Control of Ice Propagation by Using Polyelectrolyte Multilayer Coatings

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Abstract: Ice propagation is of great importance to the accumulation of ice/frost on solid surfaces. However, no investigation has been reported on the tuning of ice propagation through a simple coating process. Herein, we study the ice propagation behavior on polyelectrolyte multilayer (PEM) surfaces coated with the layer-by-layer (LBL) deposition approach. We discover that ice propagation is strongly dependent on the amount of water in the outermost layer of PEMs, that is, the ice propagation rate increases with the amount of water in the outermost layer. The ice propagation rate can be tuned by up to three orders of magnitude by changing the polyelectrolyte pairs, counterions of the outermost polymer layer, or the salt concentration during the preparation of PEMs. Because the simple, versatile, and inexpensive LBL deposition approach is generally applicable to almost all available surfaces, the PEM coatings can tune ice propagation on a wide range of substrates.

 undesired ice formation on surfaces, such as transportation vehicles, refrigeration systems, and power grids and networks, causes serious property losses.[1] Therefore, there have been continuous efforts to find anti-icing surface materials. Ice formation on surfaces initiates with heterogeneous ice nucleation and followed by ice propagation.[2] In real environments, ice nucleation occurs inevitably due to the surface defect or contamination, therefore ice propagation is critical for the ice/frost accumulation on solid surfaces.[1b,3] It has been reported that delayed ice propagation can be realized if the condensed water droplets at the front of the ice propagation are timely removed.[19] This can be achieved by substantially reducing the adhesion of condensed droplets to solid substrates, so that the self-propelled removal of condensed microdroplets can be achieved by the surface energy released during droplet coalescence.[4] It is also possible to control ice propagation by varying the heat transfer efficiency of the substrates.[4c,5] Poulikakos and co-workers found that surfaces that have better thermal conductivity are more effective in minimizing ice propagation.[5] However, for practical applications, it is often required to tune ice propagation without changing or destroying existing surfaces; therefore, it is desirable to introduce adaptive coatings on different surfaces based on simple and effective techniques.

Recently, we investigated the ice propagation behavior on the surface of polyelectrolyte brushes and found that ice propagation can be tuned by changing counterions of the polyelectrolyte brush.[6] However, the exact mechanism for the control of ice propagation remains elusive. Herein, we investigate the ice propagation behavior on PEM coatings (see in Figure 1a), which can be easily prepared by the LBL deposition process. The uniqueness of the PEMs is that water concentrates in the outermost layer, therefore the properties of PEMs are determined by the outermost layer, for example, the swelling behavior, surface wettability, and interfacial water mobility of the PEMs.[7]

To demonstrate the ability of PEM coatings to control ice propagation, we employed poly(sodium 4-styrenesulfonate)/poly (allylamine hydrochloride) (PSS/PAH) and PSS/poly(diallyldimethylammonium chloride) (PDAD), and their structures are shown in Figure 1b. Note that PDAD is a strong polyelectrolyte with quaternary amines, while PAH

Figure 1. a) Illustration of ice propagation on PEM surfaces. b) Structures of the polyelectrolytes used in this study. c) Optical images of various water macroscopic droplets (0.1 μL) frozen at −18.0°C on PSS/PAH and PSS/PDAD (n = 9) surfaces for different times. The unfrozen droplets and frozen droplets were marked by green and white circles, respectively. d) The fraction of frozen water droplets on PSS/PAH and PSS/PDAD (n = 9) surfaces as a function of freezing time. Time zero was defined as 0.1 s before the onset time of freezing.

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is a weak polyelectrolyte with primary amines. One can vary the amount of water in the outermost layer of PEMs by changing the composition of the polyelectrolyte pairs during the process of the LBL deposition, for example, the strong–strong pair or strong–weak pair of PEMs. As shown in Figure 1c, we studied the ice propagation behaviors between water macrodroplets on PSS/PAH and PSS/PDAD (n = 9) surfaces, and n is the number of layers of PEMs. Before the ice propagation tests, some macroscopic water droplets (0.1 µL) were placed atop the PEM surfaces. The as-prepared samples were cooled down to −18.0°C at a rate of 1.0°C min⁻¹ to make sure the water vapor reach equilibrium in a closed cell. On the PSS/PDAD (n = 9) surface, all water droplets froze within 0.1 s (see Figure 1c,d). In strong contrast, ice propagation on the PSS/PAH (n = 9) surface was triggered slowly by the dendrimer-like frozen droplets, one after another, through the ice bridges. The ice crystals grew at the expense of condensed water droplets via the mechanism of Wegener–Bergeron–Findeisen, that is, ice propagates through the vapor deposition with the evaporation of liquid water nearby. As a result, it took over 1600 s for all the macrodroplets to be frozen.

The profound effect of the PEM coatings on the control of ice propagation was further consolidated by the propagation of frozen condensed water. The microdroplets of water formed atop the PSS/PAH and PSS/PDAD (n = 9) surfaces through an evaporation and condensation process (as shown in the Supporting Information, Figure S1). The subsequent ice propagation was studied at −20.0°C by an optical microscope coupled with a high speed camera. Time zero was defined as the acquisition time of the frame right before the freezing (the time resolution was 1 ms). As shown in Figure 2a, the whole ice propagation process finished in 2730 ms on the PSS/PAH (n = 9) surface. In strong contrast, ice propagated spontaneously right after the freezing of any condensed droplet, and all condensed droplets froze within 5 ms on the PSS/PDAD (n = 9) surface as shown in Figure 2b. The time evolution of the fraction of frozen droplets on PSS/PAH (n = 9–12) and PSS/PDAD (n = 9–12) surfaces were obtained statistically among all of condensed microdroplets as shown in Figure 2c and the Supporting Information, Figure S2. The ice propagation times per unit area on PEMs of a variety of deposited layers are shown in Figure 2d. It can be seen that the ice propagation times on the PSS/PDAD surfaces of different deposited layers are all less than 2 s cm⁻². In comparison, all the ice propagation times on the PSS/PAH surfaces are two orders of magnitude longer. With the number of deposited layer increased from 3 to 21, the film thickness increases from approximately 4 nm to 137 (PSS/PDAD) and 37 (PSS/PAH) nm (see in Figure S3). The variation trends of ice propagation times on both PSS/PAH and PSS/PDAD surfaces show no dependence on the number of deposited layers, suggesting that the ice propagation on PEMs is not determined by the heat transfer efficiency. Interestingly, the ice propagation time on the PSS/PAH surfaces with PAH as the outermost layer (even) is longer than that on the surfaces with PSS as the outermost layer (odd), exhibiting a pronounced odd–even effect. Namely, the odd–even effect means an alternating change of surface properties depending on the outermost layer of PEMs. Similar to previous reports, we observe that both the water content and the wettability exhibit typical odd–even behavior as shown in the Supporting Information, Figures S4 and S5. As shown in the Supporting Information, Figures S6 and S7, we also studied the ice propagation behaviors on the PSS/PAH and PSS/PDAD surfaces with different outermost layers. It is found that the ice propagation times can also be tuned by up to three orders of magnitude just by changing the different outermost layer. All the results imply that the outermost layer of PEM plays an important role in the ice propagation.

Ice propagation can also be tuned by changing the salt concentration in preparing PEMs or the type of counterions in the outermost layer as shown Figure 3. Figure 3a shows the ice propagation behaviors on different PSS/PAH and PSS/PDAD surfaces prepared with NaCl concentrations of 0.1, 0.5, and 1.0 M. On PSS/PAH surfaces, the ice propagation times remain within the same order of magnitude as the salt concentration varies. In strong contrast, the ice propagation time on PSS/PDAD surfaces decreases by two orders of magnitude when the salt concentration increases from 0.1 to 1.0 M. Figure 3b exhibits the effect of the type of counterions on the ice propagation behavior on PSS/PAH and PSS/PDAD surfaces. When the Cl⁻ (well hydrated) in the outermost layer is replaced by poorly hydrated ion such as PF₆⁻, TFSI⁻, or PO₄³⁻, the ice propagation time increases significantly. For both PSS/PAH and PSS/PDAD, the ice propagation time increases in the sequence Cl⁻ < Br⁻ < NO₃⁻ < ClO₄⁻ < PF₆⁻ < TFSI⁻ < PO₄³⁻, suggesting that the ice propagation is facilitated by the increase of ion hydration ability.

The above experimental results show that the outermost polyelectrolyte layer, counterions, and the concentration of
It is known that as a water droplet freezes on the PEM surface, the time propagation of the ice front is dependent on the concentration of counterions, the hydration ability of counterions, and the mobility of polyelectrolyte chains. This in turn results in the deposition of the outermost layer of the PEM, which is critical for tuning ice propagation.

Figure 3. a) The ice propagation time per unit area on the PSS/PAH and PSS/PDAD (n = 9–12) surfaces when C_{NaCl} is 0.1 M, 0.5 M and 1.0 M. b) The ice propagation time per unit area on the PSS/PAH and PSS/PDAD (n = 10) surfaces with different counterners. c) The illustration of ice propagation on the PEM surface and the correlation between ice propagation time and water amounts in the outermost layer.

Figure 4. Ice propagation on a) PSS/PAH and b) PSS/PDAD (n = 9) surfaces triggered by a frozen AgI droplet for different times at ice supersaturation of 133%. The figures are an enlarged view of microdroplets surrounding the AgI particle in insets, and the insets show the status of the frozen AgI particle. The scale bars in figures and insets are 50 μm and 2 mm, respectively. c) The ice propagation times on the PSS/PAH and PSS/PDAD (n = 9) surfaces at different ice supersaturation from 121 % to 149 %. d) The ice propagation times on the PSS/PAH and PSS/PDAD (n = 9) surfaces on different substrates at ice supersaturation of 133 %.

Figure 5. Propagation time vs. ice supersaturation (%). The scale bars in figures and insets are 50 μm and 2 mm, respectively. a) The ice propagation times on the PSS/PAH and PSS/PDAD (n = 9) surfaces at different ice supersaturation from 121 % to 149 %. b) The ice propagation times on the PSS/PAH and PSS/PDAD (n = 9) surfaces on different substrates at ice supersaturation of 133 %.

In summary, we reported PEM coatings for the tuning of ice propagation, which can be prepared by the simple LBL deposition approach and applicable to almost all types of substrates. We found that the amount of water in the outermost layer of the PEM is critical for tuning ice propagation and can be changed by polyelectrolyte pairs, counterners in the outermost layer, or the salt concentration during the preparation of PEMs. Moreover, the investigation of ice propagation under different ice supersaturation conditions.
ditions and on different substrates showed the robustness of PEMs in controlling ice propagation. This type of coating will inspire a new strategy for the design of anti-icing materials.

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Conflict of interest
The authors declare no conflict of interest.

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