Suppressing Ice Nucleation of Supercooled Condensate with Biphilic Topography

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Preventing or minimizing ice formation in supercooled water is of prominent importance in many infrastructures, transportation, and cooling systems. The overall phase change heat transfer on icephobic surfaces, in general, is intentionally sacrificed to suppress the nucleation of water and ice. However, in a condensation frosting process, inhibiting freezing without compromising the water condensation has been an unsolved challenge. Here we show that this conflict between anti-icing and efficient condensation cooling can be resolved by utilizing biphilic topography with patterned high-contrast wettability. By creating a varying interfacial thermal barrier underneath the supercooled condensate, the biphilic structures tune the nucleation rates of water and ice in the sequential condensation-to-freezing process. Our experimental and theoretical investigation of condensate freezing dynamics further unravels the correlation between the onset of droplet freezing and its characteristic radius, offering a new insight for controlling the multiphase transitions among vapor, water, and ice in supercooled conditions.

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Anti-icing technologies have gained widespread attention due to their significance in global energy savings, safety issues for marine applications, aerospace, power transmission, and transportation [1,2]. Current industry strategies for reducing the ice accumulation primarily involve chemical deicing fluids, mechanical removal, and active heating [3,4]. These techniques are normally environmentally unfavorable, expensive, and time consuming. In comparison, the ice-free surfaces offer a safe, economical, and efficient approach to prevent ice formation. The involved icephobicity relies greatly on the nonwetting state of textured surfaces with trapped lubricants or air pockets [5–10] by reducing the contact time of impinging droplets and increasing interfacial thermal resistance to delay liquid freezing. Depending on the environmental conditions, frost forms either directly through ablation [11] or via condensation frosting where vapor first condenses on subcooled solids and subsequently freezes. In practical applications such as heat pumps and refrigerators [12,13], the operating conditions are more conducive to condensation frosting. Therefore, to maintain energy efficacy of these thermal systems, it is vital to suppress ice nucleation without degrading the condensation heat transfer. This necessitates a unique icephobic surface, which is desired to reduce the thermal barrier for efficient condensation, while preventing further heat loss to suppress icing simultaneously.

Despite extensive progress [14–24], how the structural topography mediates condensed droplet icing with continuous latent heat release and dissipation remains inadequately understood. In this work, careful experiments are reported to probe the condensate freezing dynamics on subcooled solids and associated thermal interactions. It is found that the heterogeneous ice nucleation demonstrates a remarkable dependence on the droplet radius, which involves the thermal barrier at the solid-liquid interface. By leveraging wetting contrast and hierarchical micro- or nanostructures [25–29], we showed that a properly patterned biphilic topography strikingly retarded the freezing process while sustaining rapid water nucleation. A unified model that captures the dynamics of condensed droplet growth and freezing was developed to accurately predict the characteristic length scale of droplet icing and to reveal its correlation with surface structures.

Three different surface topographies—flat hydrophobic, nanograss superhydrophobic, and biphilic—were employed in this study due to their distinct wetting features [28–30]. The advancing (receding) contact angles of water droplets on the hydrophobic, superhydrophobic, and biphilic surfaces are 118.6° (88.2°), 167.1° (164.7°), and 162.7° (160.1°), respectively. The biphilic surface consists of micropillar arrays with hydrophilic tops surrounded by superhydrophobic nanograss, shown in Fig. 1(a) inset (diameter and spacing of micropillars are 2 and 8 μm). Figures 1(a) and 1(b) capture the contrasting condensation-freezing phenomena between the biphilic topology and comparative surfaces (i.e., superhydrophobic and hydrophobic surfaces) in an experimental chamber described in
the Supplemental Material [31]. To establish a stable atmosphere, the chamber was filled with pure N₂ gas saturated with vapor at $T_{\text{sat}} = 298.05$ K for eliminating the liquid evaporation [11] and humidity fluctuation. The temperature of the substrate’s rear side was stabilized at $T_{\text{sub}} = 267.75 \pm 0.15$ K to initiate the multiphase transitions from supercooled condensation to droplet freezing.

Figures 1(a) and 1(b) show that, when vapor initially nucleated as supercooled water, the biphilic topography enhanced the droplet density owing to the extremely low water nucleation barrier on the hydrophilic micropillars [37–39]. As the condensed droplets grew, we intriguingly observed an evident retardation of ice nucleation in supercooled condensate on the biphilic structures. Specifically, for droplets of the same radius, the ice nuclei were prone to form on the hydrophobic and superhydrophobic surfaces, rather than the biphilic surface. With the droplet growth and coalescence, the supercooled droplets on the hydrophilic surface tended to spontaneously freeze when their radii approached $\sim 50 \mu$m at substrate temperature $T_{\text{sub}} = 267.75 \pm 0.15$ K. The percolation-induced frost formation is excluded from the experimental statistics because the isolated droplet icing is not driven by frost propagation [40–43]. The characteristic freezing length scale of condensed droplets was 2 orders of magnitude smaller than the typical droplet departing radius ($\sim 1.5$ mm) on the hydrophobic surface, so all the droplets inevitably froze before they could slide by gravity. By contrast, the experimental statistics demonstrated that the droplet freezing radii on the superhydrophobic ($\sim 70 \mu$m) and biphilic ($\sim 100 \mu$m) surfaces were 1.4 and 2 times of that on the hydrophobic surface during the phase transitions (see Video S1 [31]). Distinct from the gravity-driven droplet shedding on flat surface, the nonwettable nanostructures on superhydrophobic and biphilic surfaces ensure the self-propelled condensate jumping [29,44], which dramatically decreases the departing radius. In particular, the heterogeneous wettability on the biphilic surface achieved an even smaller average radius of departed droplets ($\sim 20 \mu$m) as compared to that on the homogeneous superhydrophobic surface ($\sim 40 \mu$m) (see Supplemental Material [31]). For the biphilic surface, as the droplet freezing length scale was at least 3 times larger than the average departing radius, most supercooled droplets can timely depart before they grow to the freezing length scale. Thus, the biphilic surface can maintain the active water nucleation without frost formation. The simultaneous condensation enhancement and ice suppression on the biphilic surface were also manifested by the thermal performance in the multiphase transitions [Fig. 1(c)]. At the initial stage ($t \sim 2$ min), the heat flux on biphilic surface increased by 16.6% and 42.9% over the superhydrophobic and hydrophobic surfaces, respectively, due to more intensive water nucleation on the hydrophilic patterns. As condensed droplets grew, the superhydrophobic surface, as well as the hydrophobic surface, showed obvious heat transfer degradation due to the rapid frost formation ($t \sim 15$ min). In the meanwhile, the biphilic topography achieved more than 5 times larger heat flux than the superhydrophobic surface in the supercooled condensation-to-freezing process, owing to the icing retardation caused by the larger droplet freezing radius.

To better reveal the physics underlying the size-dependent condensate freezing mechanism, we studied the phase transitions via environmental scanning electron microscopy (ESEM). In the ESEM chamber, the vapor pressure was set as $\sim 680$ Pa and the substrate temperature was controlled at 271.75 K to initiate the supercooled condensation. Figures 2(a) and 2(b) capture the distinct wetting dynamics on the superhydrophobic and biphilic
Capillary condensation

Hybrid-wetting droplets

Partial-Wenzel droplets

Interfacial thermal insulance

Droplet base temperature, T (K)

Droplet radius, r (µm)

Interfacial thermal insulance, R (K·m/W)

FIG. 2. (a) ESEM snapshots showing the formation of capillary liquid bridges between the partial-Wenzel droplet base and superhydrophobic nanogras. (b) Snapshots showing the preferential water nucleation atop the hydrophilic micropillars of the biphilic surface. The biphilic topography favors the droplet suspension and self-departure upon coalescence. (c) Schematics of the thermal resistance networks of partial-Wenzel and hybrid-wetting droplets, indicating the resistances of the droplet curvature ($\Psi_r$), liquid-vapor interface ($\Psi_{lv}$), and condensation resistances of droplet ($\Psi_d$), hydrophobic coating ($\Psi_{hc}$), liquid bridges ($\Psi_b$), micropillars ($\Psi_m$), nanopillars ($\Psi_n$), and substrate ($\Psi_{sub}$). The red dashed line represents the liquid-solid phase boundary of the supercooled droplet where the liquid water tends to freeze into ice.

surfaces in the supercooled condition. On the superhydrophobic surface, condensate preferentially nucleated within the gaps of nanostructures in the form of capillary condensation [45,46]. By locally wetting the nanocavities, the condensate formed a partial-Wenzel droplet with several capillary liquid bridges connecting the droplet base and bottom of the nanostructures, shown in Fig. 2(a). As compared to a typical Cassie droplet fully suspended on nanostructures [47,48], the capillary liquid fills the air pockets in nanocavities, therefore dramatically reducing the interfacial thermal barrier underneath the partial-Wenzel droplet [46]. We adopted a quasi-steady thermal circuit model to capture the heat transfer through the vapor, condensate, and surface [49–51], as shown in Fig. 2(c). We calculated the interfacial thermal insulance $R_i = \Psi \cdot \pi r^2 / (T_{i} - T_{sub})$ (calculated of unit area) of a partial-Wenzel droplet ($2.1 \times 10^{-7}$ K m$^2$/W), which is 2 orders of magnitude lower than that of a fully suspended Cassie droplet ($3.6 \times 10^{-5}$ K m$^2$/W). The ESEM images demonstrate that the capillary liquid bridges remained intact whether the droplet was growing or merging, that is, the wetting fraction of capillary liquid under a partial-Wenzel droplet can be theoretically described as invariant when the droplet radius far exceeds the dimension of liquid bridges (~2 µm) [52], leading to a constant $R_i$ [Fig. 3(a)].

Above the monotonic nonwettability, the biphilic topography favored the water nucleation atop the hydrophilic micropillars, which eliminated the capillary condensation and guaranteed the droplet suspension [Fig. 2(b)]. In particular, after coalescence, the droplets residing on the single hydrophilic micropillar transitioned to a hybrid-wetting morphology, where the droplet was supported by the surrounding superhydrophobic nanogras and the hydrophilic micropillars [26,29]. According to the experimental observation, the heat transfer model of a hybrid-wetting droplet was developed as shown in Fig. 2(c). The thermal resistance diagram of a hybrid-wetting droplet indicates the distinct interfacial thermal barrier on the biphilic surface, which is highly related to the wetting area fraction of the hydrophilic pillars. With the increasing radius, the droplet contact line regularly alters from the square to a quasi-circular profile, which dramatically decreases the wetting fraction of the hydrophilic structures beneath the hybrid-wetting droplet. Such hybrid-wetting state not only reduces the droplet adhesion for efficient droplet departure, but also effectively tunes the interfacial thermal barrier to regulate the heat dissipation.

For the biphilic surface tested in experiments, the interfacial thermal insulance of the hybrid-wetting droplet is given by
\[ R_{\text{i}}^{\text{bw}} = [k_{\text{si02}}k_m \varphi_m/(\delta_{\text{si02}}k_m + \delta_m k_{\text{si02}}) + k_{\text{hc}} \varphi_m (1 - \varphi_m)/(\delta_{\text{hc}}k_n + \delta_n k_{\text{hc}})]^{-1}\sin^{-2}\theta. \]

where \( k_m, k_n, k_{\text{si02}}, k_{\text{hc}} \) and \( \delta_m, \delta_n, \delta_{\text{si02}}, \delta_{\text{hc}} \) are the thermal conductivity and thickness associated with the silicon micropillar, nanograde, oxide layer, and hydrophobic coating; \( \varphi_m, \varphi_n \) are the wetting fraction of the hydrophilic structures and nanograde; and \( \theta \) is the apparent droplet contact angle. The progression of the interfacial thermal barrier with the droplet radius is plotted in Fig. 3(a). We showed that \( \varphi_m \) shrank from 1 to 0.064 in a stepwise fashion when the hybrid-wetting droplet grew to 30 \( \mu \)m with contact line distortion, leading \( R_{\text{i}}^{\text{bw}} \) to rise from \( \sim 10^{-8} \) to \( 10^{-6} \, \text{Km}^2/\text{W} \). The ascending \( R_{\text{i}}^{\text{bw}} \) on biphilic surface reduced the heat loss of the large supercooled droplets \((r > 30 \, \mu\text{m})\), and therefore retarded the decrease of liquid temperature \( T_b \) at the droplet wetting base.

The present analysis of the interfacial thermal barrier was utilized to predict the onset of condensed droplet freezing, by combining with the classical ice nucleation theory [18,22,53]. As a nonhomogeneous Poisson process \([54]\), the probability \( P_f(T) \) for initiating the heterogeneous ice nucleation in supercooled water is quantified as

\[ 1 - \exp[-J(T)\Delta T/C(T)\,dT] \]

where the water temperature at the liquid-solid phase boundary \( T = T_f \) is below the melting point of ice \( T_m = 273.15 \, \text{K} \). Here, the interfacial nucleation rate \( J(T) = K(T)A_w \exp[-\Delta G(T)/k_BT], \) \( K \) is a kinetic prefactor representing the attraction of free water molecules to a forming ice nucleus, \( \Delta G(T) \) is the Gibbs free energy barrier for the ice nucleus formation, \( K_b \) is the Boltzmann constant, and \( A_w \) is the contact area of the solid-liquid interface, based on the droplet morphology on the surface topography (see details in the Supplemental Material [31]). \( C(T) = -T \, (T') \) is the liquid cooling rate at the liquid-solid phase boundary. Figure 3(c) plots the correlations between the freezing probability \( P_f \), calculated phase boundary temperature \( T_b \) (at the droplet base), and the associated droplet radius for various surfaces. The freezing probability \( P_f \) of a condensed droplet manifests as a step-like curve that is sensitive to the droplet phase boundary temperature \( T_b \), because the ice nucleation rate \( J(T) \) shows a pseudoeponential increase with the decrease of solid-liquid interface temperature (see Fig. S5 [31]).

During the supercooled droplet condensation, \( T_b \) gradually decreases due to the increasing thermal resistance of a growing droplet and shows different dependencies on the surface topography (see the quasi-steady model for individual droplet condensation in the Supplemental Material [31]). As a result, the onset of supercooled condensate freezing exhibits a strong correlation to the droplet length scale and is considerably influenced by the interfacial thermal barrier on various surfaces. For the condensed droplets of the same radius, the enlarged thermal barrier \( R_{\text{i}}^{\text{bw}} \) on the biphilic surface raises \( T_b \), therefore suppressing the freezing probability compared to the superhydrophobic and hydrophobic surfaces. As indicated in Fig. 3(c), the mean freezing length scales of the supercooled condensate are determined by setting \( P_f = 0.5 \), which shows a good agreement with the experimental measurements (i.e., 55, 70, and 101 \( \mu \)m for the hydrophobic, nanograded, and biphilic surfaces).

This size-dependent droplet freezing mechanism was consistently validated by repeated experiments at various substrate temperatures (see Video S2 and S3 [31]). Figure 4(a) plots the probability density of the droplet freezing radii at the onset of icing, when \( T_{\text{sub}} \) ranges from 269.75 to 265.75 K. We found that all the measurements followed the nonhomogeneous Poisson distribution, where the mean and interval varied for different surface topographies and temperatures. To conveniently forecast the droplet freezing length scale in different supercooled conditions, the ice nucleation rate can be estimated as

\[ J(T) = J(T_0 + \Delta T) = \alpha \exp(-\lambda \Delta T) \]

in a narrow temperature interval \( \Delta T = T - T_0 \) around a reference temperature \( T_0 \), where \( \alpha = J(T_0) \) and \( \lambda = d[\ln J(T)/dT]_{T_0} \) [22,55]. Thus, the probability for supercooled condensate freezing is

\[ P_f(T) = 1 - \exp \left( -\frac{\alpha}{\lambda C(T_0)} \exp(-\lambda\Delta T - 1) \right). \]

Here \( T \) is set equal to the phase boundary temperature of the supercooled droplet \( T_b \), determined by our developed droplet heat transfer model [46,49,56].

\[ T_b = T_{\text{sat}} + (T_{\text{sat}} - T_{\text{sub}}) \frac{R_i + R_{\text{sub}}}{R_d + R_i + R_{\text{sub}}}. \]

where \( T_{\text{sat}} - T_{\text{sub}} \) is the temperature difference between the saturated vapor and substrate, and \( R_d, R_i, \) and \( R_{\text{sub}} \) are the thermal insulances associated with the droplet conduction, interface, and substrate. For a condensed droplet, the conduction insulance \( R_d = \rho \theta/(4k_w \sin \theta) \) depends on the droplet radius \( r \), where \( k_w \) is the thermal conductivity of water. Substituting the expression of \( T_b \) and \( R_d \) into Eq. (2), the characteristic droplet freezing radius \( r_f \), is

\[ r_f = \left( \frac{T_{\text{sat}} - T_{\text{sub}}}{T_0 - T_{\text{sat}} - \frac{1}{\eta}} - 1 \right) \frac{R_i + R_{\text{sub}}}{\theta/(4k_w \sin \theta)}. \]

where \( \eta = \ln\{-\lambda C(T_0)/\alpha \ln[1 - P_f(T)] + e^{(T_{\text{sat}} - T_{\text{sub}})}\}/\lambda \). This scaling model captures the important influence of varying the thermal barrier on the ice nucleation during supercooled condensation. For the microscaled condensed droplets, the thermal insulation caused by interfacial topography is comparable to that of the droplet conduction (Fig. S4 [31]). Thus, for identical supercooled environment \( (T_{\text{sat}} - T_{\text{sub}}) \) and substrate \( (R_{\text{sub}}) \), the characteristic droplet freezing radius \( r_f \) can be apparently enlarged by increasing the interfacial thermal barrier. In Fig. 4(b), the measured
droplet freezing radii are plotted as a function of $T_{sub}$ for different surface topographies, which are in good agreement with the scaling model prediction.

In summary, we report a concurrent enhancement of condensation and anti-icing on a biphilic surface. Such contrasting behaviors in water and ice nucleation result from the varying interfacial thermal barrier with the supercooled droplet growth. The transitioning droplet wetting morphology by biphilic topography not only reduces the thermal resistance beneath small droplets to enhance the overall heat transfer, but also retards the heat dissipation of the few anchored large droplets to delay the ice nucleation. Our dynamic ice nucleation model for supercooled condensate unravels a previously unnoticed correlation between the onset of droplet freezing and its characteristic length scale, which depends largely on the thermal interaction of the condensate and surface topography. Our fundamental understanding and the ability to control the supercooled condensate freezing in humid environments will have profound implications for designing optimal icephobic surfaces in a variety of technological applications.

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