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.[4,5] 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.[4,6] 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 with better thermal conductivity are more effective in minimizing ice propagation.[5a] 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...
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 PFO⁻, 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⁻ < PFO⁻, 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, ice propagation on a) PSS/PAH and b) PSS/PDAD (with a salt concentration of 1.0 M). The ice propagation time per unit area on the PSS/PAH and PSS/PDAD (n = 10) surfaces with different counterions. c) The illustration of ice propagation on the PEM surface and the correlation between ice propagation time and water amounts in the outermost layer.

Salts during the preparation of PEMs can be employed to tune ice propagation. The deposition of the outermost layer is driven by the increase of the entropy when the complexes between oppositely charged polyelectrolytes form accompanied by the release of small counterions. It is known that increasing the salt concentration and strengthening the hydration ability of counterions lead to a low density of complexation sites between polyelectrolytes and a high mobility of polyelectrolyte chains. This in turn results in a thick outermost layer entrapped with more free water molecules. As a water droplet freezes on the PEM surface, water molecules nearby tend to move towards the ice-growth front as the solid state of water is thermodynamic more stable (see in Figure 3c). If there is an adequate amount of free water in the PEM, ice propagation is facilitated as the ice growth front can be continuously supplied with liquid water from the PEM. On the other hand, if the PEM is devoid of free water, ice growth can only be promoted by the evaporation of water droplets nearby and thus ice propagation is slower. Therefore, we can tune the ice propagation rate by changing the amount of water in the outermost layer. For the PEMs prepared with different salt concentrations, for example, the difference in ice propagation time can be tuned up to three orders of magnitude by changing the amount of water in the outermost layer, as shown in Figures S8 and S9. Ice propagates more quickly when there are more water molecules trapped in the outermost layer.

To reveal the validity of PEM coatings in tuning ice propagation in real environments, we artificially introduced an ice nucleating agent on different PEM surface and investigated the ice propagation behavior at various ice supersaturation (see in Figure S10). A droplet of silver iodide aqueous dispersion (AgI, particle, 0.1 μL) was placed atop the PEMs (in a field of view of 10 mm × 8 mm) as the artificial ice nuclei at −6.0°C (see the Supporting Information, Figure S11). The freezing of AgI, like the fall of first domino tile, triggered the ice propagation, and time zero was defined as the onset time of the freezing of the AgI droplet (see Figure 4a,b and insets). As shown in Figure 4a, the ice propagated for 2700 s on the PSS/PAH surface after the freezing of the AgI droplet. In strong contrast, all the condensed water droplets froze in a short period (within 5 s) on the PSS/PDAD surface as the AgI droplet froze as shown in Figure 4b. We further measured the ice propagation time as the function of ice supersaturation as shown in Figure 4c. It is obvious that the PSS/PAH surface always displays a longer time than that of the PSS/PDAD surfaces when the ice supersaturation varied from 121 % to 149 %. The ice propagation behavior on different PSS/PAH- and PSS/ PDAD-coated substrates were also investigated as shown in Figure 4d. All the values of the ice propagation time on the PSS/PDAD-coated surfaces are higher than 3700 s, whereas all the ice propagation times decrease substantially (less than 5 s) on PSS/PDAD-coated surfaces. Therefore, tuning ice propagation with PEM coatings is robust.

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, counterions in the outermost layer, or the salt concentration during the preparation of PEMs. Moreover, the investigation of ice propagation under different ice supersaturation con-
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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