Sprayable superhydrophobic nano-chains coating with continuous self-jumping of dew and melting frost

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Spontaneous movement of condensed matter provides a new insight to efficiently improve condensation heat transfer on superhydrophobic surface. However, very few reports have shown the jumping behaviors on the sprayable superhydrophobic coatings. Here, we developed a sprayable silica nano-porous coating assembled by fluorinated nano-chains to survey the condensates’ dynamics. The dewdrops were continuously removed by self- and/or trigger-propelling motion due to abundant nano-pores from random multilayer stacking of nano-chains. In comparison, the dewdrops just could be slipped under the gravity effect on lack of nano-pores coatings stacked by silica nano-spheres and nano-aggregates. More interestingly, the spontaneous jumping effect also occurred on micro-scale frost crystals under the defrosting process on nano-chains coating surfaces. Different from self-jumping of dewdrops motion, the propelling force of frost crystals were provided by a sudden increase of the pressure under the frost crystal.

In real-world, formation and accumulation of dew and frost cannot be avoided on cold surfaces. As a consequence, the heat transfer efficiency was significantly impeded in energy conversion fields. In order to effectively restrain dewing and frosting on the solid-gas interface, water repellent films were largely designed because of high potential barrier for condensate nucleation. In recent years, condensed dewdrops self-ejecting (CDSE) effect was mainly developed on superhydrophobic surfaces to significantly enhance the heat transfer and dewing/frosting resistance. Evidences from the literatures suggest that rough nanostructure of the surfaces with CDSE effect were first constructed by two-tier micro-nano composite structures. Subsequently, the CDSE phenomena were also observed on treated metal surfaces, such as schistose porous Al(OH)3 films, oxidized Cu surface and electrodeposing nano-particles. Then, nano-arrays, assembled by carbon nano-tubes, ZnO nano-needles, polymer nano-cone or Al nanorods, were also reported to obtain the CDSE surfaces. In order to make superhydrophobic surfaces more widely used on various substrates, a commercial coating agent was poured on the smooth silicon wafer to characterize the CDSE effect. Therefore, it is necessary to develop a simple yet versatile approach for assembly of CDSE surfaces for application in energy saving.

Based on the principle of CDSE effect, if two or more micro-drops coalescence, the gain in surface energy was partially transferred into kinetic energy. CDSE behaviors were triggered when the adhesion force is low enough.
between the droplet and the surface. Herein, we propose that CDSE surfaces may be assembled by catenulate silica nano-particles, which is inspired by carbon nano-tubes and cerium oxide porous nanoparticles. To confirm this opinion, we fabricated the superhydrophobic coating by one-step spray methods from nano-chains, nano-spheres and nano-aggregates paints respectively for comparison of condensation performances. For another, self-propelling motion of isolated droplets or particles also could be triggered by unbalanced pressure. Thus, we designed a frosting-defrosting process to achieve local high-pressure under the frost crystal on the nano-chains coating for observation of the melting frost self-ejecting (MFSE) motion.

Results and Discussions

Coatings preparation. Sprayable paint of fluorinated silica nano-chains (F-chains) were fabricated according to literature. A spray painting apparatus equipped with S-130 airbrush (U-STAR, nozzle diameter of 0.3 mm) and U-601G gas compressor (U-STAR, 20 psi) was used to spray the paint on cleanly substrate for acquisition of superhydrophobic surfaces. The airbrush was moved (about 0.1 m·s$^{-1}$) maintaining about 10 cm distance and according to an S-style spray route from top to bottom. This process could control the thickness (5–10 μm) of the coating by spray-steps. Figure 1a displays that the F-chains coating was assembled by single-layer reticulated-like structure in the initial stage, which is interlocking by a nature of soft string-of-pearls structure with diameter of ~15 nm and length of ~80 nm (More details see Supporting Information, Figure S1). After spray painting, nano-porous foam-like coating was obtained by random multilayer stacking of nano-chains (Fig. 1b)). In contrast, we also fabricated the superhydrophobic paints using mono-dispersed silica nano-spheres (F-spheres) or fumed silica nano-aggregates (F-aggregates) to replace nano-chains. Figure S2a–c shows that the F-spheres with diameter of ~100 nm (More details see Supporting Information, Figure S1) only developed a close-packed stacking structure. Similarly, the F-aggregates coating with small amounts of nano-pores was stacked by the irregular cluster with size of ~100 × 200 nm (More details see Supporting Information, Figures S1 and S2e–f)). All of above paints were sprayed on various hard and soft substrates to fabricate superhydrophobic surfaces and their superhydrophobicity has no significant difference if measured by macroscopic water droplet. For F-chains coating, static water contact angles (SCAs) of over 160° and roll-off angles (RAs) of under 4° were demonstrated (More details see Supporting Information, Figure S3). Moreover, the substrates could repel the impacting water droplet by bouncing off due to the Cassie-Baxter state of superhydrophobicity (Fig. 1c, More details see Supporting Information, Video S1). However, it still needs further investigation whether the micro-drops can maintain the Cassie-Baxter state on the surfaces with above different coatings.

Condensation performance of dewdrops. To investigate the condensation performance on the F-chains surface, we used conventional condensation test on a cooling stage at the controlled environment. Here, condensation tests were carried out on polished copper sheet with size of 25 × 25 mm after spray-coated by nano-particle coating. Figure 2a shows the coalescence and self-expulsion processes of several adjacent condensed micro-drops without any external force (More details see Supporting Information, Video S2). Two types of CDSE phenomena...
were observed: 1) the dewdrops were firstly nucleated on the tops of F-chains coating and then growing by the Cassie-Baxter mode; the two or more droplets finally jumped out their original position after contacting and merging (Fig. 2b, More details see Supporting Information, Video S3) due to the vapor emitted by neighboring droplets41; 2) a collision could be triggered between falling droplet after ejected and static dewdrop (Fig. 2c), More details see Supporting Information, Video S4). In the past, we always focus on the self-jumping motion on the superhydrophobic surface, but pay no attention to the continuous trigger-jumping motion as an important role for rapidly propulsion of dewdrops, which is significant to more efficaciously maintain the surface as dry as possible at the condition of dewing. Intelligibly, apart from excess surface energy, the trigger-jumping effect will get more energy from surplus kinetic energy after collisions (Fig. 2d)23. Thus, the trigger-jumping behavior not only formed higher droplet velocity for accelerated removal of dewdrops, but also expedited increase of the size of droplet to easily depart from the surfaces.

Based on the continuous and periodical CDSE function on F-chains coating (More details see Supporting Information, Video S5), we also examines the statistical parameters of condensed micro-drops on a horizontal cooling stage. The coverage, numbers of unit and distribution of dewdrops on F-chains surfaces charged with times were shown in Fig. 2(e) and (f). The nucleation and growth of the condensed droplets were mainly developed at 0–200 s. At 200 s, the dimension of droplets is below 5 μm with low coverage rate (lower than 20%) and the CDSE behaviors were only detected in tiny region. When the size is growing to 10–50 μm after 400 s, the
CDSE phenomena have significantly increased. After 600 s, the CDSE effects reached the prosperous stage and various statistics of dewdrops keeping in a dynamic equilibrium. However, condensation test shows that the CDSE phenomenon was not found on the F-spheres and F-aggregates coatings although they have excellent superhydrophobicity. To further demonstrate the CDSE characteristic, we examined the morphological changes of dewdrops by environmental scanning electron micrograph (ESEM). Figure S4(a) suggests that the adjacent droplets with diameters of ~10–50 μm on the F-chains coating deviated from their original position to out of sight and presented a dry areas. Subsequently, new condensed micro-drops will nucleate again on the same location after previous droplets vanish, then the merged and jumped behaviors were surveyed again when new droplets grew to ~27 μm. Such periodical process of nucleating, growing, merging and disappearing on the same place will sequentially guarantee the statistical parameters of condensed micro-drops in dynamic equilibrium. However, we only caught the continuous consolidation process with non-jumping effect on the F-spheres and F-aggregates coatings. Figure S4(b) performed that the diameters of a dewdrop constantly increase from 18 μm to 120 μm on the F-aggregates coating. The results suggest that nano-porous structure formed by interlaced nano-chains will conducted to enhance CDSE effect on superhydrophobic surface.

MFSE motion of frost crystal. Evaporation could provide the propelling force for spontaneous movement of droplets or particles under a condition of unbalanced air pressure. In the past, the environment with vacuum39 and/or high-temperature40 was used to build the condition of low-vacuum and/or low-humidity. Inspired by this, we attempted to fabricate local environment with low-vacuum and low-humidity by a frosting process. It is well known that the frosting could not be completely restrained under super-cooling conditions44 although the CDSE behaviors provided a highly effective method to suppress it46. The environment with low-vacuum and/or low-humidity would be obtained under the frost crystal once it was formed on the nano-porous films. Now, partial vaporization was released from the frost crystal to keep the pressure balance. Then, if we rapidly elevated the temperature of substrate, the accumulated low-temperature vapor was quickly expanded to form a high-pressure for provision of propelling force.

Here, we performed the frosting-defrosting test on a cooling stage. We firstly reduced the temperature of the cooling stage to −20 °C for 20 min to insure the frost covered all the cooled surfaces. And then the temperature was rapidly increased (5 °C/s) to 20 °C for adequate defrosting. Figure 3(a) catches the defrosting process on the F-chains coating. The frost crystals were fast removed less than 30 seconds and leaving a dry surface without any evidence of damage. As shown previously38, a lubricating layer could be formed between the frost and the superhydrophobic surface before the shrinkage deformation of the frost crystal. To further demonstrate the existence of lubricating layer, we examined the dynamics of defrosting on the micro-scale. As expected, the MFSE behavior was captured on the F-chains film during the defrosting stage. Figure 3(b) displays that an irregular frost crystal with sectional dimension is ~50 × 60 μm completely departed from the substrate with self-rotation and disappeared in perspective after 8 ms. The other one with diameter of ~31.8 μm jumping up from the surface by an initial velocity is 0.1 m/s without any external force (Fig. 3(c)). The frost crystal finally landed in another
Figure 4. Relationship between the initial velocity and the value of \( \tau \). Inset: Schematic illustrations of the like-champagne cork motion model. Firstly, a sufficient pressure were obtained at the bottom surface of the frost crystal. Then, the pressure provides a propelling force for movement of the solid until it depart from the superhydrophobic surface. Finally, the escaped frost crystal gains the initial kinetic energy from the locomotion process before the vapor could diffuse from some aperture. Here, we assume the self-propelling pressure keeps invariant and the internal vapor will be diffused immediately before and after the frost crystal leave the coating surface, respectively.

\[
F_p = F_{int} - F_{atm} - G - F_w
\]

(1)

where, \( F_{int} \) and \( F_{atm} \) are the force respectively from internal and atmospheric pressure (\( P_{int} \) and \( P_{atm} \)) at the bottom and top of the frost crystal, \( F_{int} = P_{int} A \), \( F_{atm} = P_{atm} A \), \( A \) is the solid-liquid contact area, \( G \) is the gravity and \( F_w \) is wetting force from viscosity. Under the standard condition, we obtained the internal pressure \( P_{int} = P_{int-max} \) at the bottom surface of the frost crystal, a sudden increase of pressure provides the initial kinetic energy (\( \Delta P = P_{int} - P_{int-min} \)) under the frost crystal before jumping.

\[
P_{int-min} = P_{atm} + 4\gamma_{LV}/\rho_{f} \sqrt{D_0/2}
\]

(2)

To further discuss the relationship between initial velocity \( v_0 \) and the self-propelling pressure (\( \Delta P = P_{int} - P_{int-min} \)), we propose the like-champagne cork motion model (Fig. 4). The vapor were accumulated at the bottom surface of the frost crystal, a sudden increase of pressure provides the initial kinetic energy (\( E_0 = \rho AH \gamma_{LV}^{3/2} \)) of the moving solid, \( \rho \) and \( H \) is the mass density and height of the frost crystal. We propose that the frost crystal will lost the propelling pressure when it leave the nano-porous coating after motion \( h \) distances (\( \Delta E_0 = \Delta P h \)). On the basis of the law of conservation of kinetic energy (\( E_0 = \Delta E_0 \)), we could write the dynamic equation as

\[
v_0 = \sqrt{\frac{2\Delta P}{\rho}}
\]

(3)

where, \( \tau \) is defined as the ratio of \( h \) and \( H \), \( \rho = 0.9 \text{ g/cm}^3 \) is the density of the frost crystal. Figure 4 plots the changing tendency of \( v_0 \) with the increase of the \( \tau \) from 0.001 to 0.1 under the self-propelling pressure of 1, 3, 5, and 7.1 kPa.

Conclusions

In this paper, we prepared superhydrophobic coatings by spray-coating silica paint to investigate micro-scale dew and melting frost continuous spontaneous jumping behaviors. F-chains coating with nano-porous structure shows continuous micro-drops motion behaviors. Similar to previous reports, the CDSE effects were mainly observed when the size of dewdrops is growing to 10–50 \( \mu \text{m} \). Over 80% of micro-drops maintaining below 10 \( \mu \text{m} \) on the F-chains coating even after condensation for 1000 s. However, the CDSE effects were not found on the
F-spheres and F-aggregates silica coating due to lack of nano-pores. This striking property shows that construction of nano-porous is an effective mean to reduce the solid-liquid adhesion to guarantee the CDSE motion after merging. For another, the spontaneous jumping behaviors were not only triggered by the release of excess surface energy, but also promoted by unbalanced air pressure. We successfully designed a frosting-defrosting test to control the internal pressure under the frost crystal for expression of MFSE motion. The micro-scale frost crystal with size of ~50 μm deviated from their original position without any external force. These findings are significant to develop novel feasible superhydrophobic surfaces for effective elimination of micro-scale dew and melting frost, which could be extensively applied in the heat transfer equipment and self-cleaning surface.

Methods

Materials. SiO₂ sol containing with 15 wt.% SiO₂, nano-chains or 30 wt.% mono-disperse SiO₂, nano-spheres were referred by Nissan Aggressive Chemicals, Ltd. Fumed SiO₂, nano-aggregates were provided by WenhuaChem co., Ltd. 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane (PFDTES) were purchased from Sikang New Material Co., Ltd. Absolute ethyl alcohol (EtOH), deionized ammonium hydroxide (28%), tetraethyl orthosilicate (TEOS), acetone, n-butyl acetate, and other chemical reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. To remove oil contamination and oxidation film on the surface of substrate, copper sheets were orderly immersed with ultrasonic for 10 min under acetone, hydrochloric acid solution (2 mol·L⁻¹), deionized water, and EtOH. Glasses, ceramic, and polyvinyl chloride (PVC) substrates were washed by detergent, deionized water and EtOH, successively. Finally, all the above substrates were dried by blower with cold air. Other substrates were used fresh samples directly, such as wood, polyethylene terephthalate (PET), paper, and cloth.

Characterizations. The microstructure of sample surfaces were observed by field-emission scanning electron microscopy (FESEM) and atomic force microscope (AFM), which was conducted with Sirion and Dimension ICON (Nanosurf). Particle and Particle Systems Characterisation 31, 763–770 (2014). The microstructure of sample surfaces were observed by field-emission scanning electron microscopy (FESEM) and atomic force microscope (AFM), which was conducted with Sirion and Dimension ICON (Nanosurf). Particle and Particle Systems Characterisation 31, 763–770 (2014).

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**Author Contributions**

Y.Z. and S.W. conceived the initial idea of this research. Y.Z., X.Y. and C.L. guided the work. S.W. and W.Z. fabricated, functionalized, and characterized the experimental samples. S.W. and Y.Z. collected and analyzed the data. All authors were responsible for writing the paper and have given approval to the final version of the manuscript.

**Additional Information**

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