and the heating element. (b) Comparison of the deicing time and deicing power on pristine surfaces and ULSASs (reproduced with permission from [151]. Copyright (2020) John Wiley and Sons). (c) Image sequences of electrothermal deicing on different surfaces in the icing wind tunnel conditions (reproduced with permission from [168]. Copyright (2021) Elsevier). (d) Schematic showing the electrothermal mechanisms when the current is directly applied on materials, and the thermographic image sequences of electrothermal deicing processes on ULSASs (reproduced with permission from [170]. Copyright (2023) Elsevier).
4.2.2. Photothermal/Superhydrophobic Anti-Icing Surfaces

In contrast to electrothermal deicing methods, the photothermal/superhydrophobic anti-icing technology mainly utilizes solar energy in nature to convert into heat, eventually realizing passive/active combined deicing [171]. It is an environmentally friendly deicing technique without consuming any fossil fuel. Based on the photothermal conversion principles, photothermal SHSs can also be divided into two types: (i) the SHSs with structural light traps [82,172]; and (ii) the SHSs with the new phases that own the high solar-to-heat conversion efficiency [163,173,174]. Adopting various micro-nanostructures and the generated new matters enabled by ultrafast lasers, the two types of methods have been widely explored. Zhao et al. were inspired by moth eyes to fabricate the biomimetic micro-nanostructures with a femtosecond laser [175], as shown in Figure 17a. The surfaces were composed of micro-mountain arrays with micro-nanoparticles, which constructed a well-structured light trap. Under one-sun illumination, the surface temperature can rise rapidly and exceed 80 °C in 300 s. Even a large ice cube could melt and shed off the surfaces within 240 s under sunlight. Zhang et al. considered that the adhered condensates in extremely high-humidity conditions could hinder the photothermal properties and induce condensation freezing. Hence, they fabricated hierarchically structured materials by ultrafast pulsed laser deposition (PLD) technology (Figure 17b) [176]. The generated iron oxide during laser irradiation was deposited densely on substrates, not only constructing the strong light traps but also further contributing to the photothermal conversion by the thermoplasmonic effect of iron oxide nanoparticles. In the extreme environment with a temperature of −50 °C and a supersaturation degree of ~260, the photothermal anti-icing properties of the surfaces could be well maintained and the equilibrium temperature could exceed 0 °C under one-sun illumination owing to their superior condensate self-removing and high photothermal conversion capability.

Figure 17. Photothermal/superhydrophobic anti-icing surfaces. (a) Highly effective photothermal/superhydrophobic anti-icing properties enabled by the biomimetic laser-fabricated structures.
Compared to the single passive superhydrophobic anti-icing method, the passive/active combined anti-icing methods could better withstand complicated and volatile environments. However, how to realize low-cost large-scale fabrication is still a key problem for practical applications \([11,13]\). Meanwhile, different application scenarios also propose more requirements, such as the specific surface roughness and the bonding between surfaces and heating elements in the aviation field.

4.3. Exploiting Superhydrophobic Anti-Icing Surfaces in Real Applications

Based on the excellent anti-icing properties of ULSASs, many outdoor tests have been conducted to exploit their feasibility for practical applications. Vercillo et al. installed a laser-fabricated superhydrophobic Ti64 metal sheet on an A350 port-side slat for a real flight test \([177]\). The total flight duration was 171.2 h, traveling mostly across Europe and experiencing two long flights to New Zealand and the Philippines. By measuring the contact angle changes and roughness, they found that surface superhydrophobicity was mostly lost after the flight. The degrading of superhydrophobicity was mainly ascribed to the failure of the low-surface-energy coating under long-time UV exposure. Boinovich et al. conducted outdoor tests with laser-fabricated SHSs \([178]\). The test went from September 2016 to the end of March 2019 in Moscow, where regular snowfalls, sleet, and freezing rain accompanied by high humidity and frequent air temperature changes occurred frequently. They found that the bare aluminum surfaces had significant pitting corrosion in outdoor conditions, which greatly increased the snow/ice adhesion. For the SHSs, their icephobicity could be well maintained after continuous long-time rain and could effectively keep snow from accumulating when the wind speed exceeded 3–5 m/s, as shown in Figure 18. Even at a lower wind speed, the buildup of snow cups could still induce the spontaneous shedding of snow by their gravity. Although the practical test results also revealed some problems and limitations of ULSASs, these attempts and advances provided tremendous reference values for guiding ULSASs designs and accelerating their applications.

Figure 18. Long-term outdoor anti-icing tests of ULSASs and pristine surfaces (reproduced with permission from \([178]\). Copyright (2019) American Chemical Society).
5. Conclusions

Ultrafast lasers, as powerful and promising manufacturing tools, have colossal value in accelerating the development and applications of superhydrophobic anti-icing surfaces. To eliminate the undesired ice, much attention has been paid to ultrafast laser-fabricated superhydrophobic anti-icing surfaces (ULSASs), and related research has been comprehensively conducted in recent years. Here, we summarized the recent development of ULSASs, mainly including three aspects: fabricating, mechanisms, and advances and challenges. With respect to fabricating, we introduced fundamental wettability. Combining exquisite micro-nanostructures and low-surface-energy matters, biomimetic superhydrophobicity can be endowed on various substrate materials. Next, the advantages and mechanisms of ultrafast laser micro-nano fabricating were explained. Compared to other micro-nano fabricating strategies, the ultrafast laser-fabricating method possesses the significant advantages of being highly programmable, having the nm-accuracy, being contact-free, and with non-limitation for materials. Based on the light-matter interaction, many unique micro-nanostructures have been widely developed, providing more opportunities and possibilities for exploring the superhydrophobic anti-icing mechanisms and applications. In mechanisms, we introduced some recent discoveries and thus extended understanding of anti-icing on the laser-fabricated micro-nanostructures, and further elucidated the relationship between superhydrophobicity and icephobicity that superhydrophobicity is one necessary but not insufficient condition of icephobicity. Meanwhile, three common failure mechanisms of ULSASs were analyzed, including Cassie–Baxter stability, surface durability, and environmental adaptivity. Essentially, structures and coatings were two crucial factors to avoid the failure of ULSASs. In advances and challenges, we summarized the recent progress and the respective challenges of ULSASs in passive anti-icing, passive/active combined anti-icing, and some practical outdoor applications. The passive anti-icing of ULSASs mainly lies in delaying icing time, decreasing ice adhesion strengths, and achieving durable anti-icing, while the passive/active combined anti-icing technologies were introduced with the electrothermal- or photothermal-assisted methods. However, in contrast to lab-scale freezing environments, the practical application environments were more complicated and volatile, which brings tremendous challenges for the performances of ULSASs (icephobicity, durability, stability, etc.) and their engineering feasibility (large-scale fabrication, surface installation, device matching, etc.). As for the future development of ULSASs, the following opportunities are envisioned:

- Further investigations and deepened understanding of icing-related phenomena on superhydrophobic surfaces need to be explored.
- More design and optimization of structures and chemical coatings are demanded for developing more durable ULSASs.
- More novel ultrafast laser-fabrication technologies and more advanced ultrafast laser instruments are expected to meet the strictly industrial application requirements.

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