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A novel anti-icing superhydrophobic hybrid material synthesized by Surface Initiated AGET ATPR can prevent ice formation thoroughly.
A Novel Superhydrophobic Hybrid Nanocomposite Material Prepared by Surface-Initiated AGET ATRP and its Anti-icing Property

Xiaoli Zhan,* Yingdi Yan,* Qinghua Zhang* and Fengqiu Chen*

Ice aggregation is a global challenge, especially for cold regions. In this article, a novel anti-icing hybrid material synthesized by grafting fluorinated polymer chains to silica nanoparticles via surface-initiated activators generated by electron transfer atom transfer radical polymerization (SI-AGET ATRP) was proposed. It showed such properties as controllable molecular design, wonderful thermal stability and high superhydrophobicity. Most importantly, it exhibited excellent anti-icing property among coatings with different wettability varied from hydrophilic to superhydrophobic. Its large static water contact angle (WCA, 170.3°) and small contact angle hysteresis (CAH, <3°) can promote the removal of droplets efficiently. A new characterization method was put up to test the crystallization point of water, DSC, and its results demonstrated that the point can be depressed to a large extent (6.82°C). The low temperature WCA showed that it can postpone the freezing time from 196s to 10054s which indicates the surface can prevent ice formation thoroughly especially with the help of outside forces. The mechanisms were discussed based on physic-chemical property, heterogeneous nucleation theory and heat transfer theory. According to the present study, it is reasonable to predict that the organic-inorganic hybrid superhydrophobic coating will be prospective anti-icing candidate for various materials such as wind turbine blades, power lines and aircrafts.

Introduction

As we all know, ice adhesion and accumulation can lead to major inconvenience to individual daily life, such as traffic interruption, communicating destruction, loss of power and the damage of equipment relative to aviation, telecommunication, electricity and transportation.  

In fact, it can also lead to major economic loss to countries. The snowstorms of southern China have caused huge economic losses up to several billions dollars during the Spring Festival of 2008. Thus, the research on anti-icing coatings is of great significance for the whole world. Nowadays, based on preventing ice formation and reducing ice adhesion strength, anti-icing coating and icephobic coating were brought up. However, the anti-icing coating is better compared with the icephobic one for the latter one consumes energy more or less.

Preventing ice formation means retarding freezing time and reducing freezing temperature so that condensed water can roll off the substrates via outside power before it freezes, such as gravity, wind power and centrifugal forces. The classification of anti-icing coating can be described as hydrophilic, hydrophobic, and superhydrophobic. Spraying such chemicals as propylene glycol and ethylene glycol once used to delay crystallization because they can lower the freezing point of water. However, due to their hydrophilicity, the adhesion strength between water and substrate is large and it hinders the removal of condensed water. Then, hydrophobic coatings with low surface energy aroused interests because the large contact angle makes the rolling process easier. This kind of coatings mainly consists of fluorinated polymers [3, 4], organosilicone[5], fluoroalkylsilane[6, 7] and fatty acid[8]. Though it has the anti-icing effect, it is not ideal. In 1997, Barthlott et al. [9] revealed the famous lotus effect and then superhydrophobic materials began to be used as anti-icing coating and exhibited excellent performance thanks to their low surface energy and enhanced surface morphology. Up to now, it is still the research focus.[10-14]

Methods to create superhydrophobic surface are mainly attributed to two categories. One is mixing nanoparticles with low surface energy polymer physically [15]. However, for this kind of coating, it has been proved that after several ice/de-ice circles, the particle would shed off the surface [16, 17] because of the volume expansion during the process of icing or mechanical destruction during the process of de-icing, then the superhydrophobicity was weakened. The other one is fabricated by chemical modification with low surface energy materials on textured surface [18-20]. To obtain surface with hierarchical roughness, pretreatment of substrates is necessary, such as chemical etching [21, 22], crystal growth [23, 24] and lithographic method [25, 26]. So, this method requires multi-steps and is not suitable to large area application. [27, 28] Taking these shortcomings into consideration, a coating which is
suitable for large area application and with excellent durability was synthesized by initiating polymerization from the surfaces of silica nanoparticles. Since the fluorinated polymer chains were grafted to particles, the covalent bond between surface and the polymer was strong enough to prevent separation. And the abrasive resistance was improved largely. Furthermore, the coating was very rigid. Though water expand while freezing, it is likely that the pressure created by trapped air lead to crack initiation and propagation as well as ice-bonding [20].

Besides, this kind of organic-inorganic hybrid material has other fascinating properties which cannot be obtained just by mixing inorganic nanoparticles with polymers. These composite materials conceive advantages of organic polymers and inorganic material. Organic parts provide controlled molecular structure and weight and good processability, while the inorganic parts offer high modulus, wonderful thermal and mechanical stability. Due to these remarkable physicochemical properties, organic-inorganic hybrid materials are applied in diverse fields such as nanomaterial, optoelectronic devices, catalysts, biology and so on [30-32]. However, their application in anti-icing field has few reports to the best of our knowledge.

It is widely known that grafting well-defined polymers on particles needs two steps. Firstly, introduce one or two initiators to the surface of particles and then grow polymer chains away from the interface gradually. This grafting-from approach can be carried out by living/controlled polymerizations [33-36], among which atom transfer radical polymerization (ATRP) is especially attractive for its tolerance of impurities, mild polymerization conditions and compatibility with a wide range of monomers. To overcome the drawbacks of normal ATRP such as challenging inert atmosphere, ATRP using activators generated by electron transfer (AGET) was developed [37, 38].

In this work, we synthesized a kind of organic-inorganic hybrid material by grafting poly (butylacrylate-co-2-N-Ethylperfluorooctanesulphamido) acrylate) to silica nanoparticles via SI-AGET ATRP. By spin-coating the solution of this material, superhydrophobic surfaces were obtained. Its controllable polymerization, chemical composition and surface morphology were characterized by corresponding analysis methods. The anti-icing property was tested by, besides traditional contact angle hysteresis and water contact angle, differential scanning calorimetry (DSC) comparing with hydrophilic, hydrophobic and uncoated surfaces. Furthermore, the mechanisms were explored on the bases of physic-chemical property, heterogeneous nucleation theory and heat transfer theory.

Experimental

Materials

Fumed silica (SiO$_2$, >99.8%, 14nm) was purchased from Ximeng Chemical Co. 2-bromoisobutyryl bromide (BiBB, 98%), N,N,N’,N”-pentamethyldiethylenetriamine (PMDETA, 99%), and γ-aminopropyltriethoxysilane (APTES, >98%) were purchased from Aldrich Chemical Co. and as received. Toluene was purchased from Sinopharm Chemical Reagent Co. and was purified in acetone. Butyl methacrylate was purchased from Aldrich Chemical Co. and removed polymerization inhibitor by chromatography, then was stored in refrigerator under -4°C. Other reagents and organic solvents, unless specific illumination, were purchased from Sinopharm Chemical Regent Co. and used without any further purification.

Sample preparation

The approaches to prepare amino-functionalized, 2-bromoisobutyrate-functionalized and poly (BA-co-EFOA) grafted silica particles are shown in figure 1.

![Figure 1: General approaches to prepare the amino-functionalized, 2-bromoisobutyrate-functionalized and poly (BA-co-EFOA) grafted silica particles](image)

**Synthesis of amino-functionalized silica nanoparticles SiO$_2$-NH$_2$**

Typically, 15g of silica nanoparticles, 300 mL of anhydrous toluene and 21 mL of APTES were placed in a 500 mL round bottom flask equipped with a graham condenser. The reaction mixture was stirred by PTFE magnetic stir bar at 110°C under nitrogen atmosphere overnight and then cooled to ambient temperature. The nanoparticles were isolated by high-speed centrifugation and vacuum filtration. Then the sediments were redispersed in acetone and centrifuged again. The purification cycle mentioned above was repeated for several times to remove excess reagents. The product, named as SiO$_2$-NH$_2$, was dried in vacuum oven at 50°C for 6h.

**Synthesis of amino-functionalized silica nanoparticles SiO$_2$-NH-Br**

1.5g of SiO$_2$-NH$_2$ nanoparticles, 50 mL of dichloromethane and 0.5 mL of triethylamine were mixed in a round bottom flask immersed in an ice–water bath. After cooling to 0°C, the mixture of 2 mL of BiBB and 20 mL of dichloromethane were added dropwise. The solution was stirred at 0°C for 0.5 h and then air at room temperature for 24 h. The method of isolation and purification of the product was similar to procedures described for SiO$_2$-NH$_2$. The final product, named as SiO$_2$-NH-Br was also dried under vacuum oven at 50°C for 6h.

**Synthesis of SiO$_2$-P(BA-co-EFOA) nano-composites via SI-AGET ATRP**

In this step, SiO$_2$-NH-Br (0.5g, 0.25mmol of initiating sites), BA (3.2g, 25mmol), EFOA (1.1g, 2.5mmol), PMDETA (0.05 mL, 0.25mmol), DMF solution of CuBr$_2$ (5%wt) (EFOA, >95%) was synthesized according to the literature [39] and purified in acetonitrile. Butyl methacrylate was purchased from Aldrich Chemical Co. and removed polymerization inhibitor by chromatography, then was stored in refrigerator under -4°C. Other reagents and organic solvents, unless specific illumination, were purchased from Sinopharm Chemical Regent Co. and used without any further purification.
and anhydrous toluene (10mL) were added in a round bottom flask equipped with a magnetic stir bar. In order to make the SiO$_2$-NH$_3$Br nanoparticles dispersed homogeneously, the mixture was treated by ultrasonication and then immersed in an ice-water bath. After purging the system with nitrogen for 20min, the toluene solution of SiO$_2$(EH)$_2$ (5%wt) (0.061g, 0.15mmol) was added through injection syringe. The flask was then transferred to an oil bath at 80°C. The ratio of BA : EFOA : CuBr : PMDETA : SiO$_2$-NH$_3$Br was 100:10:1:1:1 in this study. After polymerization, the resulting solution was opened to air to terminate the polymerization, and then added into methanol and the nanoparticles were isolated via high-speed centrifugation. Redispersed in THF, the precipitation was isolated via centrifugation again. This purification cycle was repeated for three times. The final nanoparticles were dried at room temperature under vacuum overnight.

**Spin Coating of SiO$_2$-P(BA-co-EFOA) nano-composites** SiO$_2$-P(BA-co-EFOA) was dissolved in tetrahydrofuran (concentration 5wt%) and sonicated for 1 h prior use. The solution was spin-coated onto clean glass slides at room temperature using a chemical technology KW-4A spinning coater. A rotational speed of 1200rpm and a holding time of 30s were chosen. After that the sample was allowed to evaporate slowly for a day. Then it was dried for 12h in a vacuum oven at 80°C and annealed at 130°C for 30 min.

**Characterization of controlled polymerization** TGA was carried out on a TGA2050-TA Instrument (USA). The samples were analyzed under the nitrogen atmosphere with heating rate of 10°C/min from room temperature to 800°C. Molecular mass (Mn) and Molecular distributions (Mw/Mn) of the polymer were determined with GPC equipped with a Waters 1525 two-component high performance liquid chromatography pump, a Waters 717 automatic sampler, three Styragel HT columns and a Waters 2414 refractive index detector. A series of low-polydispersity polystyrene standards were employed for the GPC calibration. The eluent was tetrahydrofuran (THF) at 35°C with a flow rate of 1.0 mL/min. The polymer was cleaved from particles by hydrofluoric acid.

**Characterization of superhydrophobic surfaces** FTIR spectra were measured on Nicolet 5700 FT-IR spectrometer in the range of 4,000– 600cm⁻¹. The samples were dissolved in THF and cast onto KBr disks to be analyzed. $^1$H-NMR analysis was conducted with a Bruker 500 MHz nuclear magnetic resonance spectrometer (Advance DMX500) and was carried out with a 5wt% solution in CDCl$_3$ at room temperature, using tetramethysilane (TMS) as internal reference. The chemical composition was analyzed by XPS (Thermo Scientific, USA) with an Al Kα X-ray source. The X-ray gun was operated at 14 kV and 350mW, and the analyzer chamber pressure was 10-9-10-10 Pa. The morphologies of the final particles were examined by TEM with a JEOL JEM-2010 transmission electron microscope (Tokyo, Japan). The solution was dipped onto carbon-coated copper grids and dried at room temperature. TEM was done at 80 kV. SEM analysis was performed using a JEOL SM 840 scanning electron microscope at an accelerating voltage of 20 kV. AFM was operated by Multi Mode (Veeco, USA) in tapping mode. The scanning range was 5µm × 5µm and the root-mean-square (RMS) roughness value was calculated from the obtained image. TGA has been proved to give good quantitative results relative to the Br content of the.
samples in previous publications on similar systems because specific organic molecules pyrolyze at a specific temperature \cite{41}. Using the assumption that under 200°C the weight loss was caused by the removal of water absorbed physically, the additional weight losses from SiO$_2$ and SiO$_2$-NH-Br were attributed to pyrolysis of hydroxyl and the introduced APTES respectively. On the basis of the data, it is feasible to quantify the yields of the synthesis using TGA. In order to circumvent any possible influence of physically absorbed water, the results were calculated by subtracting the weight loss under 200°C, 98.26% and 97.70% for SiO$_2$ and SiO$_2$-NH-Br respectively. With this method, the hydroxyl content of the SiO$_2$ is found to be 3.34mmol/g. From the TGA curve of SiO$_2$-NH-Br, the Br content of the SiO$_2$-NH-Br is found to be 0.495mmol/g, which determines the dosage of reagents used in the next step. As the TGA curve of SiO$_2$-P(BA-co-EFOA), besides the slight weight loss at about 200°C due to dehydration, the entire curve exhibits a large mass loss only between 300°C ~ 450°C, indicating that the polymer chain structure of the SiO$_2$ is homogeneous. To see whether the polymerization was living and controlled, the grafted polymers were cleaved from nanoparticles and GPC was tested. Its result was showed in Figure 3(b). We can clearly observe that there is a single peak curve and its PDI is 1.27. In other words, the characteristic of the resulting product is quite in line with AGET ATRP polymerization mechanism.

**Characterization of superhydrophobic surface**

Superhydrophobic coatings are such coatings that are simultaneously characterized by a water contact angle greater than 150° and contact angle hysteresis smaller than 10°. The local contact angle, known as Young contact angle $\theta$, can reach no more than 120° on planar surfaces even if the most efficient fluorine containing agents form a dense monolayer on the surface of texture elements \cite{42}. By mimicking the natural superhydrophobic surfaces such as lotus leaves and insects’ legs, superhydrophobic phenomenon are formed by combining surface chemical composition with surface roughness. As Figure 4 showed, two different models are proposed to explain this phenomenon: the Wenzel model \cite{43} and the Cassie model \cite{44}. Both of them displayed the real contact angle in function of the Young contact angle $\theta$ which was measured for a flat surface. The detailed information including equations and annotations for Young, Wenzel and Cassie model are displayed in Figure 4.

**Characterization of chemical composition**

The chemical composition was tested by Fourier transform infrared (FT-IR), Nuclear magnetic resonance spectroscopy (¹H-NMR) and X-ray photoelectron spectroscopy (XPS).

The Figure 5 showed the FT-IR spectrometer of pristine SiO$_2$, SiO$_2$-NH$_2$, SiO$_2$-NH-Br and SiO$_2$-P (BA-co-EFOA). The broad absorption bands at about 1000-1250cm$^{-1}$ corresponding to Si-O-Si stretching vibrations appeared in all of the SiO$_2$ related the samples. The brand observed at about 3446cm$^{-1}$ indicated the presence of hydroxyl group in the surface of SiO$_2$ and the peak at 961cm$^{-1}$ is attributed to Si-OH vibration. Compared with the FT-IR spectrum of pristine SiO$_2$, there was a -CH$_2$ stretching vibration at 2933cm$^{-1}$. The absence of Si-OH vibration at 961cm$^{-1}$ showed hydroxyl group in the surface of silica was substituted. SiO$_2$-NH-Br macroinitiator was synthesized by the reaction of SiO$_2$-NH$_2$ with 2-bromoisobutyryl bromide. For SiO$_2$-NH-Br, C=O stretching vibrations of ester at 1629cm$^{-1}$ occurs, which indicates the initiator group is linked. The FT-IR spectrum of SiO$_2$-P (BA-co-EFOA) showed the broad peak at 1100-1250cm$^{-1}$ which is attributable to F-C-F stretching vibration. All of these proved that the graft polymerization via SI-AGET ATRP is successful.
In Figure 6, the results of $^1$H–NMR and XPS are showed together. We can infer the chemical composition of bulk and surface by analyzing them. Figure 6(a) showed the $^1$H-NMR spectrum of cleaved polymer. As the figure shown, the H and its corresponding peak were annotated. According to the value of integrations, the ratio of m and n can be calculated as 10:1 which is in accordance with feed ratio. So the ratio of fluorine to carbon was obtained subsequently as 17:83 The overall XPS spectrum of the grafted silica nanoparticles’ surface is depicted in figure 6 (b), and the silicon, oxygen, fluorine, carbon and nitrogen atomic percentage are estimated to be about 23.78%, 30.96%, 11.59%, 30.86% and 2.81% respectively. There is a high ratio of fluorine to carbon in the XPS data (11.59%: 30.86%=1: 2.66) than the realistic value of $^1$H-NMR data (1:4.88), indicating that the fluorocarbon molecule chains migrated to the surface and this segregation makes the surface hydrophobic.

**Characterization of surface morphology** Transmission electron microscopy (TEM) photographs of primary silica nanoparticles and resultant organic-inorganic hybrid material are shown in Figure 7(a-c). In Figure 7(a), the aggregation can be observed clearly due to high specific surface area and high surface free energy of silica nanoparticles, as well as presence of OH groups on the nanoparticles surface. While in the Figure 7(c), polymers surrounding the silica can be seen obviously. TEM micrographs of treated nanoparticles, Figure 7(b), showed that although grafted with polymers, the aggregation was slightly prevented. It is the key that why hierarchical surface morphology can form. Surplus OH groups facilitate aggregation but the polymer chains prevent it, the balance between the two contrary tendencies makes the treated particles form micro-nano particles with nano polymer hair among which fluorocarbon chains orientated to surface. These contribute to superhydrophobic property.

According to figure 7, the particles assembled to form hierarchical roughness and make the surface superhydrophobic. The visible images of surface morphology are received by SEM and AFM. The corresponding images are showed in Figure 8. It is seen that the surface asperities are inhomogeneous. In the case of low magnification of SEM, the protuberances in micron scale are observed obviously. After magnifying, scattered nanoparticles can be seen as well, such as the area marked by red circle in figure 8(b). The surface topography obtained by the AFM images agrees pretty well with that from the SEM images. In addition, the micro/nano composite morphology of the surfaces obtained (AFM and SEM) perfectly matches the contact angle result which is showed in the top right corner of Figure 8(b), 170±3°.

**Anti-icing property of superhydrophobic surface**
Anti-icing property mainly refers to easy removal of condensed water before it freezes and delay in the crystallization of condensed water. So that ice accumulation can be prevented thoroughly. The anti-icing property is characterized by contact angle measurement in both ambient and subzero environment and DSC measurement. In this part, five samples with different wettability were used.

**Removal of condensed water before crystallization**
The crucial factor determining whether it is easy for condensed water to roll off the surface is the force between condensed water and the surface. Lower force makes the removal procedure easier. As for superhydrophobic surface, the force is reduced by two methods, decreasing the contact area and reducing the contact angle hysteresis.

As we all know, large contact angle is echoed with small contact area. What’s more, when the superhydrophobic surface is wetted by liquid, air is trapped inside the grooves in the hierarchical structure. So the real contact area refers to the fraction of the wetted area. It has been reported that the real contact area is generally considerably less than 10% for superhydrophobic surface due to the presence of an air layer. Table 1 shows the contact angles of samples with different wettability. According to it, we can conclude that the
superhydrophobic surface decreased the contact area to a large extent.

In the case of contact angle hysteresis, it determines the force preventing the liquid rolling off the surface \cite{48}. The lower the hysteresis, the more efficiently the drops are removed from a horizontal surface of a coating under a wind force or airflow pressure. The equation is shown in equation (1)

\[ \Delta \theta = \theta_{adv} - \theta_{rec} \]  

in which \( \Delta \theta \), \( \theta_{adv} \) and \( \theta_{rec} \) represent the contact angle hysteresis, advancing contact angle and receding contact angle respectively. \( \theta \), \( \theta_{adv} \) and \( \theta_{rec} \) are marked in figure 9

Fig.9 static contact angle (\( \theta \)), advancing contact angle (\( \theta_{adv} \)) and receding contact angle (\( \theta_{rec} \))

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample</th>
<th>Sample</th>
<th>Sample</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>51.5±0.5</td>
<td>63.7±2.1</td>
<td>34.7±1.7</td>
<td>29.9±1.2</td>
</tr>
<tr>
<td>B</td>
<td>40.3±0.7</td>
<td>73.6±1.6</td>
<td>22.7±1.6</td>
<td>50.9±0.2</td>
</tr>
<tr>
<td>C</td>
<td>103.0±0.2</td>
<td>116.9±1.8</td>
<td>68.6±2.1</td>
<td>48.3±3.9</td>
</tr>
<tr>
<td>D</td>
<td>113.5±0.1</td>
<td>129.8±1.2</td>
<td>99.8±1.8</td>
<td>29.8±2.0</td>
</tr>
<tr>
<td>E</td>
<td>170.3±2.4</td>
<td>171.5±2.1</td>
<td>168.7±1.9</td>
<td>2.7±0.2</td>
</tr>
</tbody>
</table>

Table 1 Contact angle (\( \theta \)), advancing contact angle (\( \theta_{adv} \)), receding contact angle (\( \theta_{rec} \)) and contact angle hysteresis (\( \Delta \theta \)) for different surfaces achieved by CAM 200 optical contact-angle goniometer

According to the contact angle data, we can find that sample B, C, D and E exhibited hydrophilicity, double hydrophobicity and superhydrophobicity respectively. Compared with hydrophilic, uncoated and hydrophobic surfaces, superhydrophobic surface reduced both the contact area and the force between water and surface to a large extent. We can conclude that the condensed water can roll off the surface as long as it is tilted slightly. On the other hand, to investigate the low adhesion between water and coating, we applied a super-large droplet which is 7.5 times larger than normal one, 15\( \mu \)m. As Fig 10 showed, even if we pressed it hard, it is difficult for the droplet to paste on the surface. So, it is rational to say that the synthesized hybrid nanoparticles perceive good anti-icing property. Furthermore, it has been proved that the ice adhesion strength on rough hydrophobic surfaces has good correlation with wetting hysteresis \cite{49, 50}

Fig.10 The process of huge droplet failed to paste on coated surface

Delay in the crystallization of condensed water The crystallization point of water droplet on surfaces with different coatings were obtained by DSC measurement at a continuously lowering temperature and the whole icing process of condensed water was observed by CAM 200 optical contact-angle goniometer at a constant temperature, -18° C.

Through analyzing the DSC data, we can find that compared with the droplet dripped into untreated crucible, the one in superhydrophilic, hydrophobic and superhydrophobic crucible possesses lower heat flow. It is clearly caused by the heat insulation of both coatings and trapped air between water and substrate. So, the reason why freezing point can be influenced is the key and needs to be discussed. The sample coated with pure polymer, P (BA-co-EFOA), is the only planar surface. The reduced crystallization temperature is attributed to adiabatic coating which actually influenced the temperature slightly. However, for other rough samples, this phenomenon can be explained by the combination of Kelvin’s law and Clapeyron Relationship because numerous nanoparticles aggregated on the surface forming roughness especially for superhydrophobic surface, nano-hairs scattered on micron particles leading to capillaries. The formula of Kelvin’s law is

\[ P_r = P \exp \left( \frac{2 \gamma}{\alpha V_m} \right) \]  

where \( P_r \) and \( P \) are the vapor pressure and saturated vapor pressure at a given temperature respectively; \( \gamma \) is the surface energy; \( V_m \) is the molar volume of phase; \( R \) is the gas constant; \( T \) is the temperature and \( r \) is the radius of little droplet or crystal. The value of \( r \) depends on the interface. If it is concave, \( r \) is positive and if it is convex, \( r \) is negative. So, it can be obviously observed that for hydrophilic surface (pristine \( \text{SiO}_2 \)), \( P_r \) decreases while \( r \) decreases. While for \( \text{SiO}_2-P, \text{SiO}_2-PBA \) and \( P \) (BA-co-EFOA) coated surface, \( P_r \) increases when \( r \) decreases. Suspending on the surface with nano scales, \( r \) is little enough to generate a large \( P_r \). Based on Clapeyron Relationship,

\[ \frac{dT}{dp} = \frac{T \Delta^e H_m}{\Delta^e V_m} \]  

\( \Delta^e H_m \)
where $T$ is the temperature, $p$ is the vapour pressure, $\Delta^\alpha V_m$ and $\Delta^\alpha H_m$ are volume difference and enthalpy change from phase $\alpha$ to $\beta$ respectively. For solidification, the equation (3) transformed as
\[
\frac{dT}{T} = \frac{\Delta^\alpha V_m}{\Delta^\alpha H_m} dp
\]
(4)
After integral, we get
\[
\ln \frac{T_2}{T_1} = \frac{\Delta^\alpha V_m}{\Delta^\alpha H_m} (p_2 - p_1)
\]
(5)
Since in the process of solidification, $\Delta V_m > 0$ and $\Delta H_m < 0$, so, $T$ is negatively related to $p$. Therefore, compared with uncoated surface, hydrophilic surface with certain roughness possess a lower pressure, so the water droplet on it solidified at a higher temperature (-12.15°C vs. -13.37°C) and water droplet on a hydrophobic surface with a higher pressure tends to be supercooled and the freeze temperature is correspondingly decreased (-17.44°C vs. -13.37°C). Thanks to its smaller $r$, the one on superhydrophobic surface was even lower (-20.19°C).
While for the P (BA-co-EFOA) coated surface, the pressure is similar to smooth surface. This is why the temperature is in close proximity to the one on uncoated surface. According to the observation of DSC, we can conclude that the crystallization point of water can be reduced by optimizing the surface roughness and chemical composition. As for the superhydrophobic surface we applied, it decreased the temperature by 6.82°C. Besides decreasing crystallization point, the surface can delay crystallization compared with other surfaces at a constant temperature as well.

The photographs of individual water droplets on untreated glass and glass coated with different coatings in the whole freezing process are showed in figure 12. It can be obviously observed that the transparent center of condensed water vanished when the water began to freeze because the difference in reflectivity between water and ice [3]. The recorded data demonstrates that hydrophilic coating shortened the freezing process by 8s, planar and rough hydrophobic coating delayed it by 162s and 236s respectively, and most importantly, the superhydrophobic coating delayed it by 9858s which indicates this kind of coating can prevent ice formation thoroughly.

<table>
<thead>
<tr>
<th>Pristine SiO$_2$</th>
<th>Uncoated Glass</th>
<th>P(BA-co-EFOA)</th>
<th>SiO$_2$-PBA</th>
<th>SiO$_2$-P(BA-co-EFOA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water droplet</td>
<td>Begin to freeze</td>
<td>Ice</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t=0s</td>
<td>t=158s</td>
<td>t=188s</td>
<td>t=0s</td>
<td>t=385s</td>
</tr>
<tr>
<td>t=385s</td>
<td>t=196s</td>
<td></td>
<td>t=896s</td>
<td>t=10028s</td>
</tr>
<tr>
<td>t=358s</td>
<td></td>
<td></td>
<td>t=10028s</td>
<td></td>
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</table>

Fig.12 Photographs of individual water droplets on glasses with different coatings during the whole freezing process captured by a high speed CCD camera of CAM 200optical contact-angle goniometer

This phenomenon can be explained thermodynamically. It is well known that a water droplet must overcome the potential barrier to crystallize. For superhydrophobic surface, due to its roughness, the crystallization can be described as heterogeneous nucleation. Based on classic nucleation theory [31], the nucleation free energy barrier ($\Delta G$) can be calculated by the equations
\[
\Delta G = \left(\frac{2\pi R^2}{3}\Delta g + 2\pi R^2 \gamma_s f(\theta)\right)
\]
(6)
\[
f(\theta) = \frac{(2 + \cos \theta)(1 - \cos \theta)^2}{4}
\]
(7)
Where $R$ is the droplet radius, $\gamma_s$ is the solid-liquid interfacial tension, $\Delta g$ is the Gibb’s energy density difference between ice and liquid water and $\theta$ is the apparent contact angle. According to the equations, $\Delta G$ is positively proportional to $f(\theta)$ which means that the bigger $\theta$ is, the higher $\Delta G$ is. The curve of $f(\theta)$ is shown in figure 13 from which we can see $f(\theta)$ is monotonously increasing with $\theta$. So, the growing contact angle will enlarge the nucleation free energy barrier and retard the crystallization of condensed water. For treated glass with high superhydrophobicity in this study, it is inevitable to delay the water droplet freeze.

![Fig. 13 The curve of $f(\theta)$ in the function of $\theta$](chart)

Since trapped air existed between condensed water and cold superhydrophobic substrates, we believe that the droplet on surface is a system of three-phase interfaces. The process of heat transfer is changed correspondingly which also relative to the delay of crystallization. The heat transfer consists of the heat gains from air
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Notes and references

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