Droplet bouncing on hierarchical branched nanotube arrays above and below the freezing temperature

Yue Chen^{1,2}, Yuanxiang Fu², Jin Huang¹, Zhiyong Luo², Dongchuan Mo^{2*}, Shushen Lyu^{2*}

1 School of Materials and Energy, Guangdong University of Technology

2 School of Chemical Engineering and Technology, Sun Yat-sen University

*Corresponding Author: Shushen Lyu, E-mail address: lvshsh@mail.sysu.edu.cn, Fax: +86 20

84112150. Dongchuan Mo, E-mail address: modongch@mail.sysu.edu.cn.

Abstract: In this work, we investigate the droplet bouncing on the hierarchical branched nanotube (BNT) arrays surface above and below 0 °C. By anodization, we fabricate large-area arrays of BNT with the BNT spacing controlled from adjacent to sparse. We evaluate the influence of the BNT spacing on the droplet bouncing. The adjacently distributed BNT (A-BNT) outperforms the sparsely distributed BNT (S-BNT). We find that the A-BNT can repel up to 3.1 m/s droplet at 20 °C and 2.3 m/s droplet at -18 °C, while the maximum bouncing velocity on the S-BNT is below 2.3 m/s at 20 °C and below 0.9 m/s at -10 °C. For the bouncing on the supercooled A-BNT surface, the droplet bouncing contact time increases as the substrate temperature decreases for the same droplet velocity, while the bouncing contact time decreases as the droplet velocity increases for the same substrate temperature. We discuss the influence of the nanosized air cushion entrapped amid the branched-arms of the BNT on the three-phase contact line on the BNT walls and bouncing performance under supercooled conditions.

Keywords: branched nanotube, superhydrophobic, anodization, impact, anti-icing

1. Introduction

Superhydrophobic interface has attracted intense interest due to its promising applications in self-cleaning[1,2], dropwise condensation[3,4] and anti-icing[5-7]. The surface texture and the surface chemistry play a synergistic role in determining the surface wettability[8]. By rational design of the roughness features and their distribution, air cushion can be effectively entrapped in the interstices amid the surface texture, forming the Cassie-Baxter contact with the droplet and showing superhydrophobic properties[8,9]. Now, great progress has been made in design of micro/nano- textured surface to achieve superhydrophobicity under static condition[10-21]. We also notice that, increasing efforts are dedicated to investigate the water repellent performance under harsher conditions, like subjected to droplet impact[22-25] or under supercooled condition[26-31], which are usually encountered in the applications. Rational design of the surface texture to maintain superhydrophobicity under impacting and supercooled conditions is attractive and demanding.

The surfaces decorated with multiscale (micro- and nanoscales) hierarchical roughness show exciting performance of water repellency as subjected to conditions of droplet impact and below the freezing temperature. McCarthy et al.[32] showed that the hierarchical surface composed of nanostructured decorated micro-pillars arrays could resist droplet impacting at 4.3 m/s. Maitra et al.[28] reported that, the hierarchical surface composed of titanium nanowires decorated micro-pillars arrays showed droplet rebound at -30 °C for impact velocity of 2.6 m/s. The nanosized geometry element of the multi-tier texture might resist complete impalement by the impacting droplet, keeping intact air cushion between the liquid and the solid surface.

The geometry-controllable TiO₂ nanotube arrays (TNTAs) can be fabricated by anodization[33-35]. The as-prepared TNTAs surface is superhydrophilic, but can be turned into superhydrophobic after modification by low energy functional groups. The adhesion of the TNTAs can be controlled[10,12,36]. The modified TNTAs surfaces show promising performance in fields of anti-icing[10], wetting switchable surface[36]

and control drug release[37]. Despite of these achievements, the study of fabrication of nanotube arrays with desirable geometry and its superhydrophobicity is still needed.

In this work, we fabricate large-area arrays of BNT with the BNT spacing ranging from sub-micron to microns. We investigate the droplet bouncing on the superhydrophobic BNT surfaces with different BNT spacing. We evaluate the performances of the adjacently distributed BNT (A-BNT) and the sparsely distributed BNT (S-BNT) above and below 0 °C. We find that the A-BNT can repel up to 3.1 m/s droplet at 20 °C and 2.3 m/s droplet at -18 °C, while the maximum bouncing velocity on the S-BNT is below 2.3 m/s at 20 °C and below 0.9 m/s at -10 °C. We propose that the nanosized gaps between the branched-arms of the BNT entrap stable air cushion against infiltration of the impacting droplet, resulting in curved and discrete three-phase contact line (TCL) on the BNT walls, and finally decreasing the de-wetting resistance of the droplet bouncing.

2. Experimental section

2.1 Fabrication and morphology characterization of the BNT. Titanium foil with 0.3 mm thick was polished by the polishing-cloth, then successively cleaned by deionized water, acetone and deionized water in an ultrasonic bath, and finally dried by the nitrogen gas. Then, the Ti foil was anodized at 80 V (supplied by a DC power) with a round surface of 2 cm diameter exposed to the electrolyte, using a two-electrode configuration with a piece of lead plate as the counter electrode. The distance between the anode and the cathode was 1 cm. The anodization reactor was airproofed with polyethylene membrane and kept in a 25 °C bath during the anodization. The hydrofluoric acids used for the anodization experiments contain 40 wt.% HF. The surface morphology of the sample was characterized by a scanning electron microscopy (FEI Quanta 400 FEG). The as-prepared BNT was dried in the ambient air, and then stored in a glass drier. X-ray photoelectron spectroscopy (XPS) analysis was performed with two separate systems equipped with monochromatic Al

K- α sources (ESCALab250, USA) to analyze the chemical composition of the samples.

2.2 Contact angle measurement. The apparent contact angle (θ_{apparent}) measurement was conducted by the sessile drop method using a contact angle goniometer (OCA20). The sample was placed on a leveled sample table. Controlled volume (4 μL) of deionized water droplet was gently deposited on the sample surface by a micropipette. The image of the droplet on the sample surface was recorded, and the contact angle was measured by processing the captured images with the ImageJ software. The advancing and receding contact angles were recorded when water was added to and withdraw from the water droplet with the syringe respectively.

2.3 Droplet impact experiment. The droplet impact was carried out at room temperature (20 °C) and on the supercooled substrates. The collision droplet was formed using the pendant drop method, viz. 5 μL water was manually pushed through a micropipette until it detached under its own weight from the pre-determined height. The tip of the micropipette was equipped with a PTFE needle. The dynamic of the drop impact was recorded by a high-speed camera (Phantom V211 from Vision Research) at the frame rate of 10,000 Hz with a shutter speed of 2.0 μs . The impact velocity of the droplet was determined as follow: We recorded 15 frames of the instantaneous images of the dropping droplet just before the collision, measured the moving distance and calculated the terminal velocity (impact velocity).

The custom-built cold stage was used to cool and maintain the samples below the freezing temperature for the supercooled impact experiments. The temperature of the custom-built cold stage was controlled by a Peltier combined with a thermostat. The setups were placed in a chamber with humidity adjusted by the inlet pipe which can supply nitrogen gas, water vapor and their mixture. **For the droplet impact experiments on the cold substrates, the flow of nitrogen gas was used to keep the environment in the chamber dry (less than 5 % relative humidity).**

2.4 Infrared (IR) thermo-imaging analysis. The IR camera (FLIR SC325) with a recording frame rate of 30 Hz was used to perform the IR thermo-imaging analysis. The IR camera was positioned at a distance of ~0.1 m from the sample surface. The angle between the camera and the surface normal of the sample was maintained at 20°. Next to the nanotubes zone, a piece of 0.1 mm thick black tape (its emissivity is calibrated to be 0.96) was attached to the surface to monitor the substrate temperature. The emissivity of the A-BNT interface was calibrated to be 0.66. The emissivity of the water (in liquid or ice state) was determined to be 0.96 in the present study.

3. Results and discussion

3.1 Fabrication of the BNT and tailoring the BNT spacing

The branched nanotube arrays are fabricated by anodization of titanium in the ethylene glycol based electrolyte containing HF acid and water. Initially in the anodization, sparsely distributed TiO₂ nanotube arrays are formed on the anodic surface with each nanotube having an open-mouth orienting upwards and a closed-bottom buried[34,35]. Subsequently, each nanotube grows inwards the substrate with one tube splitting into two, forming the branched-tube structure. If prolonging anodization, several generations of splitting may occur, resulting in the hierarchical branched-tube structure. Notably, by manipulating the dissolution etching effect of the electrolyte, the BNT density as well as the center-to-center spacing of the BNT can be controlled. For example, by adjusting the HF acid content of the electrolyte from 1.0 wt.% to 4.0 wt.%, the average center-to-center spacing of the BNT can be controlled from sub-micron to several microns, with the thickness of the BNT varying from 4.9 μm to 2.9 μm, as shown in Figure 1. And, by adjusting the water content from 16.0 wt.% to 17.0 wt.% in the electrolyte containing 4.0 wt.% HF acid, the average center-to-center spacing of the BNT varies from sub-micron to microns scale, with the thickness of the BNT being 3.2~3.5 μm, as shown in Figure 2.

Figure 2 presents the schematic drawing and the SEM images of the A-BNT and the S-BNT, the BNT spacing of which are sub-micron and microns, respectively.

Based on the SEM images, we measured the geometrical parameters. The detailed geometrical parameters are summarized in Table 1 and indicated in Figure 2(a) and 2(b). For the S-BNT, the nanoporous layer is grown on the substrate between the BNT, with ~ 200 nm diameter cavities embedded, as shown in Figure 2(f). For both the A-BNT and the S-BNT, the inner diameter of the open mouth of the BNT is about 280 nm in average. Notably, for the A-BNT, the gaps between the branch-arms of the BNT are tens of nanometers in width, which can be evidenced in Figure 2(e) and 2(g).

Table 1. The geometrical parameters for the adjacently distributed BNT (A-BNT) and the sparsely distributed BNT (S-BNT). The geometrical parameters are indicated in Figure 2.

geometrical parameter	A-BNT	S-BNT
average BNT center-to-center spacing, p	sub-micron	microns
average gap between the branched-arms of BNT (nm), w	~ 66	~ 83
average cavity diameter of the porous layer (nm), d_c	-	~ 200
average BNT inner diameter (nm), d_i	~ 280	~ 280
average wall thickness (nm), δ	~ 25	~ 25
average thickness of BNT (μm), l	~ 3.5	~ 3.2
tube density of the BNT (tube/mm^2), T	$\sim 2.8 \times 10^6$	$\sim 6.8 \times 10^5$
calculated wetted-area-fraction for Cassie state droplet, ϕ_s	19%	11%

3.2 Superhydrophobicity after the storage

The as-prepared BNT surfaces are superhydrophilic. We stored the BNT surfaces in a glass-dryer containing silica gel to turn the samples into superhydrophobic. As is shown in Figure S1, the apparent contact angle (CA) raises upon storage, and finally reaches 150° and levels off. The increase in CA might due to the surface adsorption of

the airborne carbonaceous species during the storing process[38]. For the A-BNT, the CA is 152°; and the CA for the S-BNT is 159°. We propose that the gently-deposited droplet rests on the top of the BNT without significantly penetrates into the BNT arrays, forming the Cassie-Baxter (CB) state with the BNT interfaces. Based on the geometrical parameters in Table 1, we calculate the wetted-area-fraction (ϕ_s) of the solid in contact with the Cassie state droplet. Based on the Cassie equation, $\theta_{\text{apparent}} = \phi_s \cos \theta + (1 - \phi_s)$, we determine the effective Young contact angle, θ , to be 114° for the superhydrophobic BNT samples.

3.3 Droplet bouncing on the BNT surfaces at room temperature

For the impacting on a surface, the droplet successively experiences the spreading phase and the recoiling phase. The spreading is driven by the kinetic energy of the impacting droplet, and the spherical liquid turns into the disc-like shape. For the recoiling phase, the rim of the droplet recedes back towards the center of the impact zone, and the droplet might lift off from the substrate if the air cushion entrapped amid the surface texture remains intact. The air cushion between the solid and the liquid is affected by the balance between the droplet internal pressure and the anti-wetting capillary pressure at different length tier of the multi-tier texture[39,40]. If the droplet internal pressure exceeds the anti-wetting capillary pressure of the lowest length tier, the meniscus might fully infiltrate inwards, squeezing away the air cushion.

In fact, in the contact stage of impact, the water hammer pressure (P_{WH}) is induced by the sonic shock wave envelope in the liquid phase due to the sudden deceleration of the droplet. The P_{WH} scales as $P_{\text{WH}} = k \cdot \rho \cdot V \cdot C$, where ρ , V , and C respectively denote the water density (1000 kg/m³), impact velocity and sound velocity (1497 m/s), and k is a pre-factor suggested to be 0.2 as impacting on a flat surface[40]. The droplet internal pressure is dominated by the P_{WH} in the contact stage of impact. It is relatively large in value, and might cause liquid infiltration into the BNT texture within such P_{WH} dominated contact zone. Such locally infiltration might result in failure of the droplet complete lift-off. To evaluate the influence of the BNT spacing

on the droplet bouncing, we carried out the droplet impact experiments at room temperature (20 °C), as shown in Figure 3.

For the S-BNT, the microsize BNT spacing provides relatively lower capillary pressure. Upon impact, the meniscus might readily infiltrate into the microsize BNT spacing, further touching the substrate decorated with the nanoporous layer, as shown in Figure 2f. The SEM image of Figure 2f shows that, the nanoporous layer is embedded with ~200 nm diameter nanocavities. The anti-wetting capillary pressure of the nanocavity is calculated to be 0.59 MPa, based on the equation of $P_{c,cavity} = 4\gamma \cos(\theta)/d_c$, where γ , θ , and d_c respectively denote the surface tension (72 mN/m), the **effective** Young contact angle (114°) and the diameter of the nanocavity (~200 nm in average). The experimental results show that, the droplets are able to completely rebound for the impact velocity from 0.6 m/s to 2.0 m/s, and the bouncing contact time increases from 10.0 ms to 11.3 ms, as is shown in Figure 3f. But, for the 2.3 m/s droplet impact, partial pinning of the droplet occurs (with ~160 μm in pinned diameter), as is evidenced in Figure 3a and 4a. This is because the $P_{WH,2.3m/s}$ is calculated to be 0.66 MPa, slightly larger than the $P_{c,cavity}$, which results in liquid infiltration into the nanoporous layer.

For the A-BNT interface, Figure 3b-3d present the instantaneous images of the droplets impacting at different velocity. The maximum contact diameter (D_{max}) increases for higher impact velocity. For the recoiling phase, when impacting at low velocity of 0.9 m/s, the receding rate is almost linear. But for elevated impact velocity to 2.3 m/s, the outer layer of the disk-shape droplet lifts off from about 4.0 ms. Such partial lift-off state is evidenced by the typical images (at 5.0 ms) of Figure 3c and 3d: The outer layer of the droplet hangs above the substrate while the droplet center remains in contact with the solid surface. Although, in the final stage of the recoiling phase, the receding rate slows down, the droplets completely lift off. Figure 3f shows the contact time of the droplets bouncing on the A-BNT as a function of impact velocity. For the impact velocity between 0.6 m/s and 3.1 m/s, the contact time ranges

from 9.5 ms to 11.7 ms, which is close to the reported characteristic time for the non-wetting impact[22,23].

We notice that, for the gaps between the branched-nanotubes at the lower layer of the A-BNT, the gap width, w , is about 66 nm in average, as summarized in Table 1. Its anti-wetting capillary pressure ($P_{c,gap}$) can be briefly calculated to be 0.89 MPa, based on the equation of $P_{c,gap} = 2\gamma \cos(\theta)/w$, where w denotes the gap width. Here, we assume that that very few water infiltrates into the BNT for our tested velocity, since additional pressure would be built up for the air-pocket inside the BNT if the liquid further infiltrated into the BNT. The experimental results show that the 3.1 m/s droplet can be well repelled by the A-BNT interface leaving negligible liquid pinned. So, the maximum bouncing velocity of the adjacently distributed BNT outperforms that of the sparsely distributed BNT. To ensure the robustness of superhydrophobicity under droplet impact condition at room temperature, it is necessary to integrate finer length tier into the surface texture

3.4 Droplet impacting on the BNT surfaces below 0 °C

For the droplet impacting on the surface at supercooled condition, the liquid might be effectively cooled down. As is well known, the viscosity of the supercooled water increases with decrease in its temperature. Such increase in viscosity would result in increased viscous shear resistance against the spreading and the recoiling motions of the droplet. To evaluate the influence of the solid surface temperature on the droplet bouncing, we carried out the droplet impact experiments on the S-BNT and the A-BNT surfaces at -10 °C and -18 °C.

For the impacting on the supercooled S-BNT, the droplet rebound is prominently affected. For example, for the case of impacting on room temperature S-BNT, the 0.9 m/s droplet can completely bouncing with negligible de-wetting resistance. But for the case of impacting on the -10 °C S-BNT, the 0.9 m/s droplet is fully pinned, as is evidenced in Figure 4a. The contact diameter evolution in Figure 4e shows that, the receding rim of the droplet is pinned at the earlier stage of the recoiling phase. The

results suggest that, for droplet impacting on the S-BNT, prominent viscous shear resistance would be induced by the supercooled condition, thus hindering the droplet rebound.

For the case of adjacently distributed BNT, Figure 4e presents the contact diameter evolution for different impact velocity on the -10 °C and -18 °C A-BNT. For the higher impact velocity to 1.9 m/s, the $D_{\max}$ decreases slightly with decrease in temperature of the A-BNT. For the recoiling phase, the receding rate is slower on colder substrate for the same impact velocity, and the bouncing contact time increases as the A-BNT temperature decreases from -10 °C to -18 °C, as is shown in Figure 4f. **Figure 4b-4d** presents the images of the droplets bouncing at different velocity on the -18 °C A-BNT. The transient receding contact angle is lower than 90°. These results indicate that, for the droplet bouncing on the supercooled A-BNT, the de-wetting resistance increases as impacting on the colder A-BNT. Nevertheless, the droplet can successfully bounce for impact velocity up to 2.3 m/s even on the -18 °C A-BNT.

In order to study the influence of the droplet impact on the transient temperature of the impact zone, we employed the infrared camera to capture the temperature profile of the A-BNT during the impact. Figure 5a and 5b present the infrared thermal images of the impact zones about 33 ms after the droplet striking, from which we can see the moments as the droplets just lift off. In Figure 5c and 5d, we draw the line-distributed temperature profiles of the impact zones for the images in Figure 5a and Figure 5b, respectively. For the impact at the same velocity, the transient temperature of the impact zone is lower when the A-BNT original temperature decreases from -10 °C to -18 °C. Interestingly, for the same original temperature of A-BNT but with larger velocity from 0.9 m/s to 2.3 m/s, the transient temperature of the impact zone increases, and the bouncing contact time decreases, as shown in Figure 4f. It suggests that higher impact velocity might weaken the effect of the supercooled induced viscous shear resistance and decrease the droplet bouncing contact time on the A-BNT.

Obviously, the droplet bouncing on the A-BNT outperforms that on the S-BNT. During the bouncing process, the air cushion might be effectively entrapped in the gaps between the branched-arms of the A-BNT. The droplet-solid contact state might be in the Cassie-Baxter (CB) state or the partial CB state, as illustrated in Figure 6. Even in the partial CB state, as illustrated in Figure 6d, we propose that, due to the stable air cushion amid the branch-arms of the nanotubes, the partial infiltrated liquid can form heterogeneous contact with the BNT walls, resulting in curved, discrete TCL on the nanotubes walls. Under such contact state, the detaching resistance of the TCL is relatively small[14,18,41], thus completely bouncing of the droplets can be finally accomplished under supercooled conditions.

4. Conclusions

In this work, by controlling the HF content of the electrolyte from 1.0 wt.% to 4.0 wt.% and the water content from 16.0 wt.% to 17.0 wt.% for the anodization, we fabricate large-area arrays of BNT with the average BNT spacing controlled from sub-micron scale to microns scale. We investigate the droplet bouncing on the superhydrophobic BNT surfaces with different BNT spacing above and below 0 °C. We find that the A-BNT can repel up to 3.1 m/s droplet at 20 °C and 2.3 m/s droplet at -18 °C, while the maximum bouncing velocity on the S-BNT is below 2.3 m/s at 20 °C and below 0.9 m/s at -10 °C. For the bouncing on the supercooled A-BNT surface, the droplet bouncing contact time increases as the substrate temperature decreases for the same impact velocity, while the droplet contact time decreases as the impact velocity increases for the same substrate temperature. The results indicate that, stable air cushion can be effectively entrapped inside the nanosized gaps between the branched arms of the A-BNT, resulting in relatively small de-wetting resistance as the droplet bouncing on the A-BNT interface under supercooled conditions.

Acknowledgement

The authors gratefully acknowledge the financial support of the National Science Foundation of China (51206193, 51476038). YC also thanks the support from the Nature Science Foundation of Guangdong University of Technology (14QNZD009).

References

- [1] W. Barthlott, C. Neinhuis, Purity of the sacred lotus, or escape from contamination in biological surfaces, *Planta* 202 (1997) 1-8.
- [2] Y. Lu, S. Sathasivam, J. Song, C.R. Crick, C.J. Carmalt, I.P. Parkin, Robust self-cleaning surfaces that function when exposed to either air or oil, *Science* 347 (2015) 1132-1135.
- [3] J.B. Boreyko, C.H. Chen, Self-propelled dropwise condensate on superhydrophobic surfaces, *Phys. Rev. Lett.* 103 (2009) 184501.
- [4] N. Miljkovic, R. Enright, E.N. Wang, Effect of droplet morphology on growth dynamics and heat transfer during condensation on superhydrophobic nanostructured surfaces, *ACS Nano* 6 (2012) 1776-1785.
- [5] L. Cao, A.K. Jones, V.K. Sikka, J. Wu, D. Gao, Anti-icing superhydrophobic coatings, *Langmuir* 25 (2009) 12444-12448.
- [6] P. Guo, M. Wen, L. Wang, Y. Zheng, Strong anti-ice ability of nanohairs over micro-ratchet structures, *Nanoscale* 6 (2014) 3917-3920.
- [7] L. Mishchenko, B. Hatton, V. Bahadur, J.A. Taylor, T. Krupenkin, J. Aizenberg, Design of ice-free nanostructured surfaces based on repulsion of impacting water droplets, *ACS Nano* 4 (2010) 7699-7707.
- [8] L. Wen, Y. Tian, L. Jiang, Bioinspired super-wettability from fundamental research to practical applications, *Angew. Chem. Int. Ed.* 54 (2015) 3387-3399.
- [9] A.B.D. Cassie, S. Baxter, Wettability of porous surfaces, *Trans. Faraday Soc.* 40 (1944) 546-551.
- [10] Z. Hu, X. Zhang, Z. Liu, K. Huo, P.K. Chu, J. Zhai, L. Jiang, Regulating water adhesion on superhydrophobic TiO₂ nanotube arrays, *Adv. Funct. Mater.* 24 (2014) 6381-6388.
- [11] A. Lafuma, D. Quéré, Superhydrophobic states, *Nature Mater.* 2 (2003) 457-460.
- [12] Y. Lai, X. Gao, H. Zhuang, J. Huang, C. Lin, L. Jiang, Designing superhydrophobic porous nanostructures with tunable water adhesion, *Adv. Mater.* 21 (2009) 3799-3803.
- [13] A. Marmur, Superhydrophobic and superhygrophobic surfaces: From understanding non-wettability to design considerations, *Soft Matter* 9 (2013)

7900-7904.

- [14] D. Öner, T.J. McCarthy, Ultrahydrophobic surfaces. Effects of topography length scales on wettability, *Langmuir* 16 (2000) 7777-7782.
- [15] J. Shieh, F.J. Hou, Y.C. Chen, H.M. Chen, S.P. Yang, C.C. Cheng, H.L. Chen, Robust airlike superhydrophobic surfaces, *Adv. Mater.* 22 (2010) 597-601.
- [16] A. Tuteja, W. Choi, M. Ma, J.M. Mabry, S.A. Mazzella, G.C. Rutledge, G.H. McKinley, R.E. Cohen, Designing superoleophobic surfaces, *Science* 318 (2007) 1618-1622.
- [17] W. Wu, X. Wang, D. Wang, M. Chen, F. Zhou, W. Liu, Q. Xue, Alumina nanowire forests via unconventional anodization and super-repellency plus low adhesion to diverse liquids, *Chem. Commun.* (2009) 1043-1045.
- [18] X. Yao, Q. Chen, L. Xu, Q. Li, Y. Song, X. Gao, D. Quéré, L. Jiang, Bioinspired ribbed nanoneedles with robust superhydrophobicity, *Adv. Funct. Mater.* 20 (2010) 656-662.
- [19] Z. Yoshimitsu, A. Nakajima, T. Watanabe, K. Hashimoto, Effects of surface structure on the hydrophobicity and sliding behavior of water droplets, *Langmuir* 18 (2002) 5818-5822.
- [20] X. Cao, A. Gao, H. Lv, H. Lan, Q. Cheng, N. Zhao, Superhydrophobic surface formation and modulation in a biphenyltetracarboxylic dianhydride derivative self-assembly system via changing alkyl chain lengths, *RSC Adv.* 5 (2015) 48500-48505.
- [21] X. Cao, A. Gao, N. Zhao, F. Yuan, C. Liu, R. Li, Surfaces wettability and morphology modulation in a fluorene derivative self-assembly system, *Appl. Surf. Sci.* 368 (2016) 97-103.
- [22] D. Richard, C. Clanet, D. Quéré, Contact time of a bouncing drop, *Nature* 417 (2002) 811-811.
- [23] K. Okumura, F. Chevy, D. Richard, D. Quéré, C. Clanet, Water spring: A model for bouncing drops, *Europhys. Lett.* 62 (2003) 237-243.
- [24] J.C. Bird, R. Dhiman, H.M. Kwon, K.K. Varanasi, Reducing the contact time of a bouncing drop, *Nature* 503 (2013) 385-388.
- [25] Y. Liu, L. Moevius, X. Xu, T. Qian, J.M. Yeomans, Z. Wang, Pancake bouncing on superhydrophobic surfaces, *Nature Phys.* 10 (2014) 515-519.
- [26] V. Bahadur, L. Mishchenko, B. Hatton, J.A. Taylor, J. Aizenberg, T. Krupenkin, Predictive model for ice formation on superhydrophobic surfaces, *Langmuir* 27 (2011) 14143-14150.
- [27] S. Jung, M.K. Tiwari, N.V. Doan, D. Poulikakos, Mechanism of supercooled droplet freezing on surfaces, *Nat. Commun.* 3 (2012) 615.

- [28] T. Maitra, M.K. Tiwari, C. Antonini, P. Schoch, S. Jung, P. Eberle, D. Poulikakos, On the nanoengineering of superhydrophobic and impalement resistant surface textures below the freezing temperature, *Nano Lett.* 14 (2014) 172-182.
- [29] Y. Wang, J. Xue, Q. Wang, Q. Chen, J. Ding, Verification of icephobic/anti-icing properties of a superhydrophobic surface, *Acs Appl. Mater. Interfaces* 5 (2013) 3370-3381.
- [30] T.M. Schutzius, S. Jung, T. Maitra, P. Eberle, C. Antonini, C. Stamatopoulos, D. Poulikakos, Physics of icing and rational design of surfaces with extraordinary icephobicity, *Langmuir* 31 (2015) 4807-4821.
- [31] T.M. Schutzius, S. Jung, T. Maitra, G. Graeber, M. Koehme, D. Poulikakos, Spontaneous droplet trampolining on rigid superhydrophobic surfaces, *Nature* 527 (2015) 82-85.
- [32] M. McCarthy, K. Gerasopoulos, R. Enright, J.N. Culver, R. Ghodssi, E.N. Wang, Biotemplated hierarchical surfaces and the role of dual length scales on the repellency of impacting droplets, *Appl. Phys. Lett.* 100 (2012).
- [33] P. Roy, S. Berger, P. Schmuki, TiO₂ nanotubes: Synthesis and applications, *Angew. Chem. Int. Ed.* 50 (2011) 2904-2939.
- [34] Y. Chen, H.H. Lu, X.M. Wang, S.S. Lu, Large-scale sparse TiO₂ nanotube arrays by anodization, *J. Mater. Chem.* 22 (2012) 5921-5923.
- [35] Y. Chen, X.M. Wang, S.S. Lu, X. Zhang, Formation of titanium oxide nanogrooves island arrays by anodization, *Electrochem. Commun.* 12 (2010) 86-89.
- [36] D. Wang, Y. Liu, X. Liu, F. Zhou, W. Liu, Q. Xue, Towards a tunable and switchable water adhesion on a TiO₂ nanotube film with patterned wettability, *Chem. Commun.* (2009) 7018-7020.
- [37] Y.Y. Song, F. Schmidt-Stein, S. Bauer, P. Schmuki, Amphiphilic TiO₂ nanotube arrays: An actively controllable drug delivery system, *J. Am. Chem. Soc.* 131 (2009) 4230-4232.
- [38] D.H. Shin, T. Shokuhfar, C.K. Choi, S.H. Lee, C. Friedrich, Wettability changes of TiO₂ nanotube surfaces, *Nanotechnology* 22 (2011).
- [39] S. Dash, M.T. Alt, S.V. Garimella, Hybrid surface design for robust superhydrophobicity, *Langmuir* 28 (2012) 9606-9615.
- [40] T. Deng, K.K. Varanasi, H. Ming, N. Bhate, C. Keimel, J. Stein, M. Blohm, Nonwetting of impinging droplets on textured surfaces, *Appl. Phys. Lett.* 94 (2009) 133109.
- [41] L. Wang, M. Wen, M. Zhang, L. Jiang, Y. Zheng, Ice-phobic gummed tape with nano-cones on microspheres, *J. Mater. Chem. A* 2 (2014) 3312-3316.

Figure captions

Figure 1 The SEM images of the top view (left panels) and the side view (right panels) of the branched nanotube (BNT) formed by anodization at 80 V for 12 h in the ethylene glycol based electrolyte containing 17.5 wt.% water and (a,b) 1.0 wt.%, (c,d) 3.0 wt.% and (e,f) 4.0 wt.% HF acid.

Figure 2 Schematic drawing (a,b) and the SEM images (c-h) of the adjacently distributed branched nanotube (A-BNT) arrays (left panels) and the sparsely distributed branched nanotube (S-BNT) arrays (right panels). The A-BNT and S-BNT are formed by anodization at 80 V for 12 h in the ethylene glycol based electrolyte (with 4.0 wt.% HF) containing (c,e,g) 16.0 wt.% and (d,f,h) 17.0 wt.% water, respectively. (c-f) present the top view of the samples while (g,h) present the side view of the samples. The values of the parameters in (a) and (d) are shown in Table 1.

Figure 3 Instantaneous images of the droplet impacting (a) on the S-BNT at 2.3 m/s and (b-d) on the A-BNT at (b) 0.9 m/s, (c) 2.3 m/s and (d) 3.1 m/s. (e) Evolution of the droplet non-dimensional contact diameter (contact diameter, D , divided by the initial spherical droplet diameter, D_0) at different impact velocity on the S-BNT and the A-BNT. (f) Droplet bouncing contact time as a function of the impact velocity. The experiments are carried out at 20 °C.

Figure 4 Instantaneous images of the droplet impacting (a) on -10°C S-BNT at 0.9 m/s and (b-d) on -18°C A-BNT at (b) 0.9 m/s, (c) 1.9 m/s and (d) 2.3 m/s. (e) Evolution of the droplet non-dimensional contact diameter at different impact velocity on the S-BNT and the A-BNT at -10 °C or -18 °C. (f) Droplet bouncing contact time as a function of the substrate temperature at different impact velocity.

Figure 5 Infrared (IR) thermal images for droplet bouncing on (a) -10 °C and (b) -18 °C A-BNT: Recording the instant as the bouncing droplet just lifts off (about 33 ms after the striking). (c) and (d) present the line-distributed temperature profile of the

impact zones for the images in (a) and (b), respectively. The vertical axes in (c) and (d) represent the non-dimensional contact diameter.

Figure 6 Schematic drawing of the liquid-solid contact conditions for (a,c) Cassie-Baxter (CB) state and (b,d) partial CB state. (a) and (b) present the side view while (c) and (d) present the ‘A-A’ section view of (a) and (b). The red dash lines in (c) and (d) illustrate the three-phase contact line (TCL) on the BNT walls.

Figure 1 The SEM images of the top view (left panels) and the side view (right panels) of the branched nanotube (BNT) formed by anodization at 80 V for 12 h in the ethylene glycol based electrolyte containing 17.5 wt.% water and (a,b) 1.0 wt.%, (c,d) 3.0 wt.% and (e,f) 4.0 wt.% HF acid.

Figure 2 Schematic drawing (a,b) and the SEM images (c-h) of the adjacently distributed branched nanotube (A-BNT) arrays (left panels) and the sparsely distributed branched nanotube (S-BNT) arrays (right panels). The A-BNT and S-BNT are formed by anodization at 80 V for 12 h in the ethylene glycol based electrolyte (with 4.0 wt.% HF) containing (c,e,g) 16.0 wt.% and (d,f,h) 17.0 wt.% water, respectively. (c-f) present the top view of the samples while (g,h) present the side view of the samples. The values of the parameters in (a) and (d) are shown in Table 1.

Figure 3 Instantaneous images of the droplet impacting (a) on the S-BNT at 2.3 m/s and (b-d) on the A-BNT at (b) 0.9 m/s, (c) 2.3 m/s and (d) 3.1 m/s. (e) Evolution of the droplet non-dimensional contact diameter (contact diameter, D , divided by the initial spherical droplet diameter, D_0) at different impact velocity on the S-BNT and the A-BNT. (f) Droplet bouncing contact time as a function of the impact velocity. The experiments are carried out at 20 °C.

Figure 4 Instantaneous images of the droplet impacting (a) on -10°C S-BNT at 0.9 m/s and (b-d) on -18°C A-BNT at (b) 0.9 m/s, (c) 1.9 m/s and (d) 2.3 m/s. (e) Evolution of the droplet non-dimensional contact diameter at different impact velocity on the S-BNT and the A-BNT at -10 °C or -18 °C. (f) Droplet bouncing contact time as a function of the substrate temperature at different impact velocity.

Figure 5 Infrared (IR) thermal images for droplet bouncing on (a) $-10\text{ }^{\circ}\text{C}$ and (b) $-18\text{ }^{\circ}\text{C}$ A-BNT: Recording the instant as the bouncing droplet just lifts off (about 33 ms after the striking). (c) and (d) present the line-distributed temperature profile of the impact zones for the images in (a) and (b), respectively. The vertical axes in (c) and (d) represent the non-dimensional contact diameter.

Figure 6 Schematic drawing of the liquid-solid contact conditions for (a,c) Cassie-Baxter (CB) state and (b,d) partial CB state. (a) and (b) present the side view while (c) and (d) present the 'A-A' section view of (a) and (b). The red dash lines in (c) and (d) illustrate the three-phase contact line (TCL) on the BNT walls.

Graphical Abstract