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Energy-Effective Frost-Free Coatings Based on Superhydrophobic Aligned Nanocones

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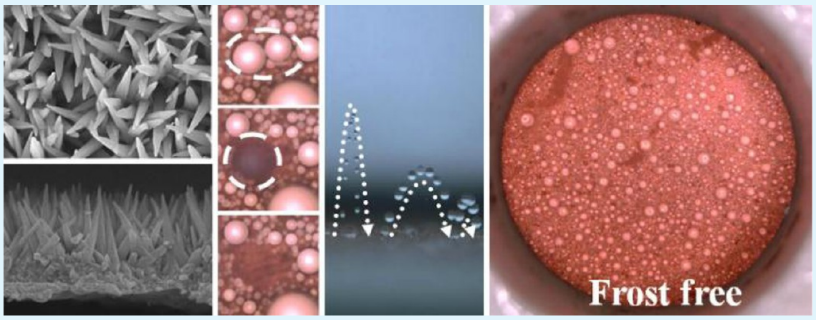
Supporting Information



ABSTRACT: We demonstrate the feasibility of superhydrophobic aligned nanocones as energy-effective frost-free coatings. Exemplified by $Co(OH)_2$ nanocone films with condensed microdrop self-removal ability, their edge and whole-surface frosting time can be delayed to about 10 and 150 min, respectively. By using a Teflon gasket to shield edges, the samples can keep frost-free state over 90 min. Further, the lasting frost-free state can be realized by intermittent weak airflow heating, which is energy-effective in contrast to usual high-power heating for defrosting flat surfaces. These findings are significant to develop antifrosting nanotechnologies for energy-effective heat exchangers such as heat pumps and refrigerators.

KEYWORDS: *antifrosting coatings, superhydrophobic, nanostructure, condensate jumping, energy effective, weak heating*

With the advance of bioinspired superhydrophobic nanotechnologies,[1−3] engineering surfaces that can prevent frost formation and accumulation in an energy-effective way has attracted great interest because of their significance in basic research and technological innovations. It is known that condensation frosting, i.e., formation of subcooled condensates and subsequent freezing into frost, inevitably occurs on subzero common metal surfaces under humid environments, which is undesired in daily life and industrial processes. For example, the frost formation and accumulation can dramatically degrade the heat transfer efficiency of heat pump and defrosting also consumes a large amount of energy.[4,5] Very recently, sporadic reports showed that superhydrophobic nanostructures[6] or hierarchical structures[7−9] with the self-propelled jumping ability of condensed microdrops can effectively retard frosting while superhydrophobic surfaces with impaled condensates[10−12] exhibit poor antifrosting effects (defrosting more difficultly)[13−15] in comparison with flat surfaces. However, it is still a great challenge to fully prevent the frost formation because of the inevitable occurrence of edge-induced interdrop freezing wave propagation across the entire surface.[6−9] To date, there is no report about energy-effective frost-free surfaces, especially suitable for metal substrates. Thus, we wonder if the frost-free surfaces can be realized by the delicate design of surface nanostructure and surface chemistry integrated with external energy-effective heating measures.

Here, we demonstrate that condensed microdrop self-propelling surface can be used as energy-effective frost-free coatings. Exemplified by superhydrophobic $Co(OH)_2$ nanocone films with the self-propelled jumping ability of condensed microdrops, in situ grown on copper foils, the frosting time at their edge and whole surface can be delayed to about 10 and 150 min, respectively. By using a Teflon gasket to shield edges, the samples can keep frost-free state over 90 min. Further, the lasting frost-free state can be realized by intermittent weak airflow heating, which is energy-effective in contrast to high-power heating commonly used for defrosting flat surfaces. These findings are significant to develop innovative antifrosting nanotechnologies for energy-effective heat exchangers such as heat pumps and refrigerators.

Figure 1a shows typical scanning electron microscopic (SEM) top-view (top) and side-view (bottom) of the as-synthesized brucite-type cobalt hydroxide aligned nanocone films, which can be obtained by immersing rinsed glass slides in

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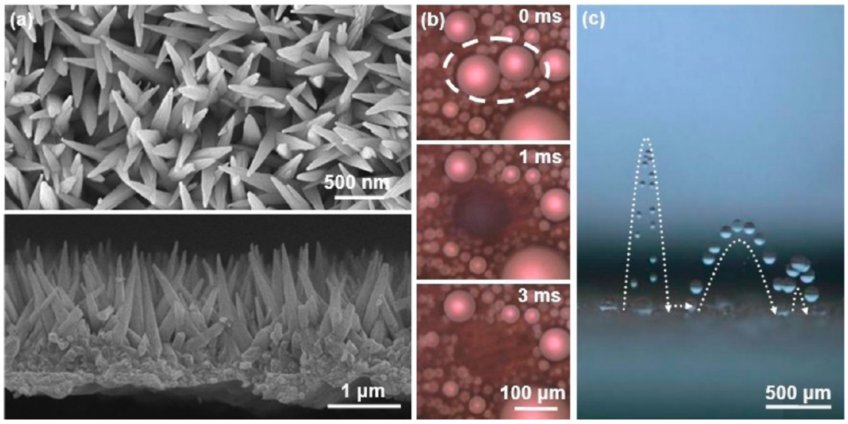

Figure 1. (a) SEM top-view (top) and side-view (bottom) of the as-synthesized cobalt hydroxide nanoneedle films. (b) Optical images showing the coalescence-induced self-removal of condensed microdrops on the nanostructured surface. (c) An overlapped optical image showing a continuous coalescence-induced jumping process of condensed microdrops, accompanied by its size scaling up. These optical images are captured at the controlled environment of T_{sub} = 1 °C, T_{air} = 25 °C, and RH = 90%.

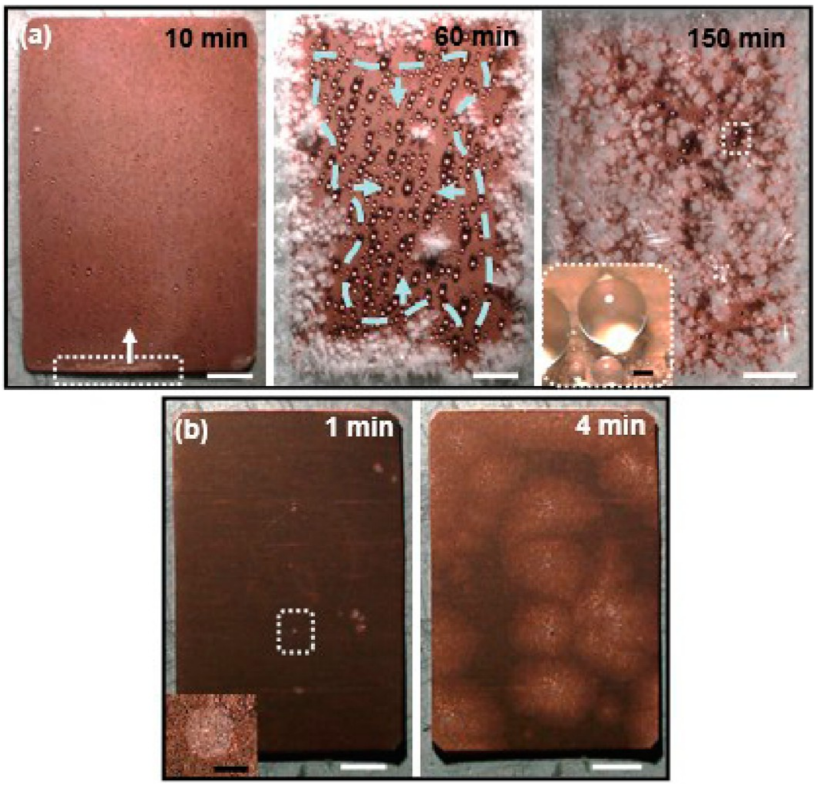

Figure 2. Time-lapse optical images of (a) nanostructured and (b) flat surfaces at the controlled environment of T_{sub} = −10 °C, T_{air} = 25 °C, and RH = 60%. The insets are spherical condensed microdrops and initially formed frost islands, corresponding to the dotted rectangle. Scale bar: 5 mm (white), 200 μm (black).

a mixed aqueous solution of 0.15 M $CoCl_2 \cdot 6H_2O$ and 0.33 M $(NH_2)_2CO$ at 60 °C for 11 h (see Experimental Section in the Supporting Information).[16] These nanocones are almost perpendicular to the substrate surface with average top diameters of 28 nm, end diameters of 188 nm, opening interspaces of 219 nm and heights of 1.9 μm, respectively. After modifying fluorosilane molecules, the aligned nanocone films show ideal quasi-static and dynamic superhydrophobic non-stickiness to macroscopic water droplets (see Figure S1 in the Supporting Information). However, condensed microdrops are still pinned on the surfaces because their diameters are far less than water capillary length (~2.7 mm) so that the gravitation effect is unavailable. Although the microdrops themselves are immobile via the traditional shedding-off way, they can self-remove by coalescence-induced out-of-plane jumping (Figure 1b), powered by excess surface energy released from mutual coalescence.[17−23] Note that the coalescence-induced jumping events can continuously occur on horizontally placed samples (Figure 1c).

Our measurement indicated that the as-synthesized super-hydrophobic aligned nanocone films indeed own remarkable antifrosting performance. As shown in Figure 2a, frost crystals can only emerge at the edge of the nanostructured surface of −10 °C after a relatively longer refrigeration period (around 10 min). Condensed microdrops at the central regions almost keep the liquid state and the frost crystals propagate inwardly at an extremely slow rate (~0.1 mm/min). Even as the refrigeration time extends to 150 min, the surface is still not fully covered by frost crystals. This is because that the inward frost crystal propagation on the nanostructured surfaces can be effectively inhibited by delaying the ice-bridging process based on the violent self-propelled jumping of condensed microdrops and evaporation-induced gaps between frozen droplets and condensed microdrops (see Figure S2 in the Supporting Information).[7,8] As a result, the formed frost layer is loosen, consisting of spicule-like crystals (see Figure S2c in the Supporting Information). Note that the frost wave propagation can also be induced by frost crystals randomly emerging in the central area, caused by the defects of locally larger voids distributed on the surface of nonaligned nanocones. In contrast, condensed microdrops on the hydrophobic flat surfaces freeze randomly within less than ~1 min once the substrate temperature is below zero because of the rapid liquid−solid phase transition (Figure 2b) and frost wave propagation (see Figure S2d in the Supporting Information). Subsequently, frost crystals can grow over the entire surface by both the direct condensation frosting and ice bridging within less than 5 min.

To understand such a remarkable antifrosting property, we explored the intrinsic antifreezing ability of the superhydrophobic aligned nanocone films. A sessile droplet (9 μL) is placed on the central region of nanostructured surface at substrate temperature (T_{sub}) of −10 °C and covered with a watch glass to reduce the influence of humidity, while the ambient temperature is ~25 °C. It is found that the droplet can maintain liquid state on the nanostructured surface until the refrigeration duration extends to 286 min (see Figure S3 in the Supporting Information), far higher than that in the previous reports.[24−26] Similarly, spherical condensed microdrops can also intrinsically maintain the liquid state under long-term refrigeration. It may be understood that the intriguing antifreezing performance of the aligned nanocone films is ascribed to the higher energy barrier of ice crystal nucleation caused by minimized nanotips[27,28] and the higher thermal resistance of thin films caused by the existence of stable air cushion.[24−26] However, frost crystals could inevitably form at the edge defects due to geometric singularity with low free energy barrier of heterogeneous nucleation.[6−9] Although the inward ice crystal propagation on the nanostructured surfaces can be slowed down by delaying the ice-bridging process based on the coalescence-induced self-propelling of condensed microdrops and evaporation-induced gaps between frozen droplets and condensed microdrops,[7,8] the frost still can grow over the entire surface by the edge-induced interdrop freezing wave propagation.

On the basis of the above analysis, we believe that the prevention of the edge-induced freezing events is crucial to maintain the frost-free state of the as-synthesized aligned nanocone films. In principle, microscopic building blocks at the sample edge show geometrical singularity nature so that there are more exposed lateral surfaces for condensation frosting at microscale.[6,8] In view of far higher energy barrier of frost crystal nucleation for hydrophobic flat surfaces in comparison with hydrophilic flat surfaces,[29] we suppose that the edge's side-effect of the superhydrophobic nanocoatings may be effectively delayed by employing edge shielding and hydrophobicization. To verify the feasibility of this idea, we briefly put a Teflon gasket with flat top and inner surfaces onto the nanostructured surface to shield the edge (Figure 3a). Remarkably, the onset time of frosting on the sample edge can be dramatically

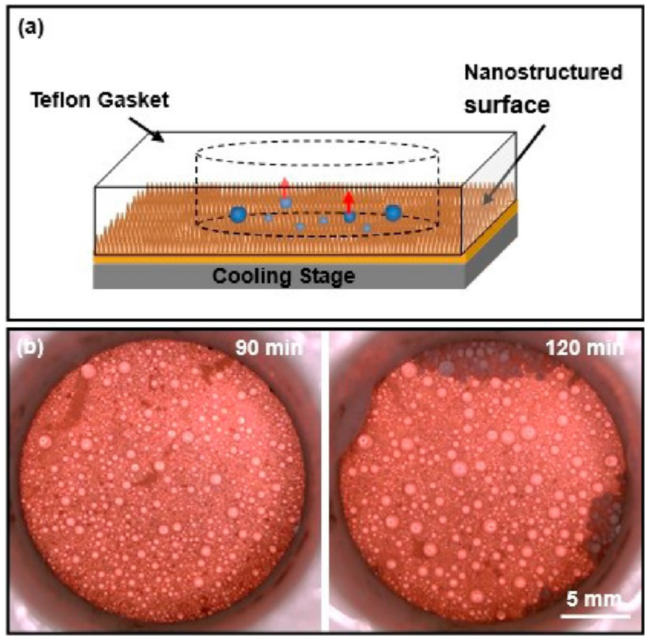

Figure 3. (a) Schematic of edge shielding of the nanostructured sample by covering a Teflon gasket. b) Optical top-view of the edge-shielding nanostructured sample at the refrigerated time of 90 min (left) and 120 min (right), respectively. Condensates can still keep the liquid state within 90 min while frozen microdrops near the circular junction emerge as the time extending to 120 min. They were taken in a controlled environment of T_{sub}= −10 °C, T_{air} = ~25 °C and RH = ~60%.

delayed, where no freezing event occurs and condensed microdrops are still in the liquid state within 90 min (Figure 3b). Compared with the previous reports, we present the longest frost-free state on superhydrophobic surfaces without any additional energy supply. However, the frosting event still inevitably occurs on the junction of the nanostructured surface and the Teflon gasket after longer time, e.g., observable frost is found in 120 min (Figure 3b).

Further, the aligned nanocone films may be frost-free by introducing low-energy-consumption heating, e.g., blowing intermittent airflow (21 °C, 3 m/s) for 1 min at the intervals of 9 min. After the first cycle of 9 min refrigerating test, only a small quantity of frost crystals emerged at the nanosample edge. Interestingly, after heating for 1 min, the loosen accumulation of frost crystals at the edge could instantly melt into mobile spherical droplets (Figure 4a). It is found in the experiments that with the times of frosting/defrosting cycles increasing, the edge-induced frost front propagation would be slightly aggravated, resulting in the larger frost crystal area around the edges (Figure 4b, c). We suppose that the residual big droplets of melting water around the edges may accelerate the inward propagation of frost crystals and microscopic capillarity during the process of frosting/defrosting repetition might also lead to the structural damage around the edges.[30] Even so, the nanostructured surfaces can still keep the "frost-free" state in longer duration, e.g., see the 12th cycle of tests as shown in Figure 4c. In contrast, a layer of dense frost crystals can easily accumulate on the hydrophobic flat surface after 9 min refrigerating and became thicker, rather than thinning

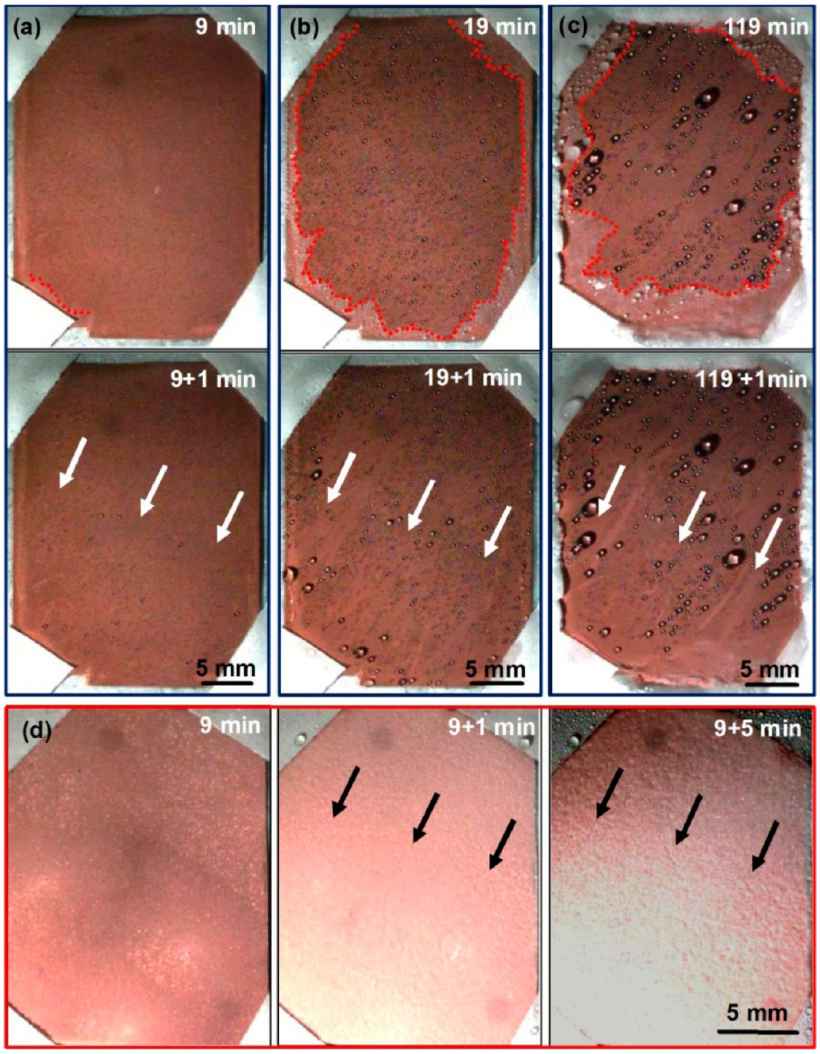

Figure 4. (a−c) Optical images showing the energy-effective frosting prevention of nanostructured surfaces under the 1st, 2nd, and 12th intermittent cyclic heating of airflow (21 °C, 3 m/s) for 1 min every 10 min. (d) Optical images showing that the aggravated frosting (rather than defrosting) of hydrophobic flat surfaces after airflow heating for 1 min (middle), even 5 min (right). The airflow direction is denoted as arrows. All samples are placed on the cooling stage of −10 °C during the whole test process.

(melting), after the same heating treatment for 1 min. Even as the heating time is elongated to 5 min, the frost layer covered on the entire surface still cannot be removed (Figure 4d). Clearly, such energy-effective frost-free nanocoating is highly desirable because the traditional energy-swallowed defrosting approach suitable for common hydrophobic surfaces or coatings requires long-term and high-power heating.[5] Besides, the previously reported defrosting approach based on the integrated detachment of frost blocks on the condensate jumping nanostructured surfaces[6,8] is not suitable for small-scale applications, e.g., heat pump equipped with millimeter-interspaced heat exchanger fins.[4]

We demonstrate that the condensed microdrop self-propelling surfaces, exemplified by the in situ grown super-hydrophobic cobalt hydroxide nanocones on the copper foils, can be used as energy-effective frost-free nanocoatings. Our studies revealed that the superhydrophobic aligned nanocone films have ideal intrinsic antifreezing ability to subcooled water droplets and thus controlling over the edge shielding can effectively prevent the condensation frosting within tens of minutes. Further, to fully avoid the condensation frosting, it is necessary to take the low-energy-consumption heating measures, where energy consumption is extremely low in comparison with the traditional energy-swallowed high-power heating approach. Therefore, these findings are significant to develop antifrosting coatings for energy-effective heat exchangers such as heat pumps and refrigerators.[4,5] It should be also pointed out that any nanostructure or hierarchical structure with condensed microdrop self-propelling functions may be used as effective candidates. Future research should be focused on the development of robust superhydrophobic coatings suitable for metal (e.g., copper and aluminum) substrates and investigation into the integral effects of practical energy-effective heating approaches toward different applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental Section, ideal superhydrophobicity to macroscopic water droplets (Figure S1), details about the frost front propagation on the nanostructured and the contrast flat samples (Figure S2), and striking intrinsic antifreezing ability of the nanostructured samples (Figure S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Wisdom, K. M.; Watson, J. A.; Qu, X. P.; Liu, F. J.; Watson, G. S.; Chen, C. H. Self-Cleaning of Superhydrophobic Surfaces by Self-Propelled Jumping Condensate. *Proc. Natl. Acad. Sci. U.S.A.* **2013**, *110*, 7992−7997.

(2) Yao, X.; Song, Y.; Jiang, L. Applications of Bio-inspired Special Wettable Surfaces. *Adv. Mater.* **2011**, *23*, 719−734.

(3) Gao, X.; Yan, X.; Yao, X.; Xu, L.; Zhang, K.; Zhang, J.; Yang, B.; Jiang, L. The Dry-Style Antifogging Properties of Mosquito Compound Eyes and Artificial Analogues Prepared by Soft Lithography. *Adv. Mater.* **2007**, *19*, 2213−2217.

(4) 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.

(5) Wang, W.; Xiao, J.; Guo, Q. C.; Lu, W. P.; Feng, Y. C. Field Test Investigation of the Characteristics for the Air Source Heat Pump under Two Typical Mal-Defrost Phenomena. *Appl. Energy* **2011**, *88*, 4470−4480.

(6) Boreyko, J. B.; Srijanto, B. R.; Nguyen, T. C.; Vega, C.; Fuentes-Cabrera, M.; Collier, C. P. Dynamic Defrosting on Nanostructured Superhydrophobic Surfaces. *Langmuir* **2013**, *29*, 9516−9524.

(7) Boreyko, J. B.; Collier, C. P. Delayed Frost Growth on Jumping-Drop Superhydrophobic Surfaces. *ACS Nano* **2013**, *7*, 1618−1627.

(8) Chen, X.; Ma, R.; Zhou, H.; Zhou, X.; Che, L.; Yao, S.; Wang, Z. Activating the Microscale Edge Effect in a Hierarchical Surface for Frosting Suppression and Defrosting Promotion. *Sci. Rep.* **2013**, *3*, 2515.

(9) Zhang, Q.; He, M.; Chen, J.; Wang, J.; Song, Y.; Jiang, L. Anti-Icing Surfaces Based on Enhanced Self-Propelled Jumping of Condensed Water Microdroplets. *Chem. Commun.* **2013**, *49*, 4516−4518.

(10) Zheng, Y.; Han, D.; Zhai, J.; Jiang, L. In Situ Investigation on Dynamic Suspending of Microdroplet on Lotus Leaf and Gradient of Wettable Micro- and Nanostructure from Water Condensation. *Appl. Phys. Lett.* **2008**, *92*, 084106.

(11) Wier, K. A.; McCarthy, T. J. Condensation on Ultrahydrophobic Surfaces and Its Effect on Droplet Mobility: Ultrahydrophobic Surfaces are Not Always Water Repellant. *Langmuir* **2006**, *22*, 2433−2436.

(12) Lafuma, A.; Quéré, D. Superhydrophobic States. *Nat. Mater.* **2003**, *2*, 457−460.

(13) Jung, S.; Dorrestijn, M.; Raps, D.; Das, A.; Megaridis, C. M.; Poulikakos, D. Are Superhydrophobic Surfaces Best for Icephobicity? *Langmuir* **2011**, *27*, 3059−3066.

(14) Varanasi, K. K.; Deng, T.; Smith, J. D.; Hsu, M.; Bhate, N. Frost Formation and Ice Adhesion on Superhydrophobic Surfaces. *Appl. Phys. Lett.* **2010**, *97*, 234102.

(15) Kulinich, S. A.; Farhadi, S.; Nose, K.; Du, X. W. Superhydrophobic Surfaces: Are They Really Ice-Repellent? *Langmuir* **2011**, *27*, 25−29.

(16) Hosono, E.; Fujihara, S.; Honma, I.; Zhou, H. Superhydrophobic Perpendicular Nanopin Film by the Bottom-Up Process. *J. Am. Chem. Soc.* **2005**, *127*, 13458−13459.

(17) Boreyko, J. B.; Chen, C. H. Self-Propelled Dropwise Condensate on Superhydrophobic Surfaces. *Phys. Rev. Lett.* **2009**, *103*, 184501.

(18) Chen, C. H.; Cai, Q.; Tsai, C.; Chen, C. L.; Xiong, G.; Yu, Y.; Ren, Z. Dropwise Condensation on Superhydrophobic Surfaces with Two-Tier Roughness. *Appl. Phys. Lett.* **2007**, *90*, 173108.

(19) Chen, X.; Wu, J.; Ma, R.; Hua, M.; Koratkar, N.; Yao, S.; Wang, Z. Nanograssed Micropyramidal Architectures for Continuous Dropwise Condensation. *Adv. Funct. Mater.* **2011**, *21*, 4617−4623.

(20) Feng, J.; Pang, Y.; Qin, Z.; Ma, R.; Yao, S. Why Condensate Drops Can Spontaneously Move Away on Some Superhydrophobic Surfaces but Not on Others. *ACS Appl. Mater. Interfaces* **2012**, *4*, 6618−6625.

(21) Feng, J.; Qin, Z.; Yao, S. Factors Affecting the Spontaneous Motion of Condensate Drops on Superhydrophobic Copper Surfaces. *Langmuir* **2012**, *28*, 6067−6075.

(22) He, M.; Zhang, Q.; Zeng, X.; Cui, D.; Chen, J.; Li, H.; Wang, J.; Song, Y. Hierarchical Porous Surface for Efficiently Controlling Microdroplets' Self-Removal. *Adv. Mater.* **2013**, *25*, 2291−2295.

(23) Nam, Y.; Kim, H.; Shin, S. Energy and Hydrodynamic Analyses of Coalescence-Induced Jumping Droplets. *Appl. Phys. Lett.* **2013**, *103*, 084106.

(24) Guo, P.; Zheng, Y.; Wen, M.; Song, C.; Lin, Y.; Jiang, L. Icephobic/Anti-Icing Properties of Micro/Nanostructured Surfaces. *Adv. Mater.* **2012**, *24*, 2642−2648.

(25) Tourkine, P.; Le Merrer, M.; Quéré, D. Delayed Freezing on Water Repellent Materials. *Langmuir* **2009**, *25*, 7214−7216.

(26) He, M.; Wang, J.; Li, H.; Song, Y. Super-Hydrophobic Surfaces to Condensed Micro-Droplets at Temperatures below the Freezing Point Retard Ice/Frost Formation. *Soft Matter* **2011**, *7*, 3993−4000.

(27) Liu, X. Y. A New Kinetic Model for Three-Dimensional Heterogeneous Nucleation. *J. Chem. Phys.* **1999**, *111*, 1628.

(28) Cao, L.; Jones, A. K.; Sikka, V. K.; Wu, J.; Gao, D. Anti-Icing Superhydrophobic Coatings. *Langmuir* **2009**, *25*, 12444−12448.

(29) Na, B.; Webb, R. L. A Fundamental Understanding of Factors Affecting Frost Nucleation. *Int. J. Heat Mass Transfer* **2003**, *46*, 3797−3808.

(30) Wang, Y.; Xue, J.; Wang, Q.; Chen, Q.; Ding, J. Verification of Icephobic/Anti-Icing Properties of a Superhydrophobic Surface. *ACS Appl. Mater. Interfaces* **2013**, *5*, 3370−3381.