Superhydrophobic coatings using nanomaterials for anti-frost applications – review

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Frost formation and accretion on various outdoor structures like aircraft, wind turbines, heat exchanger coils etc. as well as on glass doors of indoor refrigerators is a serious issue as it presents economic as well as safety challenges. Most of the research done on anti-frost coatings is based on the theme of making the surface super hydrophobic (contact angle \(>150^\circ\), Sliding angle \(<10^\circ\) mimicking a lotus leaf which provides low or zero ice adhesion. Nanomaterials have played a significant role in such coatings as they help in tuning the surface properties which are surface roughness and surface energy. In this paper, we have tried to investigate why all superhydrophobic surfaces may not be ice-phobic and how nanomaterials improve super hydrophobicity of the surface, in turn, making them anti-frosting. This paper is a detailed study of anti-frosting strategies based on nanosystems which have been developed to date.

Keywords: Anti-frost coatings, superhydrophobic, icephobic, nano fillers, surface roughness, surface energy, contact angle.

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1. Introduction

When moist air comes in contact with a cold surface, whose temperature is below the triple point of water, frosting or icing takes place on the surface [1].

Considering the phase equilibrium of water-system, if pressure is applied to the system at the triple point (where all the three phases coexist); the effect of applying pressure will be to cause condensation of vapor to liquid or solid phase. Ultimately, the vapor phase will disappear and only two phases, solid and liquid, will stay and further application of pressure will cause increase of pressure with change of temperature along the fusion curve on phase diagram [2]. This implies that pressure exerted by humid air is responsible for frosting or icing on many outdoor structures in colder regions such as wind turbines, aircrafts, heat exchangers (air-conditioners/heaters), as well as domestic and industrial refrigerators/freezers. Thus, frosting is a condensation phenomenon and temperature of the (cold) surface, percent relative humidity (% RH) and temperature of air, are the factors which influence frosting and defrosting.

Frost formation and accretion on various infrastructures is a serious issue as it presents economic as well as safety challenges. For example, the ice accretion on aircraft results in drag increase and sometimes may lead to dangerous loss of lift force, which may cause tragic crashes [3]. Ice accretion on wind turbine blades can cause a production loss of as much as 50 % of the annual production [4]. Furthermore, frost and ice accumulation in refrigerators and heat exchangers results in a decrease of heat transfer efficiency up to 50 – 75 % [5].

Several conventional defrosting/de-icing techniques include electric heating which accelerates ice melting or breaking the accretion by direct scraping which neither safe nor efficient. In addition, Automatic robots, electromagnetic forces [6] are reported for the de-icing of overhead transmission lines. Thus, most of these conventional anti-frosting strategies are often inefficient, energy-consuming, high-cost, or environmentally harmful. Applying an anti-frost or defrosting coating on the cold surface has been found as the most promising and interesting method in the past two decades, realizing the objective of preventing frosting and saving energy.

Initially freezing point depressants such as Ethylene glycol were incorporated into the resin or a hydrophilic polymer was impregnated with an anti-freeze, for defrosting in heat exchangers [7]; which was later replaced by- developing an ‘ice-phobic’ surface where the substrate is mostly made superhydrophobic which exhibit water contact angles exceeding 150 °C, mimicking a lotus leaf. Today, many such anti-frosting strategies have been developed by incorporating various nanomaterials in the coating formulation.

This paper clarifies the terms ‘superhydrophobicity’ and ‘ice-phobicity’. It reviews the significance of nanomaterials for tuning the surface properties of a glass or a metal substrate so as to make it ‘anti-frost’; along with some important anti-frosting strategies which have been developed till date.
2. Superhydrophobicity and ice-phobicity

The wettability of a flat surface is directly related to the surface energy and is expressed by contact angle (CA) \( \theta \) of a water droplet given by Young’s equation:

\[
\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}},
\]

where, \( \gamma_{SV}, \gamma_{SL}, \gamma_{LV} \) refer to the interfacial surface tensions with \( S(\text{solid}), L(\text{liquid}) \) and \( V(\text{gas}) \) respectively. Surfaces with water contact angles (CA’s) greater than 150° are considered superhydrophic or ultraphobic. The dynamic CA’s are measured during the growth (advancing) and shrinkage (receding) of a water droplet as contact angle hysteresis \( \Delta \theta = \theta_a - \theta_r \). The values of \( \Delta \theta \) can be as low as below 10° on some surfaces, whereas many surfaces show much larger hysteresis, due to chemical heterogeneity and roughness [8].

The superhydrophobic surfaces are usually covered with micro- or nanoscale asperities (rough). Water can either penetrate the asperities (Wenzel state: wet-contact mode) or be suspended above the asperities (Cassie Baxter state: nonwet-contact mode). In either case, much higher contact angles are observed than those obtained for the corresponding flat surface. For a hydrophobic surface, in the Wenzel’s regime, the contact angle and its hysteresis increase as the roughness factor increases until it exceeds 1.7, from where the CAH starts to decrease. The decrease in the contact angle hysteresis is attributed to the switching from the Wenzel to the Cassie–Baxter state due to the formation of hierarchical rough morphology with sufficient air trapped in the gap to reach Cassie state of suspension of water droplet on top of the asperities as shown in Fig. 1 [8, 9].

![Fig. 1. Wenzel model (a); Cassie-Baxter model (b); Behaviour of a liquid droplet on lotus leaf (Cassie state) (c); Behaviour of a liquid droplet on rose petal (Cassie impregnating wetting state) (d)](image)

Thus, when a rough surface reaches ‘Cassie’ state it can show the ‘self-cleaning’ effect from where the dust particles or frost roll off when surface is slightly tilted, mimicking a Lotus leaf. (Also known as ‘lotus effect’ characterized by high CA and low CAH). Another special case of Cassie state is ‘rose petal’ inspired surfaces where the water droplets enter into the larger scale grooves of the petal but not into the smaller ones, thus forming a Cassie impregnating wetting state (characterized by high CA and high CAH due to adhesive property of the petal). These two effects can be attributed to difference of the microstructures and chemical composition between the petal and the lotus leaf [9].

Now, talking about ice-phobicity, a surface should be called ice-phobic if it delays frost formation from incoming water (moisture) or delays ice formation from condensed droplets (frost crystals) in the situation where normally ice would form and/or there is low adhesion force between ice and the solid surface [10]. Considering this definition, it is clear that to achieve ice-phobicity or anti-frost property on a cold surface, the surface can be made superhydrophobic with low adhesion force i.e. low CAH so that the incoming water droplets (moisture) roll off as soon as they condense and before converting into the frost; thus, frost accumulation can also be avoided due to low or non-adhesion.
This implies that lotus leaf inspired surfaces (high CA, low CAH) can show ice-phobicity and not the rose petal inspired ones. However, it has been also studied that every superhydrophobic surface which shows self-cleaning behavior (lotus effect) may not necessarily show ice-phobicity. There are several other parameters, such as surface roughness, mechanical robustness of the surface so as to maintain the same superhydrophobicity at sub-zero temperatures and with subsequent icing /de-icing events. This can be explained by the following example:

S. A. Kulinich et al. studied the ice-releasing properties of rough hydrophobic coatings based on different materials with different surface topographies [11]. Three samples were investigated for ice-phobic properties: 1. Etched aluminium alloy coated with an organosilane (ODTMS). 2. TiO$_2$ nanopowder functionalized with perfluoroalkyl methacrylic copolymer (Zonyl) applied on the substrate by spin coating. 3. TiO$_2$-Zonyl applied by spray coating. Fig. 2 shows both CA and CAH values obtained for the above three samples. Table 1 shows root mean square roughness values for the three samples at various icing-de-icing events. From Table 1 and Fig. 2 it can be seen that sample 3 though maintains high roughness after 6 de-icing cycles, high CAH 80° leads to high ice adhesion strength. Sample 1 and 2 show higher contact angles 153° and 152° respectively along with low CAH values (5.7° and 6.1° respectively).

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Sample Description</th>
<th>Root-mean-square roughness (nm) at event:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>Etched Al/ODTMS</td>
<td>240</td>
</tr>
<tr>
<td>2</td>
<td>TiO$_2$ spin</td>
<td>210</td>
</tr>
<tr>
<td>3</td>
<td>TiO$_2$ spray</td>
<td>310</td>
</tr>
</tbody>
</table>

Fig. 2. Contact angle and contact angle hysteresis for three different samples

However, there is a gradual decrease in roughness for sample 2 due to the sharper and much taller asperities which were believed to be gradually damaged during icing/de-icing cycles, whereas sample 1, also having sharp and tall asperities, seemed to be more resistant to damage during icing/de-icing. This was likely due its more rigid asperities (built of Al$_x$O$_y$) compared to those in sample 2 (based on fluoropolymer heavily loaded with TiO$_2$ nanoparticles). Thus, the more robust nanostructured surface prepared by etching the aluminium substrate maintained the ice-releasing properties better compared to its counterparts.

3. Role of nanomaterials

Nanomaterials play a significant role in the tuning of surface properties of the substrate which is desired to be superhydrophobic and also ice-phobic. As mentioned in section 2, to achieve ice-phobicity, the surface has to reach the Cassie state (high CA, low CAH), which can be accomplished by increasing the surface roughness. Nanomaterials such as carbon nanotubes, hydrophobic nanosilica, ZnO nanorods etc. are often used both as fillers and for functionalization, to impart roughness to the surface, and also to improve the mechanical properties of the surface.
Qi Tao Fu et al. prepared mechanically robust sol-gel type of ice-phobic coatings and once again clarified the significance of nanofillers in designing superhydrophobic surfaces and also that all superhydrophobic surfaces may not be ice-phobic [12]. Two sets of samples were prepared, one having coating samples prepared by using MTEOS, GLYMO and varying amounts (5 – 20 wt %) of silica nanoparticles; and the other having coating samples prepared by adding varying amounts of FAS (4 – 16 wt %) to the above formulations. The first set of samples showed increase in water CA i.e. increase in superhydrophobicity with an increase in nanofiller content as a result of increased surface roughness. However, such samples with high silica content failed in maintaining the superhydrophobicity below room temperature (high ice adhesion). On the other hand, a second set of samples containing a low surface energy fluoroalkylsilane showed ice-phobicity to temperatures as low as $-10 \, ^\circ C$. With $0.31 \pm 0.35 \, \text{µmol/gm}$ of FAS in sol and 16 wt % silica nanoparticles, the surface maintained CA $\sim 170 \, ^\circ C$, SA $\sim 4.4 \, ^\circ$ at $-10 \, ^\circ C$. The samples containing only FAS without nanofiller or with up to 8 % nanofillers were able to give CAs up to $120 \, ^\circ$ and higher sliding angles ($60 - 80 \, ^\circ$) and therefore failed to show both superhydrophobicity and ice-phobicity.

Carbon nanotube-based composite materials have been investigated for superhydrophobic coatings to improve mechanical strength. Yoonchul Sohn et al. developed an anti-frost coating with reliable thermal cyclic properties [13]. A superhydrophobic multi-walled carbon nanotube (MWCNT)-silicone composite film (Cassie structure) that can endure over 4000 thermal cycles ($-30 \, ^\circ C$ to room temperature, 40 % RH) was fabricated by controlling the composition and microstructure of the composite. The nanofiller content of this coating was 20 vol %, showing thermo-mechanical reliability without significant change in the contact angle ($\sim 160 \, ^\circ$). A composite structure having higher nanofiller content (20 – 30 %), which contains numerous pores, can accommodate high levels of thermal stress. The stress relaxation can reach 48 % and 84 % of the reference point for the 20 and 30 vol % MWCNT specimens, respectively. Since the coefficient of thermal expansion (CTE) of silicone (310 ppm $^\circ C$) is much larger than that of MWCNTs (7 ppm $^\circ C$), the large expansion and shrinkage of silicone matrix compared to MWCNT fillers resulted in cracking of specimens containing lesser nanofiller content, after 1000 thermal cycles. Though the 30 vol % MWCNT-silicone film is better for stress relaxation, the 20 vol % film shows superior ice-phobic properties (lower CAH).

Thus nanopores in superhydrophobic coatings, constituting air pockets in a Cassie structure, are of great importance not only for wetting characteristics but also for superior reliability induced by stress relaxation. Although a more open structure can help relax more stress arising from a CTE mismatch, the composition of a superhydrophobic coating should be carefully selected to optimize its wetting characteristics while maintaining its mechanical reliability.

4. Superhydrophobic anti-frost coatings using nanotechnology

Min He et al. also developed anti-frost coatings for glass substrates. They prepared superhydrophobic surfaces using ZnO nanorod arrays, which could maintain superhydrophobicity to condensed micro-droplets at temperatures below the freezing point. ZnO nanorod arrays were employed because of their controllable morphologies. Materials with different ZnO nanorod arrays were fabricated by the method of low-temperature wet chemical bath deposition and modified with a fluoroalkylsilane (FAS-17) to obtain super-hydrophobicity, even at temperatures lower than 0 $^\circ C$ [14]. Firstly, ZnO seeds layer was obtained on the cover glass by treating it with zinc acetate and then it was immersed into an equimolar solution of Zn(NO$_3$)$_2$ and hexamethylenetetramine, and kept sealed at a temperature of 90 $^\circ C$ for different times ($t_{ZnO}$) to control the growth (size) of the ZnO nanorods. Table 2 shows the change in contact angle with $t_{ZnO}$ at room temp., $-5 \, ^\circ C$ and $-10 \, ^\circ C$. The values of sliding angle have been mentioned only at room temperature as 1 $^\circ$, 1 $^\circ$ and 2 $^\circ$ for $t_{ZnO}$ 1 h, 2 h and 3 h respectively. The ice-phobic behavior when compared with that of a hydrophobic glass surface, it has been observed that the time of condensed droplets maintaining a liquid state is much longer on the superhydrophobic ZnO nanorod array surfaces. Furthermore, the shorter growth time ($t_{ZnO}$) of ZnO nanorods, increases the time period for maintaining condensed droplet in the liquid state, thus providing better anti-frost performance.

Hao Wang et al. fabricated anti-frosting copper surfaces for evaporator coils of industrial refrigerators and air-conditioners. This coating was based on nanosized CaCO$_3$ particles modified with heptadecafluorodecyl trimethoxysilane mixed in an ordinary polyacrylate binder [15]. The coating, when applied on glass, showed superhydrophobic behavior (with CA $= 155 \, ^\circ$) and maintained the same superhydrophobicity on copper plate for subsequent 10 frosting-thawing treatments at temperature $-7.2 \, ^\circ C$ and 55 % humidity. In this case, frost formation was not totally inhibited, but the rate of frosting was greatly reduced as compared to bare copper or ordinary hydrophobic surfaces and formed frost was able to roll off the plate when mounted vertically as a result of roughness (nano CaCO$_3$) and low surface energy FAS.
Yanfen Huang et al. developed ice-phobic coatings to protect aluminium ground wires and phase conductors of overhead power lines from icing [16]. The coating was prepared by a simple, inexpensive method using silica/fluorinated acrylate copolymers. The nano silica sol was mixed with fluorinated acrylic copolymers in different weight ratios. The films showed good hydrophobicity (CAUs up to 141.7 °C) and especially excellent mechanical properties of adhesion strength and pencil hardness as compared to other superhydrophobic surfaces. The coated Al surface can delay icing for 90 min. compared with the glass surface at −5.6 °C.

Hyomin Lee et al. prepared a zwitter-wettable surface, i.e. one that has the ability to rapidly absorb molecular water from the environment while simultaneously appearing hydrophobic when probed with water droplets [17]. This can be prepared by using hydrogen-bonding-assisted layer-by-layer (LbL) assembly of poly (vinyl alcohol) (PVA) and poly(acrylic acid) (PAA). An additional step of functionalizing the nano-blended PVA/PAA multilayer with poly (ethylene glycol methyl ether) (PEG) segments produced a significantly enhanced antifrost and frost-resistant behavior. The addition of the PEG segments was needed to further increase the non-freezing water capacity of the multilayer film. The desirable high-optical quality of these thin films arises from the nanoscale control of the macromolecular complexation process that is afforded by the LbL processing scheme. The author justifies the inhibition of frost formation on glass due to this type of coating by the fact that in this case, the water molecules are presumably molecularly dispersed as a result of strong polymer-water hydrogen bonding interactions and hence are not capable of freezing at the usual temperature. Also, the above-prepared nanoscale LbL assembly ensures that crystallisation of PVA molecules will be limited or non-existent, which is helpful to accommodate more amount of non-freezing water.

William Tong et al. designed transparent glass windows with antifrost/anti-fog capabilities in order to maintain the aesthetic appearance of glass windows for vehicles and modern buildings [18]. The nanostructured metamaterials can be coated on the window’s outside surface. A tungsten-silica-tungsten (at nanoscale) metamaterial coating was used as the solar absorber to coat on window’s outside surface. The top layer of the absorber is a 1D tungsten planar stack, the dielectric SiO2 spacer works as optical cavity and the bottom tungsten film as non-perfect or perfect mirrors. The profile of this three-layer structured coating can be designed by adjusting the thickness of bottom and top layers in such a way that sufficient visible light transmits through the window glass for enough lightening in the room, while maximum infrared waves can be absorbed for heating. The coating was deposited using closed field magnetron sputtering (CFM). This nanoscale metamaterial structure with periodic metal-dielectric interfaces efficiently absorbs solar radiation and with proper design, the window surface temperatures can be well controlled which is useful for efficient anti-frosting and anti-fogging. The transparency can be adjusted by changing the tungsten layer thickness (∼300 nm) meanwhile the absorption performance of the solar absorber has no significant variation.

Aeree Kim et al. fabricated a ‘nanostructured’ and therefore superhydrophobic Al surface for anti-frosting applications due to its property of enhanced self-propelled jumping by condensate droplets. This Al surface was fabricated in three following steps: 1. Alkali treatment (0.05 M NaOH) to produce an aluminium hydroxide (Al(OH)3) layer. 2. Boiling the specimens in deionized water to induce formation of nanostructures. 3. A self-assembled monolayer (SAM) of fluorochlorosilane was applied to render it superhydrophobic as well as ice-phobic. It can be seen from Fig. 3 that the time for which the specimens are immersed in boiling water governs the surface’s nanostructure and hence, the CA and CAH. All four specimens were alkali treated for the same time (5 min) and coated with SAM layer, however, different CA and CAH values were obtained for those samples having different boiling times. Samples had higher CA and lower CAH for 5 – 30 minutes boiling, as shown in Fig. 3. Self-Propelled Jumping (SPJ) by condensate droplets that occurs on superhydrophobic surface, shows significant dependency on the super saturation $S = PV/PW$, where $PV$ is the vapor pressure and $PW$ is the saturation pressure that corresponds to the specimen surface temperature. Frost formation on the above ‘nanostructured’ aluminium was delayed more than 4 times at $S = 3.41$ and $S = 6.39$ compared to smooth Al surface [19].

<table>
<thead>
<tr>
<th>$t_{ZnO}$</th>
<th>Contact angle</th>
<th>Room temp.</th>
<th>−5 °C</th>
<th>−10 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 hr</td>
<td>170.9 °</td>
<td>167.9 °</td>
<td>163.4 °</td>
<td></td>
</tr>
<tr>
<td>2 hr</td>
<td>166.1 °</td>
<td>160.3 °</td>
<td>158.2 °</td>
<td></td>
</tr>
<tr>
<td>3 hr</td>
<td>165.8 °</td>
<td>154.6 °</td>
<td>155.4 °</td>
<td></td>
</tr>
</tbody>
</table>
The lotus leaf-inspired superhydrophobic surfaces show promising ice-phobicity but at high humidity conditions, they may fail. Due to their high surface area and increased nucleation site density to condensing droplets, they may induce ice nucleation at an even faster rate than smooth surfaces of the equivalent materials at high humidity conditions [20]. Slippery liquid infused porous surfaces (SLIPS) have attracted great interest as anti-icing coatings. The ‘pitcher plant’ inspired slippery surfaces capable of repelling condensing water droplets have been created by infiltrating a micro/nanoporous substrate with a lubricating liquid to produce a thin, ultra-smooth lubricating layer that repels almost any immiscible materials. Such SLIPS have been fabricated on industrially-relevant metals like aluminium and thus can be used as antifrosting surfaces for aircraft, refrigeration etc. The criteria for designing SLIPS are: 1) the lubricating fluid repellent fluid (e.g. water, oil) have to be immiscible; 2) the chemical affinity between the lubricating fluid and the solid should be higher than that between the repellent fluid and the solid; 3) the solid surface should preferably have roughened nanostructures to provide increased surface area for the adhesion and retention of the infiltrated lubricating fluid [21].

Kim et al. developed aluminium based SLIPS by the electrodeposition of highly textured polypyrrole (PPy) on Al substrates followed by fluorination of the structured coating and infiltration with the lubricant. PPy/Al surfaces having rough and globular morphology were fluorinated with a fluorochlorosilane and infiltrated with a low viscosity perfluorinated lubricating fluid which has freezing point less than $-70\, ^\circ\text{C}$, immiscible with water and strong chemical affinity to the modified solid substrate. The contact angle hysteresis (CAH) which decides the surface retention force was found to be lowest as below $3\, ^\circ\text{C}$ for the SLIPS-Al specimens when compared with the bare Al, hydrophobically modified Al and even with superhydrophobic PPy coated Al (without lubricant). While checking the ice-phobic behavior, it has been observed that SLIPS-Al surface delays frost formation. After 100 min of freezing (at $-2\, ^\circ\text{C}$, 60 % RH), only 20 % surface is covered with ice. After a prolonged exposure to deep freezing, ice accumulates on the surface, however, during the defrost cycle, the large ice patches slide off the surface immediately upon melting at the interface, leaving the surface clean and ready for the next cooling cycle within 1 minute. The average ice adhesion strength on SLIPS/Al has been reported as 15.6 kPa. This low adhesion strength is attributed to the ultrasmooth solid-liquid interface present at the SLIPS surface which has significantly fewer defects/ heterogeneities/pinning points than the solid-solid interface found in conventional superhydrophobic surfaces [22].

Though SLIPS are promising for anti-icing, the most challenging point is their durability. Water tolerance, lubricant retention ability after subsequent icing-deicing cycles are the parameters to be considered while designing a SLIPS. Q Liu et al. developed hierarchically micro structured high temperature vulcanized silicone rubber (HTV) infiltrated with a perfluoropolyether lubricant to form SLIPS. These surfaces showed water contact angle more than $162\, ^\circ\text{C}$ and lubricant contact angle nearly $0\, ^\circ\text{C}$, which suggests that the lubricant can infiltrate completely into the substrate. As the no. of icing/deicing cycles increased the freezing and thawing times accelerate which is related to the lubricant depletion. The lubricant retention rate (LRR) at $-14\, ^\circ\text{C}$, 80 % RH and air at $18\, ^\circ\text{C}$ for the above surface was found to be nearly 37 % after 4 cycles. Also, these samples showed best results for delayed ice formation. Ice adhesion strength was nearly 250 kPa up to 5 cycles and maximum 700 kPa for 20 cycles [23].

Recently, Chanda et al. studied and compared the advantages and disadvantages of superhydrophobic and hydrophilic surfaces with respect to their anti-frosting properties and came to the conclusion that neither purely (super)hydrophobic polymeric surfaces, nor ‘antifreeze’ hydrophilic ones provide an ideal solution for the problem of icing [24].
5. Conclusion

Frost formation and accretion on various infrastructures is a serious issue, as it presents economic as well as safety challenges. Considering the current anti-frosting strategies based on superhydrophobic surfaces, it should be made very clear that superhydrophobicity and ice-phobicity are different phenomena as far as practical applications are concerned. Nanotechnology is the backbone of such coatings which helps in tuning the morphology of the surface by providing the required surface roughness for a coating’s superhydrophobic nature and mechanical strength. The amount of nanofillers to be incorporated or the procedures to be followed while fabricating a nanostructured surface are also important in order to obtain the desired anti-frosting properties.

There is still scope for development of more bio-inspired anti-frosting strategies, such as grafting nanomaterials on smart interface materials, the use of different binder combinations for naofiller, fluorinated system or simplifying the design methods for ‘slippery’ surfaces.

References