

Preview

Bio-inspired Hydrogels as Multi-task Anti-icing Hydrogel Coatings

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In a recent report in *Matter*, Zhu, Wang, He and co-workers report a straightforward and effective strategy for the design of icephobic hydrogel coatings on the basis of polydimethylsiloxane (PDMS)-grafted polyelectrolyte hydrogels. These passive anti-icing and de-icing coatings were demonstrated to synergistically suppress ice nucleation, ice propagation, and ice adhesion.

Water is essential to life on Earth and it also plays a diverse and structural role in cell biology.¹ Water can exist as solid, liquid, and gas within the range of temperatures found on Earth, has a unique structure and mediates all life's chemical reactions. Although water is central to our lives and survival, covering more than 70% of the Earth's surface, it can also have undesirable effects on the society because of ice formation. Icing is a phenomenon causing numerous and significant problems in many areas such as buildings and power supplies, transportation, and telecommunication. Besides the aspects concerning human safety, icing is also causing high economic losses due to energy waste and reduced operating efficiency.² Ice formation generally occurs through a nucleation and crystal growth mechanism.³ The nucleation process is complicated because it can take place in bulk water or at interfaces, and it is highly influenced by the temperature and other environmental conditions. Consequently, ice formation processes can widely vary, and the different ice-formation mechanisms have to be taken into account in order to design efficient anti-icing materials that can successfully be used in real-life applications.

Two different approaches have been developed to reduce ice formation, namely *anti-icing* that aims to prevent

ice growth from a surface and *de-icing* that focuses on the removal of the ice after it grows on a surface. Both approaches can be active when an input of energy is used (electrical or human power) or passive when no input of energy is required from the user. Various active strategies have been employed to inhibit ice accretion and remove ice, including vapor heating, mechanical means, and the use of ice-melting agents.⁴ However, active methods are generally costly, inefficient, design-complicated, and environmentally harmful. Therefore, passive anti-icing materials, i.e., icephobic materials, that have the capability to prevent accumulation of ice with "zero-energy" consumption have attracted intensive interests in the last decade.⁵ Successful strategies used for passive anti-icing are (1) timely removal of water droplets and (2) control of the ice formation, whereas passive de-icing aims to reduce ice adhesion. Best anti-icing behavior is commonly achieved using either microscopically rough superhydrophobic surfaces (SHSs) or slippery liquid-infused porous surfaces (SLIPs).^{6,7} It has been reported that SHSs can effectively prevent ice accretion through sliding or bunching off water droplets before they can freeze.⁶ The construction of rough surfaces via the creation of micro- or nanostructures on hydrophobic substrates is of vital importance for the preparation

of artificial anti-icing SHSs.⁸ However, the ice adhesion strength values of such rough SHSs are several times higher than that of the corresponding smooth SHSs because of interlocking between the ice crystals and the micropatterned SHS. In contrast, the SLIPs exhibit low adhesion strength, superior anti-icing and frost-resisting characteristics.⁷ However, the costly infused lubricant and weak resistance to mechanical abrasion still limit their practical applications.

Natural anti-freeze proteins (AFPs) can control ice formation by selectively binding to ice crystal surfaces. Wang et al. have examined both depression and promotion effects of AFPs on ice nucleation by selectively linking the ice-binding face (IBF) and non-ice-binding face (NIBF) of the AFPs to solid substrates.⁹ The ice nucleation was found to be inhibited by the NIBF because of the lack of hydrophobic or hydrophilic patterns as well as the presence of charged groups, whereas the IBF facilitated the ice nucleation. The synergy between hydrogen bonding and hydrophobic interactions was found to be responsible for the regulation of interfacial water and the outstanding anti-icing properties of the NIBF. This exciting discovery was developed toward NIBF coatings, which could prevent ice formation down to temperatures of -28°C . It is, however, still a great challenge to design more robust and economically viable synthetic materials that can function in a similar way by simultaneously suppressing ice nucleation, ice propagation, and adhesion.

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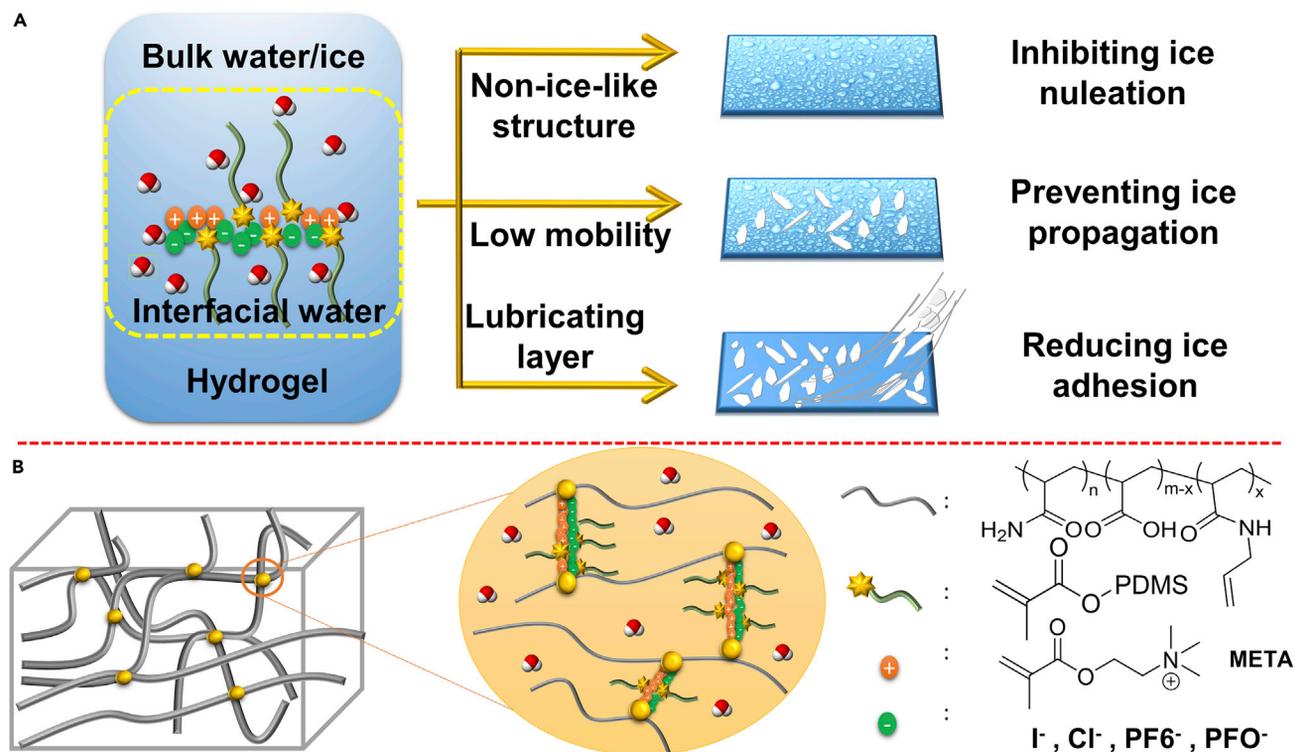


Figure 1. Design of Icephobic Hydrogels Inspired by Natural Anti-freeze Proteins

(A and B) Shown in (A), polyelectrolyte hydrogel coating functions that suppress all ice formation mechanisms; in (B) are the chemical structure of the hydrogel and precursors that were investigated by He and coworkers. Adapted and reprinted from He et al.¹⁰ with permission from Elsevier.

Recently, Zhu, Wang, He and coworkers addressed this challenge by developing synthetic AFP-inspired anti-icing materials that synergistically target all ice formation processes, unlike previous reports that commonly only focused on a single process (Figure 1).¹⁰ They designed a synthetic hydrogel platform with unprecedented water structuring ability to obtain icephobic hydrogel coatings with superior anti-icing properties. More specifically, the hydrogel design combines hydrophilic acrylamide (AAM) units as well as negatively charged acrylic acid (AAC) and positively charged [2-(methacryloyloxy)ethyl]trimethylammonium (META) units with hydrophobic polydimethylsiloxane (PDMS) grafts. The hydrophilic and charged groups are hypothesized to suppress ice nucleation and ice propagation, whereas the hydrophobic grafts should reduce ice adhesion strength.

To validate this hypothesis, a hydrogel platform was developed that allows accurate tuning of the hydrophilic-hydrophobic balance, which is required to suppress the different aspects of ice formation. Therefore, a poly(acrylamide-co-acrylic acid-co-*N*-allylacrylamide)-(poly(AAm-co-AAc-co-AAene))-based hydrogel carrying multiple hydrophobic and charged functional groups was prepared by *in situ* photocrosslinking with cationic PMETA and monomethacrylate-functionalized PDMS monomers having different PDMS chain length. The hydrophobicity of this PDMS containing polyelectrolyte hydrogel coating could be easily tuned by incorporation of PDMS macromonomers with different PDMS chain length, whereas potential ion-specific effects could be regulated by ion exchange reactions.

To evaluate the anti-icing performance of these hydrogels, the authors investi-

gated the heterogeneous ice nucleation (HIN) temperature (T_H), which is the temperature at which ice nucleation is observed. The presence of ions in the hydrogels that induced a more ice-like water structure show a higher T_H (e.g., -17.7°C for iodine), whereas ions that promote a liquid-like water structure induced a lower T_H (e.g., -29.9°C for perfluorooctanoate). This latter hydrogel surface even remained unfrozen up to 4,800 s at -28°C , demonstrating its high ice nucleation inhibition performance. Increasing the thickness of the hydrogels in the range from 50 nm to 1,000 nm raised the T_H significantly, regardless of the nature of the counterion, indicating that thinner coatings are more efficient for suppressing ice nucleation. Furthermore, the incorporation of longer PDMS macromonomers overruled the ion-specificity leading to a T_H of around -24°C , independent of the counter anions.

Even if a hydrogel coating fully suppresses ice nucleation, ice-crystals can be induced by contaminants, e.g., dust or defects. Therefore, it is also important to prevent propagation of formed ice crystals for efficient anti-icing performance. The effect of the anti-icing hydrogel composition on the ice propagation rate was investigated in the highlighted study by monitoring the area that is covered by ice in time, revealing that it also depends on ion-specific and hydrophobic interactions. Similar to the ice nucleation, the propagation rate decreased when the counterions were changed from iodine to perfluorooctanoate as the water in the hydrogel has a more liquid-like structure with perfluorooctanoate counter anions. Furthermore, the incorporation of longer PDMS chains decreased the ice propagation time because water can no longer penetrate in the hydrogel obstructing the ion-specific interactions that suppress ice nucleation and propagation. In general, it could be concluded that the hydrophobicity and ion specificity of the hydrogel act in a synergistic manner leading to the effective control of ice nucleation and ice propagation.

If both the suppression of ice nucleation and suppression of ice propagation are ineffective, anti-icing can only be achieved by de-icing, that is removal of the formed ice crystals. Therefore, the authors also studied the de-icing properties of the PDMS containing polyelectrolyte hydrogels by determining the ice adhesion strength. The ice adhesion strength of the hydrogels was found to be reduced by more than one order of magnitude upon incorporation of the PDMS chains that enable the retention of a viscous lubricating liquid-like water layer at the hydrogel-ice interface, whereas the different counterions had no significant effect on the ice adhesion strength.

The PDMS containing polyelectrolyte hydrogel with short PDMS grafts of ~ 900 g/mol and perfluorooctanoate counterions was found to be the most efficient anti-icing hydrogel coating, which was shown to maintain low ice adhesion values after 50 icing/de-icing cycles. Furthermore, the authors demonstrated that the coating could be applied to a wide range of substrates (metal, ceramic, glass, and polymer) after oxygen plasma activation followed by surface functionalization with dopamine methacrylamide. A real-life test of the coating at -25°C revealed that ice nucleation could be suppressed for 1,900 s, whereas full coverage of the surface with ice took around 4,000 s. Nonetheless, the authors claim that due to the low ice adhesion strength, the ice layer could be removed by a mild wind breeze of 2 m/s.

Altogether, the highlighted study offers valuable insights into the mechanism as well as applications of hydrogels in anti-icing, especially the importance of counterions for the polyelectrolytes to control water structuring as well as the hydrophilic-hydrophobic balance. Nonetheless, the mechanical strength and robustness of the reported hydrogels are still limited as the authors reported that the surface of the hydrogels showed cracks after mechanical abrasion tests. The authors propose that this limitation could potentially be overcome by making use of dual crosslinked hydrogels, double network hydrogels, or composite hydrogels. It is anticipated that the versatility and functionality of the reported strategy to synergistically suppress ice formation, ice propagation, and ice adhesion opens up a new era for the development of anti-icing materials. As such, it might open up real-life applications for icing prevention, and it will inspire new directions for the development of next-generation anti-icing materials.

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