Article

Preparation and Anti-frost Performance of PDMS-SiO₂/SS Superhydrophobic Coating

Li Jia ^{1,2}, Jun Sun ^{1,*} , Xiaoxiao Li ¹, Xian Zhang ¹, Lin Chen ¹ and Xinyou Tian ^{1,*}

¹ Key Lab of Photovoltaic and Energy Conservation Materials, Institute of Solid State Physics, HFIPS, Chinese Academy of Sciences, Hefei 230031, China; jial2008@mail.ustc.edu.cn (L.J.); lixiaoxiao@rntek.cas.cn (X.L.); xzhang@issp.ac.cn (X.Z.); chenlin@issp.ac.cn (L.C.)

² University of Science and Technology of China, Hefei 230026, China

* Correspondence: jsun@rntek.cas.cn (J.S.); xytian@issp.ac.cn (X.T.); Tel.: +86-551-65393564 (J.S.); +86-551-65591418 (X.T.); Fax: +86-551-65591434 (X.T.)

Received: 24 September 2020; Accepted: 27 October 2020; Published: 30 October 2020

Abstract: Polydimethylsiloxane modified SiO₂/organic silicon sol (PDMS-SiO₂/SS) hybrid coating was synthesized via a simple two-step modification route. The nanoparticles (NPs) of PDMS-SiO₂ were synthesized through a high temperature dehydration reaction by using silica and excessive PDMS. The NPs lapped with each other and formed a branch and tendril structure. Organic silicon sol (SS) added as basement introduced a hydrophobic group and protected the structure of the NPs. The PDMS-SiO₂/SS hybrid coating exhibits a superhydrophobic performance with a maximum water contact angle of 152.82°. The frost test was carried out on a refrigerator evaporator, and the results showed that the coating did not merely delay the frost crystal time about 113 min but also increased the frost layer process time. Meanwhile, the defrosted water droplets rolled off from the coated surface easily which is a benefit for frost suppression performance of the next refrigeration cycle.

Keywords: SiO₂; PDMS; nanoparticles; superhydrophobic; antifrosting

1. Introduction

It is well known that frost will occur when water vapor in the air contacts a cold surface with a surface temperature lower than the dew point in refrigeration, low temperature storage, air conditioning heat pumps and other low temperature fields [1–3]. As the frost layer is a porous material composed of ice crystals and air, its effective thermal conductivity is low. Therefore, the existence of a frost layer on structures will increase the heat transfer resistance and reduce the heat transfer coefficient, then cause serious problems, such as power transmission, economic losses, and even inability to work normally in cold regions [4–7]. Numerous methods and techniques for inhibiting frosting have been reported, which can be classified into three categories, one is reducing air humidity [8]; the second is using the effect of external field energy [9]; the third is surface modification treatment [10]. The methods of air humidity control and external field energy are seldom used in engineering. This is because air humidity has to be maintained at a certain level to ensure its specific function in some engineering fields, while the method of external field energy has some disadvantages such as space limitations, equipment complexity, and a limited antifrost effect. Comparatively, the surface modification method has broad application prospects because of its advantages such as low cost, convenient processing, and so on.

Surface modification, generally using hydrophilicity or hydrophobicity to modify the surface, affects the frost layer growth by regulating the contact angle and binding force between the droplets and the cold surface. Hydrophilic coating research began in the early 1980s. Highgate et al. [11] reported that a hydrophilic coating could absorb a large amount water and store part of the latent cooling, so that

the adsorbed water would not freeze even at $-20\text{ }^{\circ}\text{C}$. Okoroafor et al. [12] observed that surfaces with hydrophilic polymers could delay the frosting rate and reduce frost mass by about 10%–30% after two hours of experimental measurement. However, a hydrophilic surface is unfavorable for the defrosting process. A large amount of defrosting water would be retained in the hydrophilic surface because of its excellent wettability, and the retained water would be directly frozen when the next frost period started to form a permafrost area [13–16]. The heat consumed by the evaporation of defrosting water is about eight times as much as that of the frosting layer, meanwhile, the evaporation of defrosting water could also prolong defrosting time and reduce defrosting efficiency. In recent years, the study of the special properties of natural species, i.e., superhydrophobic surfaces, has been developed and applied in many fields both in daily life and in industrial production. It has been found that the surface of a lotus leaf has a nano-multistructure and the contact angle is generally above 150° , so that water droplets can roll off smoothly and easily. Based on this phenomenon, many scientists have carried out research of superhydrophobic frost suppression. Wang et al. [17] prepared superhydrophobic surfaces by a chemical etching method and carried out the frost experiment. They found that the superhydrophobic surface can delay the formation of frost crystals and decrease the amount of frost crystals at the end of a frost experiment, while both a hydrophobic and a bare aluminum surface were covered by frost. Liu et al. [18] prepared a superhydrophobic surface by the biomimetic synthesis. It was found that the bionic superhydrophobic surface had excellent frost suppression ability that could delay the initial frost crystal appearance time by more than 55 min. Zheng et al. [19] prepared the hydrophobic surface with a nano-microstructure through electrostatic spinning. The results of the frosting experiment showed that the hydrophobic surface could delay the appearance of initial frost crystals and decrease the surface coverage ratio. Therefore, the hydrophobic or superhydrophobic surfaces are beneficial to impede frosting. But hydrophobic or superhydrophobic surface treatment methods have been complicated and expensive in previous literature, i.e., the etching method, biomimetic synthesis, electrostatic spinning and so on, which are only suitable for laboratory and academic research, and are not suitable for batch production.

On the other hand, research into frost suppression on the heat exchanger has always been an important theme in industrial engineering. However, the current studies for frost suppression have attracted more attention on water retention and drainage performance on the uncoated or coated microchannel heat exchanger. For example, Xu and Han [20] investigated the influences of the water retention effect on the frosting and defrosting performance on microchannel heat exchangers in heat pump systems. Xia et al. [21] investigated the water retention effect on different uncoated tube microchannel evaporators. Padhmanabhan et al. [22] pointed out that removing the water residual at the end of the defrost cycle could only reduce the next frost cycle time by 4%. Zhong et al. [23] and Joardar et al. [24] pointed out that, compared with hydrophobic coating surfaces, the hydrophilic coating surface was beneficial to water residue, but had no significant effect on water drainage behavior. Liu and Jacobi [25] investigated the differences in condensation and water drainage mechanisms between wind-tunnel experiments and dip tests by using spray or droplet spray. Ehsan Moallem et al. [16] studied the effect of hydrophilic and hydrophobic surface coatings and water retention on their frosting performance and frost growth rates. The range of surface contact angles was from hydrophilic (5°) to hydrophobic (105°) surface with a workpiece surface temperature range of -9 – $-4\text{ }^{\circ}\text{C}$. The results showed that the surface properties and temperature played a key role in the frosting formation rate and frosting cycle time. However, there are few studies on the antifrost effect of a superhydrophobic surface with the surface temperature lower than $-20\text{ }^{\circ}\text{C}$.

To address the existing gap in the literature about frost growth on the surface of a microchannel heat exchanger, especially on a surface with a superhydrophobic coating, Polydimethylsiloxane modified SiO_2 /organic silicon sol (PDMS- SiO_2 /SS) hybrid coatings have been prepared through mixing PDMS-modified SiO_2 NPs with organic silicon sol under vigorous ultrasonication. The hybrid coatings were characterized by scanning electron microscope (SEM), transmission electron microscopy (TEM),

energy dispersive spectroscopy (EDS), and water contact angle (WCA), then the effect of antifrost on the evaporator was investigated.

2. Materials and Methods

2.1. Materials

Fumed silica particles with mean diameter of 20 nm were supplied by Xinhong Chemical Co. Ltd. (Taicang, China), polydimethylsiloxanes (PDMS400, industrial products) were purchased from Foshan Vago Organic Silicon Co. Ltd. (Foshan, China), organic silicon sol (ss-01) was purchased from Laiyang Zixilai Environmental Protection Technology Co. Ltd. (Laiyang, China). Acetone (A.R.), ethanol (A.R.), potassium persulfate (KPS, A.R.), sodium dodecyl sulfate (SDS, A.R.), alkyl phenol polyoxyethylene ether OP-10) were acquired from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). All the reagents were used as received.

2.2. Synthesis of PDMS-SiO₂ Hybrid

Firstly, PDMS and SiO₂ were heated at 110 °C in a vacuum oven for 8 h. Secondly, PDMS and SiO₂ were mixed into a Teflon-lined autoclave with a mass ratio of 2.5 to 20.5, and anhydrous calcium chloride was put into the Teflon-lined autoclave and used as desiccant. Thirdly, the sealed mixture under nitrogen atmosphere was heated at 180 °C for above 10 h to react completely. The PDMS-SiO₂ nanoparticles were repeatedly washed using acetone by vacuum filtration and the filtrate cake was put in an oven at 70 °C for 10 h. Lastly, the as-prepared powder was ground to obtain the PDMS-SiO₂.

2.3. Synthesis of PDMS-SiO₂/SS Hybrid Coating

The hydrophobic PDMS-SiO₂/SS hybrid coating synthesis route is shown in Figure 1. PDMS-SiO₂ NPs and ethanol (with mass ratio of 1:15) were mixed into a clean beaker under vigorous ultrasonication. Then organic silicon sol was added into the mixed solution and the mixture was ultrasonicated for 15 min. Finally, the PDMS-SiO₂/SS hybrid coating was fabricated onto the sample piece through spraying the mixture with a spray gun, and then placed in an oven at 70 °C for 1 h to promote solvent volatilization and film forming.

Figure 1. Schematic diagram of fabricating PDMS-SiO₂/SS coating.

2.4. Frosting Test

The frosting tests were performed in the air-cooled refrigerator evaporator of a BCD-330 (MIDEA, Hefei, China). The PDMS-SiO₂/SS hybrid coating was fabricated onto the surface of the evaporator fins by spray gun. For comparison, the frost test was performed on the same evaporator where half the evaporator was sprayed with PDMS-SiO₂/SS hybrid coating, while the other half was not treated. During the test, a microsquare camera monitoring system was utilized to capture the frostiness.

2.5. Characterization

Micromorphology observations were taken with a transmission electron microscopy (TEM) instrument (JEOL JEM-2010, Tokyo, Japan) at an acceleration voltage of 200 kV, the sample solution was placed on the copper grid and dyed with phosphotungstic acid, and dried in air before observation. Scanning electron microscopy (SEM) images were examined with a Sirion 200 field-emission scanning electron microscopy (SEM, FEI, Sirion 200, Hillsboro, OR, USA) under an acceleration voltage of 15 kV, and the element analysis was performed with an energy dispersive spectroscopy (EDS) unit from SEM. Water contact angle (WCA) was determined by a contact angle analyzer (KRÜSS DSA10Mk2, Hamburg, Germany) with 5 μ L of distilled water. Digital photos were taken with a digital single lens reflex camera (Sony, Tokyo, Japan). The processes of frosting and defrosting on the evaporator pipe were recorded by the software of a microsquare camera monitoring system.

3. Results and Discussion

3.1. Surface Morphology and Compositions

The superhydrophobic PDMS-SiO₂ NPs were synthesized through dehydration at high temperature by using silica and excessive polydimethylsiloxane (PDMS). Typical scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of PDMS-SiO₂ NPs are shown in Figure 2. The PDMS-modified SiO₂ NPs overlapped with each other by PDMS chains to form a branching structure with a micron size of a nanocluster, while the single NP size was about 10 to 20 nm. As shown in Figure 2 by SEM, the PDMS-SiO₂ composite surface had a structure similar to an island, with high roughness and the nanoparticles tightly attached to each other, which also showed partial agglomeration (Figure 2b). Then the as-prepared PDMS-SiO₂ NPs and ethanol were mixed into a clean beaker under vigorous ultrasonication. After that, organic silicon sol was added into the mixed solution and ultrasonicated for another 15 min to obtain the PDMS-SiO₂/SS hybrid coating mixture. As shown in Figure 3, the pure SS can only form amorphous nanoparticles of several nm after gel, while the PDMS-SiO₂ NPs hybrid can form a film well, possibly due to the interaction between the PDMS-SiO₂ NPs and SS. The surface morphology results showed that the film-forming property of the PDMS-SiO₂/SS was so good that the PDMS-SiO₂ NPs could also be effectively coated to protect its nano-microstructure.

Figure 2. (a,b) SEM and (c,d) TEM images of PDMS-SiO₂.

Figure 3. TEM images of (a,b) pure SS and (c,d) PDMS-SiO₂/SS.

The element analysis of the obtained samples was examined with energy dispersive spectroscopy (EDS) and the results were summarized in Table 1. It is clearly seen from Table 1 that the PDMS-SiO₂ sample was mainly composed of C, O and Si elements with 26.78%, 55.90% and 17.32% atoms, respectively. A large presence of C element in the PDMS-SiO₂ hybrid indicated that PDMS with low free energy had been successfully introduced into silica NPs through the reaction. For the PDMS-SiO₂/SS sample, the atomic percentage of C, O and Si elements was 30.38%, 51.21% and 14.59% in the PDMS-SiO₂/SS-1 coating (with the mass ratio of PDMS-SiO₂ to SS of 1:1) and 31.28%, 38.45% and 29.50% in the PDMS-SiO₂/SS-2 coating (with the mass ratio of PDMS-SiO₂ to SS of 2:1), respectively. The further increase of the atomic percentage of the C element of 30.38% and 31.28% in PDMS-SiO₂/SS-1 and PDMS-SiO₂/SS-2 coatings, respectively, indicated that certain organic silicone groups had been introduced into the sample, which was conducive to fabricating superhydrophobic surfaces.

Table 1. Contact angle, atomic percentage of C, O, Si Na, Al, of PDMS-SiO₂ and PDMS-SiO₂/SS samples, according to EDS data.

Sample Designation	Atomic Percentage (%)					Contact Angle (°)	PDMS-SiO ₂ :SS (wt %)
	C	O	Si	Na	Al		
PDMS-SiO ₂	26.78	55.90	17.32	–	–	–	–
PDMS-SiO ₂ /SS-1	30.38	51.21	14.59	2.18	1.64	152.82	1:1
PDMS-SiO ₂ /SS-2	31.28	38.45	29.50	–	0.77	150.22	2:1

3.2. Surface Morphology and Wettability of PDMS-SiO₂/SS Hybrid Coatings

The SEM images of PDMS-SiO₂/SS hybrid coatings with different PDMS-SiO₂ content are shown in Figure 4. The surface had become rough with the PDMS-SiO₂ particles added. The amount of PDMS-SiO₂ was an important factor affecting surface roughness, with the PDMS-SiO₂ content in the nanocomposites increasing, the distribution uniformity of surface nanoparticles and the surface roughness was at first increased and then decreased. When PDMS-SiO₂ nanoparticles and organic silicon sol were added with a mass ratio of 1:10, there were nanoparticle aggregates composed of PDMS-SiO₂ nanoparticles in 10–50 nm sizes appearing on the surface. When PDMS-SiO₂ nanoparticles and organic silicon sol were added with a mass ratio of 1:2, the coating showed a rough surface morphology consisting of microscale bumps and protrusions superimposed with nanoparticles. However, with a further increase of PDMS-SiO₂ nanoparticles content, many defects (particle agglomeration and cracking phenomena) appeared in the picture (Figure 4d,e).

Figure 4. SEM images of PDMS-SiO₂/SS hybrid coating with different mass ratios of PDMS-SiO₂ to SS. (a) 1:10; (b) 1:5; (c) 1:2; (d,e) 1:1; (f) 2:1.

The WCAs of PDMS-SiO₂/SS hybrid coatings with different PDMS-SiO₂ content are recorded in Figure 5. As shown in Figure 5a, inset image, the pure SS coating showed weak hydrophobicity with a WCA value of 93.15°. After adding PDMS-SiO₂ NPs into the SS, the WCA values of the hybrid coating increased at first and then decreased, meaning that the amount of PDMS-SiO₂ was a critical factor affecting the surface properties of the hybrid coating, which was consistent with the results from the SEM test. In the sample with the mass ratio of PDMS-SiO₂ to SS of 1:10, the WCA was up to 99.15°. The WCA of the hybrid coating with a mass ratio of 1:2 increased to 150.05°, showing that the introduction of PDMS-SiO₂ content could significantly improve the coating's superhydrophobic performance. However, the WCAs showed little change with further increases in the PDMS-SiO₂ and it has been stable above 150°, the mass ratio of PDMS-SiO₂ to SS was 1:1, the WCA was up to 152.82°. However, the WCA decreased to 150.22° with the mass ratio of PDMS-SiO₂ to SS up to 2:1, the reason could have been that the superfluous PDMS-SiO₂ NPs in the composite could not be coated perfectly and the excess NPs were agglomerated, leading to a decrease of dispersion and surface roughness. The results show that a suitable loading content of PDMS-SiO₂ NPs is crucial for the surface roughness of the PDMS-SiO₂/SS hybrid coating. Briefly, too many PDMS-SiO₂ NPs agglomerate and lead to many cracks on the coating surface. Thus, based on the comprehensive consideration of processing technology and material cost, our study selected the sample with the mass ratio of 1:1 for PDMS-SiO₂ to SS (PDMS-SiO₂/SS-1) for the antifrosting study. The PDMS-SiO₂/SS hybrid coating was fabricated onto the surface of evaporator fins by spray gun. As shown in Video S1 (supporting information Video S1), water droplets easily rolled off the surface of the as-prepared PDMS-SiO₂/SS-1 coating, indicating that the coating had good hydrophobicity and low rolling angle.

Construction of nano-microstructures on the surface of materials and the introduction of the low surface free energy modification are the two main methods for the preparation of a hydrophobic surface [26,27]. In this study, PDMS-modified silica NPs were prepared through a dehydration reaction at high temperature. On the one hand, the hydrophobic properties of the hybrid coating surface could be enhanced by introducing the low surface free energy of organic silicon (PDMS) groups. Silica NPs modified by PDMS to form a branching structure gave rise to different sizes of clusters. In addition, PDMS-SiO₂ NPs overlapped with each other to further form the convex–concave coating structure. On the other hand, it can be seen from the TEM figure that different size holes were also formed between the clusters. This structure can form a solid–air–water contact mode, which belongs to the Cassie–Baxter model and can enhance the hydrophobic performance of the material [28,29]. Thirdly, the organic silicon membrane of the hybrid coating effectively wraps PDMS-SiO₂ NPs, which can reduce the aggregation of NPs and enhance the strength of the hole structure forming from overlap

with clusters to protect the solid–air–water patterns, this could ultimately lead to the surface become more hydrophobic with the surface roughness increased [28–32]. When the content of PDMS-SiO₂ was further increased, excess NPs which could not be covered by SS would tend to agglomerate together. As a result, the hydrophobic performance of the hybrid coating could diminish with dispersion and roughness decreased.

Figure 5. Water contact angles (WCAs) of PDMS-SiO₂/SS hybrid coating with different mass ratios of PDMS-SiO₂ to SS. (a) 1:10; (b) 1:5; (c) 1:2; (d) 1:1; (e) 2:1. (f) WCA curve of PDMS-SiO₂/SS hybrid coating with different mass ratio of PDMS-SiO₂ to SS. Inset image in (a) is the WCA of pure SS coating.

3.3. Frosting Characteristics

In order to study the frosting performance and frost growth rates of PDMS-SiO₂/SS-1 hybrid coating, the dynamic frost formation process on the air-cooled refrigerator evaporator of a BCD-330 (MIDEA) was investigated. For comparison, the frost test was on the same evaporator where half of the evaporator was sprayed with PDMS-SiO₂/SS-1 hybrid coating and the other half was not treated. Frostiness on both sides of the evaporator was observed using a microsquare camera monitoring system at the same experiment time.

When the refrigerator ran in equilibrium state, the temperature and humidity in the freezer were stable at −21.5 °C and 38.1% RH, respectively, and the surface temperature of the evaporator was −28.9 °C. As shown in Figure 6, mostly needle-like frost crystals appeared on the normal evaporator surface within 22 min and distributed randomly on the edge and surface of the fin, while the frosted crystals appeared on the coated evaporator at 135 min and the first frost crystals appeared at the edge of the fins, which may be due to a certain defects in the small range of the fin that provided nucleation points for the frost and promoted the formation of frosted crystals [26,27,30]. The appearance time of the first frost crystals was delayed by about 113 min. The reason may be that the PDMS-SiO₂/SS-1 superhydrophobic surface with low surface free energy could improve the frost crystal nucleation barrier which could delay frost formation time and loosen the frost layer. As shown in Figure 6, the frost on the uncoated surface was thicker than that on PDMS-SiO₂/SS-1 coated surface as time elapsed. With the extension of operation time, the frost layer thickness on the evaporator surface with no coating increased continuously until the uncoated surface was basically covered by a thin frost layer at 405 min, and was covered with a thicker frost layer after operation for 2325 min. At the same time, when the frost degree of the PDMS-SiO₂/SS-1 coated evaporator surface was compared to it, only a few independent frost crystals had appeared on the coated surface at 405 min and only a thin and sparse layer of frost crystals covered the surface at 2325 min. Therefore, the PDMS-SiO₂/SS-1 superhydrophobic coating synthesized in our study had a better antifrost effect that could delay the appearance time of the first frost crystals for 113 min. Meanwhile, the surface with superhydrophobic coating had few breeding points for frost branches, and the frost layer was shorter and looser, which

were similar findings to a previous study [33]. It is worth noting that during the whole refrigeration process, due to the temperature of the evaporator surface and refrigerator room being -28.9 and -21.5 °C, respectively, which were far below the frost crystal temperature, the water vapor in the air directly condensed into frost crystals on the evaporator surface without water droplets forming.

Figure 6. Frost formation process and variation of frost mass with time for (a) uncoated and (b) PDMS-SiO₂/SS hybrid coated surfaces.

Subsequently, the refrigerator went into the defrost mode and then started the next frost cycle. It can be seen from Figure 7 that the melt frost water spread into filmwise and dropwise condensation on the uncoated evaporator surface. The filmwise and dropwise condensation were quickly frozen into ice crystals after refrigeration once again at about 25 min, the frost increased quickly and covered the entire normal evaporator surface at 120 min, and then the frost thickness increased as time elapsed and a batch of ice branches were formed at about 240 min. Meanwhile, the evaporator surface with the PDMS-SiO₂/SS-1 superhydrophobic coating had a few small droplets due to low surface free energy, and the small droplets coalesced with each other and jumped off the surface similar to the previous study [34]. The frost crystals were observed after refrigeration for about 60 min, with only a thin frost layer on the PDMS-SiO₂/SS-1 superhydrophobic coated surface at about 240 min, indicating that under the same cooling time, the evaporator with the PDMS-SiO₂/SS-1 superhydrophobic coating displayed excellent antifrost performance compared to the uncoated evaporator. The frosting experiment was

carried out again in the refrigerator and the times for frosting crystal appearance and frost thickness were basically consistent with the second circulation. This may be because the PDMS in the hybrid coating can perform some deformation to adapt to the relative volume change to improve the durability of the coating [35], which is an important fact for industry use. In order to verify the frost-suppression stability of the PDMS-SiO₂/SS-1 hybrid coating, we ran the refrigerator continuously for more than 5000 min (more than ten frosting and defrosting cycles), and the dynamic frost formation process on the evaporator surface was observed by using SLR camera at different times. As shown in Figure 8, there was always a thick frost layer on the surface of the evaporator fins without coating. In contrast, only a thin and loose frost layer appears on the PDMS-SiO₂/SS-1 superhydrophobic surface. As shown in Figure 8 (from 1832 to 3272 min), small pieces of ice were observed on the edge of the evaporator fins with PDMS-SiO₂/SS-1 superhydrophobic coating, which could be caused by defects in the coating on the edge of the evaporator fins. In general, the results show that the as-prepared superhydrophobic coating can function effectively as an antifrost for a long time. It can be seen that this developed synthesis strategy could be useful for the design of the superhydrophobic coatings and other potential applications in the field of antifrosting.

Figure 7. Frost formation process and variation of frost mass with time for various surfaces after defrosting. (a) Normal surfaces; (b) PDMS-SiO₂/SS hybrid coated surfaces.

Figure 8. Frost formation process and variation of frost mass with time for various surfaces after defrosting. (a) normal surfaces; (b) PDMS-SiO₂/SS hybrid coating surfaces.

4. Conclusions

In this study, PDMS-SiO₂/SS hybrid coatings have been prepared through mixing PDMS-modified SiO₂ NPs with organic silicon sol under vigorous ultrasonication. SEM, TEM, EDS and WCAs results revealed the surface morphology, compositions and hydrophobic properties of the as-prepared NPs and hybrid coatings. The PDMS-modified SiO₂ NPs overlapped with each other to form the convex–concave coating structure and built a solid–air–water contact mode, which was beneficial to the hydrophobic properties of the coating materials. The addition of organic sol in the coatings not only introduced a hydrophobic group to protect the NPs’ convex–concave structure which could be conducive to improving hydrophobic performance, but also improved the manufacturability of the hydrophobic coating. The amount of PDMS-SiO₂ is a critical factor affecting the surface hydrophobic performance of the PDMS-SiO₂/SS hybrid coatings and the maximum water contact angle is 152.82°. In addition, the frost test of PDMS-SiO₂/SS hybrid coating was carried out on a refrigerator evaporator. The results showed that the coating did not merely delay frost crystal formation but also increased the frost layer process time. Meanwhile, the defrosted water droplets rolled off the coated surface easily which is a benefit for frost suppression performance in the next refrigeration cycle. This implies that the PDMS-SiO₂/SS hybrid coating has a better antifrosting performance. Above all, it is believed that as-prepared PDMS-SiO₂/SS hybrid coatings have potential applications in self-cleaning surfaces, defrosting and frost-resistant areas.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2079-6412/10/11/1051/s1>, Video S1: Video of Water Spray Experiment about the Evaporator Fins with the PDMS-SiO₂/SS-1 Superhydrophobic Coating.

Author Contributions: L.J.: conceptualization, methodology, investigation, data curation, writing—original draft preparation. J.S.: Conceptualization, methodology, investigation, data curation, writing—original draft preparation, writing—review and editing, funding acquisition. X.L.: methodology, writing—review and editing, funding acquisition. X.Z.: methodology, writing—review and editing, funding acquisition. L.C.: conceptualization, data curation, writing—review and editing, funding acquisition. X.T.: conceptualization, writing—review and editing, funding acquisition. All authors have read and agreed to the published version of the manuscript.

Funding: This research is funded by the National Key Research and Development Program of China under 2017YFC0703200 and Youth Innovation Promotion Association, CAS (2015268).

Acknowledgments: All the coauthors thank Key Lab of Photovoltaic and Energy Conservation Materials, Chinese Academy of Sciences. All the authors thank Hefei Midea refrigerator Co. Ltd. for their support in the refrigerator experiment.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Li, K.; Luo, S.X.; Yu, J.; Tang, Q.T.; Su, L.; Fang, Y.D. An experimental investigation on frosting characteristics of a microchannel outdoor heat exchanger in an air conditioning heat pump system for electric vehicles. *Int. J. Energ. Res.* **2020**, *44*, 7807–7819. [\[CrossRef\]](#)
2. Laforte, J.L.; Allaire, M.A.; Laflamme, J. State-of-the-art on power line de-icing. *Atmos. Res.* **1998**, *46*, 143–158. [\[CrossRef\]](#)
3. Bragg, M.B.; Heinrich, D.C.; Valarezo, W.O. Effect of under-wing frost on a transport aircraft airfoil at flight Reynolds number. *J. Aircr.* **1994**, *31*, 1372–1378. [\[CrossRef\]](#)
4. Stone, H.A. Ice-Phobic surfaces that are wet. *ACS Nano* **2012**, *6*, 6536–6540. [\[CrossRef\]](#)
5. Boutar, Y.; Naïmi, S.; Mezlini, S.; Silva, L.F.M.d.; Hamdaoui, M.; Ali, M.B.M. Effect of adhesive thickness and surface roughness on the shear strength of aluminium one-component polyurethane adhesive single-lap joints for automotive applications. *J. Adhes. Sci. Technol.* **2016**, *30*, 1913–1929. [\[CrossRef\]](#)
6. Frankenstein, S.; Tuthill, A.M. Ice adhesion to locks and dams: Past work; future directions? *J. Cold Reg. Eng.* **2002**, *16*, 83–96. [\[CrossRef\]](#)
7. Ayres, J.; Simendinger, W.H.; Balik, C.M. Characterization of titanium alkoxidesol-gel systems designed for anti-icing coatings. *J. Coat. Technol. Res.* **2007**, *4*, 463–471. [\[CrossRef\]](#)
8. Kondepudi, S.N.; O'Neal, D.L. Effects of different fin configurations on the performance of finned-tube heat exchangers under frosting conditions. *ASHRAE Trans.* **1990**, *96*, 439–444.
9. Adachi, K.; Saiki, K.; Sato, H. Suppression of frosting on a metal surface using ultrasonic vibrations. *ICE Tech. Rep. Ultrason.* **1998**, *98*, 9–12.
10. Bharathidasan, T.; Vijay Kumar, S.; Bobji, M.S.; Chakradhar, R.P.S.; Basu, B.J. Effect of wettability and surface roughness on ice-adhesion strength of hydrophilic, hydrophobic, and superhydrophobic surfaces. *Appl. Surf. Sci.* **2014**, *314*, 241–250. [\[CrossRef\]](#)
11. Highgate, D.; Knight, C.; Probert, S.D. Anomalous 'Fresszing' of water in hydrophilic polymeric structures. *Appl. Energy* **1989**, *34*, 243–259. [\[CrossRef\]](#)
12. Okoroafor, E.U.; Newborough, M. Minimizing frost growth on cold surfaces exposed to humid air by means of crosslinked hydrophilic polymeric coatings. *Appl. Therm. Eng.* **2000**, *20*, 737–758. [\[CrossRef\]](#)
13. Gong, J.Y.; Hou, J.Q.; Yang, L.W.; Wu, W.F.; Li, G.J.; Gao, T.Y. Mesoscopic investigation of frost crystal nucleation on cold surface based on the lattice-Boltzmann method. *J. Mech. Sci. Technol.* **2019**, *33*, 1925–1935. [\[CrossRef\]](#)
14. Liang, C.H.; Wang, F.; Lü, Y.; Yang, M.T.; Zhang, X.S. Experimental and theoretical study of frost melting water retention on fin surfaces with different surface characteristics. *Exp. Therm. Fluid Sci.* **2016**, *71*, 70–76. [\[CrossRef\]](#)
15. Li, L.T.; Wang, W.; Sun, Y.Y.; Feng, Y.C.; Lu, W.P.; Zhu, J.H.; Ge, Y.J. Investigation of defrosting water retention on the surface of evaporator impacting the performance of air source heat pump during periodic frosting-defrosting cycles. *Appl. Energy* **2014**, *135*, 98–107. [\[CrossRef\]](#)

16. Moallem, E.; Cremaschi, L.; Fisher, D.E.; Padhmanabhan, S. Experimental measurements of the surface coating and water retention effects on frosting performance of microchannel heat exchangers for heat pump systems. *Exp. Therm. Fluid Sci.* **2012**, *39*, 176–188. [[CrossRef](#)]
17. Wang, F.C.; Li, C.R.; Lv, Y.Z.; Lv, F.C.; Du, Y.F. Ice accretion on superhydrophobic aluminum surfaces under low-temperature conditions. *Cold Reg. Sci. Technol.* **2010**, *62*, 29–33. [[CrossRef](#)]
18. Liu, Z.L.; Gou, Y.J.; Wang, J.T.; Cheng, S.Y. Frost formation on a super-hydrophobic surface under natural convection conditions. *Int. J. Heat Mass Transf.* **2008**, *51*, 5975–5982. [[CrossRef](#)]
19. Zheng, J.F.; He, A.H.; Li, J.X.; Xu, J.; Han, C.C. Studies on the controlled morphology and wettability of polystyrene surfaces by electrospinning or electrospraying. *Polymer* **2006**, *47*, 7095–7102. [[CrossRef](#)]
20. Xu, B.; Han, Q.; Chen, J.P.; Li, F.; Wang, N.J.; Li, D.; Pan, X.Y. Experimental investigation of frost and defrost performance of microchannel heat exchangers for heat pump systems. *Appl. Engery* **2013**, *103*, 180–188. [[CrossRef](#)]
21. Xia, Y.; Zhong, Y.; Hrnjak, P.S.; Jacobi, A.M. Frost, defrost, and refrost and its impact on the air-side thermal-hydraulic performance of louvered-fin, flat-tube heat exchangers. *Int. J. Refrig.* **2006**, *29*, 1066–1079. [[CrossRef](#)]
22. Padhmanabhan, S.; Cremaschi, L.; Fisher, D. Comparison of frost and defrost performance between microchannel coil and fin-and-tube coil for heat pump systems. *Int. J. Air-Cond. Refrig.* **2011**, *19*, 273–284. [[CrossRef](#)]
23. Zhong, Y.F.; Joardar, A.; Gu, Z.P.; Park, Y.-G.; Jacobi, A.M. Dynamic dip testing as a method to assess the condensate drainage behavior from the air-side surface of compact heat exchangers. *Exp. Therm. Fluid Sci.* **2005**, *29*, 957–970. [[CrossRef](#)]
24. Joardar, A.; Gu, Z.; Jacobi, A.M. Off-Cycle Condensate Drainage Behavior of Compact Heat Exchangers: Assessment and Enhancement. In Proceedings of the International Refrigeration and Air Conditioning Conference at Purdue, West Lafayette, IN, USA, 17–20 July 2006.
25. Liu, L.P.; Jacobi, A.M. Issues affecting the reliability of dynamic dip testing as a method to assess the condensate drainage behavior from the air-side surface of dehumidifying heat exchangers. *Exp. Therm. Fluid Sci.* **2008**, *32*, 1512–1522. [[CrossRef](#)]
26. Boreyko, J.B.; Srijanto, B.R.; Nguyen, T.D.; Vega, C.; Fuentes-Cabrera, M.; Collier, C.P. Dynamic defrosting on nanostructured superhydrophobic Surfaces. *Langmuir* **2013**, *29*, 9516–9524. [[CrossRef](#)] [[PubMed](#)]
27. Cao, L.L.; Jones, A.K.; Sikka, V.K.; Wu, J.Z.; Gao, D. Anti-icing superhydrophobic coatings. *Langmuir* **2009**, *25*, 12444–12448. [[CrossRef](#)] [[PubMed](#)]
28. Cassie, A.B.D.; Baxter, S. Wettability of porous surfaces. *Trans. Faraday Soc.* **1944**, *40*, 546–551. [[CrossRef](#)]
29. Cassie, A.B.D. Contact angles. *Discuss. Faraday Soc.* **1948**, *3*, 11–16. [[CrossRef](#)]
30. Hobbs, P.V.; Rangno, A.L. Ice particle concentrations in clouds. *J. Atmos. Sci.* **1985**, *42*, 2523–2549. [[CrossRef](#)]
31. Wenzel, R.N. Resistance of solid surfaces to wetting by water. *Trans. Faraday Soc.* **1936**, *28*, 988–994. [[CrossRef](#)]
32. Wenzel, R.N. Surface roughness and contact angle. *J. Phys. Colloid Chem.* **1949**, *53*, 1466–1467. [[CrossRef](#)]
33. Yoshimura, Y.; Fukiba, K.; Sato, S. Heat transfer improvement of a cooling tube using a splitter plate under frosting condition. *Trans. JSRAE* **2016**, *33*, 221–230.
34. Miljkovic, N.; Wang, E.N. Condensation heat transfer on superhydrophobic surfaces. *MRS Bull. Mater. Res. Soc.* **2013**, *38*, 397–406. [[CrossRef](#)]
35. Wang, L.; Gong, Q.H.; Zhan, S.H.; Jiang, L.; Zheng, Y.M. Robust anti-icing performance of a flexible superhydrophobic surface. *Adv. Mater.* **2016**, *28*, 7729–7735. [[CrossRef](#)]

Publisher’s Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).