Water-Repellent Surfaces Consisting of Nanowires on Micro-Pyramidal Structures

Wenjing Zhang, Wenwu Ding, Maria Fernandino,* and Carlos A. Dorao

Department of Energy and Process Engineering. Norwegian University of Science and Technology,

Trondheim, 7491, Norway

E-mail: maria.fernandino@ntnu.no

Phone: +47 73595352

Abstract

Super-repellent surfaces are relevant for several practical applications, such as water collection and self-cleaning and anti-icing surfaces. However, designing surfaces that can maintain their super-repellency when the surface is subjected to a humid environment is still a challenge. Here, we present a two-tier roughness surface consisting of nanowires on micro-pyramidal structures. We compare the wetting properties of this surface with other single-level roughness surfaces and surfaces with nanowires on micro-pillars, so as to investigate the role of the two-tier roughness with micro-pyramidal structures. Surfaces are characterised by both the static contact angle and sliding angle of a water droplet on the surfaces. The characterization is performed also for the surfaces after these ones have been subjected to condensation conditions. Compared to the single-level roughness surfaces and surfaces with nanowires on pillars, the surface with nanowires on pyramidal structures shows no degradation of water repellency properties during condensation, and shows better performance in terms of low droplet adhesion than similar surfaces comprised of the more commonly used pillar structures. This is thanks to the nanowires roughness that minimizes the contact area of the droplets with the base surface and the V-shaped cavities between the pyramids that provide the droplets with an upward driving force due to Laplace pressure. Furthermore, this study shows the importance of characterising surface wetting properties not only on dry but on wet conditions as well. The combination of a nano-scale roughness with micro-pyramidal structures appears as an attractive solution for super-repellent substrates under humid and wet conditions.

Keywords

contact angle, sliding angle, micro-pyramids, Cassie-Wenzel transition, two-tier roughness, dropwise condensation

1 Introduction

Superhydrophobic surfaces have been the focus of research during the last years due to their significance in several practical applications such as self-cleaning surfaces,¹⁻⁴ water collection⁵⁻¹⁰ and anti-icing surfaces.¹¹⁻¹⁸ For a surface to behave as superhydrophobic and super-repellent, both contact angle larger than 150° and low contact angle hysteresis are required. Approaches to make a surface superhydrophobic include the use of chemical coatings,¹⁹ modification of the surface structure to present several roughness levels,²⁰⁻²³ slippery liquid-infused porous surfaces (SLIPSs)^{16,24-26} and active methods of droplet removal.²⁷⁻³⁰ A current tendency is to design surfaces inspired on insects wings^{23,31-33} and plant leaves.³⁴⁻³⁸ For instance, the Lotus leaves show an amazing self-cleaning property with apparent water contact above 150° and contact angle hysteresis below 10°. Thus, at low inclinations angles millimetre drops can roll off easily resulting in a super-repellent surface. This low surface adhesion property is attributed to the air trapped below the droplet allowing it to reach a Cassie-Baxter superhydrophobic state.³⁹⁻⁴² However, when subjected to humid conditions where the surface gets wet, most of these types of surfaces lose their super-repellent properties.

In a humid atmosphere droplets can nucleate and grow within the surface texture resulting in a Wenzel state and consequent strong pinning of the water to the surface.^{43–45} Once the surface is already wet, deposited droplets will also pin to the existing liquid between the structures and many times show a transition to a Wenzel state. In this Wenzel state, droplets will remain attached to the surfaces even at high tilting angles, although the surface was originally showing non-wetting properties. This increase in the adhesion property of the wet surface represents a serious drawback in many applications such as water harvesting, dropwise condensation and in the case of self-cleaning surfaces. For this reason the dry wetting property of hydrophobic and superhydrophobic surfaces can be misleading. For dry conditions, many micro-structures surfaces (both from nature or artificially fabricated) have been shown to be able to reach a superhydrophobic state. From these ones, the work of Wilke et al.⁴⁶ has reported a surface structure, based on nanoscale reentrant cavities, that retains its repellency during condensation conditions without any low surface coatings. However, even when droplets were able to stay in a Cassie-Baxter wetting state during condensation, reentrant cavities show a large contact angle hysteresis (CAH) reducing droplet mobility and the possibility of easy droplet shedding. Reaching a super-repellent state where both contact angle and CAH remain unchanged in wet conditions still remains a major challenge.

Here, we present surfaces with a hierarchical architecture consisting of a micro-texture in the form of pyramids with a superimposed nano-texture in the form of nanowires. These surfaces are capable of remaining in superhydrophobic state and maintain their super-repellent properties (i.e. large contact angle and high droplet mobility due to a low CAH) even during wet conditions, while keeping the fabrication process based on simple wet etching techniques. This surface design allows to reduce the surface adhesion energy by maintaining newly deposited droplets above the micro-structure level even when smaller droplets have been previously nucleated below within the surface structure. While the nano-level roughness decreases the effective surface contact area, the micro-pyramidal structures help in providing the nucleated droplets with a mechanism to migrate upwards and outside the surface structure.

To demonstrate the capabilities of these surfaces, we experimentally characterise contact angle and sliding angles of water droplets on different surface structures in order to compare their behaviour under wet conditions. Pyramidal structures are compared with cylindrical pillars, highlighting the role of the former in providing the necessary mechanism for droplet migration towards the top of the structures. The insights gained from this work offer new opportunities to tailor surfaces to realise super-repellent states also during wet conditions.

2 Materials and methods

In this work, we used 2-inch single-side polished silicon wafers ({100}, P-type) as substrates to produce four kinds of structures. The surfaces fabricating methods are as follows.

2.1 Fabrication of Si nanowires

Nanowires on a silicon wafer were produced through metal-assisted etching, which is simple, fast and inexpensive. First, the silicon wafers were rinsed with acetone, ethanol and isopropanol (IPA) to remove organic impurities and then dried with nitrogen (N₂) flow. Then a film of 2 nm thickness of gold particles was deposited on the wafer at rate of 5 Å/s using an electron-beam evaporator (AJA International Inc. Custom ATC-2200V). To generate the nanowires, the silicon wafer was etched in a mixed solution of hydrofluoric acid (HF), hydrogen peroxide (H₂O₂) and deionized (DI) water. After etching, the silicon wafer was rinsed with deionized water and then dried by nitrogen airflow. Gold particles were finally removed by a gold etchant. A schematic representation of the fabrication process is shown in Figure 1a. An SEM image of the fabricated nanowire surfaces can be seen in Figure 2a.



Figure 1: Fabrication process for (a) surfaces with nanowires, (b) surfaces with micro-pillars, and (c) surfaces with micro-pyramids.



Figure 2: SEM images of fives kinds of surfaces produced on silicon wafers. All surfaces were covered with a monolayer of silane after fabrication. Oblique view and cross section view of (a) nanowires, (b) micro-pillars, (c) pillars with nanowires, (d) pyramids, and (e) pyramids with nanowires. The height of the nanowires on the pillars and on the pyramids is $\sim 1.5 \ \mu$ m. The pitch sizes of pillars and pyramids are 10 μ m and 8 \sim 11 μ m, respectively.

2.2 Fabrication of micro-pillars

Micro-pillars were fabricated on silicon wafers using photolithography and dry etching. The silicon wafers were rinsed with acetone, ethanol and IPA in sequence and then dried with N_2 flow. Additionally, the wafers were treated with UV cleaning to remove impurities and contaminants. The silicon wafers were then placed on a heating plate at 200 $^{\circ}C$ for 5 minutes to evaporate the water moisture on the wafer. Then photolithography was conducted to imprint micro-patterns on the wafers, which consisted of squares with 5.5 μm side length and distance between two squares of 4.5 μm . For the lithography process, a film of 4 μm thickness of DWL-5 negative photoresist was spin-coated on the silicon wafers. The wafers were then soft-baked on a heating plate at 50 $^{\circ}C$, 90 $^{\circ}C$ and 50 $^{\circ}C$ for 5 minutes in sequence, respectively. After the pre-baking step, ultraviolet (UV) light exposure was conducted on the coated wafers, with a wavelength of 405 nm and exposure dose of $200 \text{ mJ} \cdot \text{cm}^{-2}$. After the UV light exposure, the wafers were hard-baked at 50 $^{\circ}C$ and 90 $^{\circ}C$ for 5 minutes, respectively. At last, the patterns were developed in a Mr-DeV 600 bath for about 3 minutes, cleaned with IPA and then dried with flow of N₂. The micro-pillars were etched in ICP-RIE Chiller (Plasmalab System 100 ICP-RIE 180, Oxford Instruments, UK) using sulfur hexafluoride (SF_6) and trichloromethane (CHF_3) for 15 minutes. Then oxygen (O_2) plasma was used to remove the rest of photoresist. A schematic representation of the fabrication process is shown in Figure 1b. A scanning electron microscope (SEM) image of the fabricated micro-pillar surfaces can be seen in Figure 2b.

2.3 Fabrication of micro-pillars with nanowires

The first step of this process was to produce micro-pillars on the substrate in the same way as the preparation process described above. The next step was to make nanowires on the micro-pillars, in the procedure as described for the fabrication of nanowires alone. An SEM image of the surfaces with micro-pillars and nanowires can be seen in Figure 2c.

2.4 Fabrication of Si pyramids

Silicon pyramids were produced by one-step anisotropic etching. First, the silicon wafers were rinsed with acetone and ethanol to remove organic impurities, and then dried with N_2 flow. Then the wafer was immersed in a mixed solution of potassium hydroxide (KOH) with 2.5 wt% and IPA (4 vt%) at 80 °C while stirring. After etching, the silicon wafers were rinsed with deionized water and then dried with a nitrogen flow. A schematic representation of the fabrication process is shown in Figure 1c. An SEM image of the fabricated micro-pyramids surfaces can be seen in Figure 2d.

2.5 Fabrication of Si pyramids with nanowires

The preparation process was similar to the process above. The first step was to prepare pyramids on the silicon wafers and then to produce the nanowires on the pyramids in the same way as described for each separate process. An SEM image of the surfaces with pyramids and nanowires can be seen in Figure 2e.

2.6 Hydrophobic coating

The surfaces are rendered hydrophobic by vapour deposition of 1H,1H,2H,2H-Perfluorooctyltrichlorosilane. On a smooth silicon surface this treatment provides an equilibrium contact angle of $107^{\circ} \pm 3^{\circ}$, a contact angle hysteresis of $32^{\circ} \pm 2^{\circ}$ and a sliding angle of $33^{\circ} \pm 2^{\circ}$.

2.7 Surface characterization

Scanning Electron Microscope: An FEI Helios dual-beam focused ion beam scanning electron microscope (FIB-SEM) was used to characterize the microstructures and nanostructures on the silicon wafers.

2.8 Contact angle measurement

An optical tensiometer (Attension Theta, Biolin Scientific, Sweden) was used to measure the static contact angle and sliding angle on both the dry and wet surface of all the samples. For the measurements on the wet surfaces, the samples were exposed to condensation conditions over a cold plate for one hour in a controlled ambient environment with temperature of $0-1^{\circ}C$ and relative humidity of 40%. A 10 μ L droplet was used to measure the contact angle and tilting angle for all samples on both dry and wet surface. After dripping 10 μ L of water droplet on the surface to measure the static contact angle, the stage was tilted progressively until the water droplet rolled off, thus determining the sliding angle. The contact angle and sliding angle values are the averaged values of 5 different measuring points on each surface.

2.9 Condensation experiments

The samples were fastened to a cooling stage, in open ambient conditions with a relative humidity of 40% during one hour. The samples were cooled down from ambient temperature $(\sim 22 \ ^{\circ}C)$ to 0-1 $^{\circ}C$ with a cooling rate of 10 $^{\circ}C$ /min. Surfaces were left under condensation conditions during 1 hour before starting the contact angle experiments.

3 Results and discussion

Motivated by the promising properties of conical structures as super-repellent surfaces,^{45,47} surfaces with micro-pyramidal structures were fabricated. The fabrication procedure used for these micro-pyramids (namely wet-etching) is much simpler and cheaper than the dry-etching procedure needed for micro-cones. As it is widely accepted in the literature, surfaces with two-tier roughness enhance superhydrophobicity.^{20,45,48} The pyramidal structures were therefore covered with nanowires.

The wetting properties of the surfaces during dry conditions were studied by measuring the static contact angle of a deposited dionized water droplet on each surface. To characterise the lateral adhesion properties, the surfaces were inclined and the sliding angle of the water droplet is reported. In order to characterize the lateral adhesion force of the already wetted surfaces, the same procedure is repeated after the surfaces have been subjected to condensation of the humidity in the environment for one hour. A water droplet is then deposited on the surface already covered with small droplets grown from condensation.

Experiments performed on the surface with pyramids with nanowires show that during dry conditions, the static contact angle and sliding angle are $165^{\circ}\pm1^{\circ}$ and $0.5^{\circ}\pm0.1^{\circ}$, respectively, while for wet conditions, the same angles are $162^{\circ}\pm0.9^{\circ}$ and $4.8^{\circ}\pm0.7^{\circ}$, respectively. These results imply that the wetting and lateral adhesion properties of the surface have not been significantly affected by the wet conditions.

3.1 Contact angle during dry and wet conditions

To explain the observed phenomena, we study the wetting properties of selected structured surfaces in order to isolate the effect of the micro- and nano-structures. Micro-pyramids with and without nanowires are compared to surfaces with only nanowires on them. In addition, pillars with nanowires were chosen in order to test the effect of having a two-level roughness on any geometrical structure as compared to two-levels of roughness with pyramidal structures in particular. The center-to-center distance and height of the pillars were 10 μm and 5 μm , respectively. These dimensions are of the same order as the corresponding geometrical parameters for the pyramids.

A summary of the results is shown in Figure 3. All surfaces except the pyramids are superhydrophobic during dry conditions. For all the tested surfaces, the static contact angle is deteriorated during condensation conditions. This can be attributed to the extra adhesion generated by the liquid already existing below the deposited droplet.⁴⁴ While on a given dry surface a droplet may remain in Cassie state, during condensation conditions small liquid droplets are nucleated in between the surface structures. When a droplet is deposited on this surface, the liquid pockets below the deposited droplet merge with the liquid above. This

creates a larger adhesion force due to the droplet transitioning to a local Wenzel condition and results in a change of apparent contact angle. This decrease in apparent contact angle occurs even when a total transition from Cassie to Wenzel state may not happen.

In particular, for the case of pillars and pyramids alone, the apparent contact angle is reduced by 50° and 30°, respectively, from dry to wet conditions. This is attributed to the large space available between the structures, allowing nucleated droplets to grow within the structure, adhering to the lateral walls and with no mechanism strong enough to lift them above the structures. When a droplet is deposited in these conditions, the small droplets nucleated in-between the structures merge with this big droplet. As observed in previous works,⁴⁴ the sudden merge of these small droplets can in some situations generate sufficient kinetic energy for the small droplets to be lifted by the larger droplet above. However, since the small droplets have already grown enough so that they are in contact with both the bottom and lateral walls of the pillars and pyramids, the gained kinetic energy is not enough to overcome this force of adhesion and the small droplets pull the larger droplet towards the bottom of the surface. This results in a transition of the droplet to Wenzel state when the surface is wet.

In the case of pillars with nanowires, this transition is avoided due to the two-tier roughness created by the nanowires. The presence of nanowires reduces the force of adhesion between the small condensed droplets and the lateral walls of the structure, promoting sudden movement of the droplets above the pillars surface, a similar phenomenon as observed previously.⁴⁹ Thus, with a two-tier roughness the small droplets nucleated within the structure are lifted when in contact with the deposited droplet above, maintaining a Cassie wetting state. As explained, the lifting of the small droplets when coalescing with the droplet above is possible due to the lower liquid-to-surface contact area between these droplets and the side walls of the larger structures (pillars/pyramids). This same phenomenon has been recently referred to as shaded coalescence and was attributed to the Laplace pressure difference arising from the droplet radii mismatch.⁵⁰



Figure 3: Static contact angles and sliding angles for the five tested types of surfaces during dry and wet conditions, the latter after condensation for 1 hour. (a) measured values of contact angle and sliding angle for each surface; (b) SEM pictures of the surfaces; (c) pictures of static contact angle on five samples during dry conditions; (d) pictures of static contact angle on five samples during wet conditions; (e) schematic representation of the deposited droplet and the condensed droplets. For the contact angle from images on wet conditions, the base line of the surface has been added on the figures to makes it easier to see the contact angle.

In the surfaces with pyramids+nanowires, the decrease in contact angle during wet conditions was smaller than for pillars+nanowires, since the droplets growing in between pyramids have an extra Laplace pressure driving force arising from the V-shaped space between the pyramids. Surfaces with only nano-level roughness, namely nanowires, also showed a small decrease in static contact angle during wet conditions. This small change in contact angle can be attributed to the nano-structures characteristic size being smaller than the nucleating droplets.⁴⁶ However, as it will be discussed in the next section, the sliding contact angle of nanowire surfaces increased significantly during wet conditions, showing the need of a combined nano- and micro-structure level to achieve super-repellency.

3.2 Sliding angle during dry and wet conditions

The most significant effect of the wet conditions on the wettability of the surfaces is its effect on the sliding angle. The sliding angle is a direct measure of the surface lateral adhesion, characterising droplet mobility on the surface. It is possible to observe in Figure 3 that surfaces with only pillars showing low sliding angles during dry conditions make it almost impossible for a droplet to slide on a wet surface even at inclinations of 80°. Surfaces with only micro-pyramidal structures do not show droplet shedding by gravitational force at all neither for dry nor for wet conditions, even when the surface shows hydrophobic properties. For the surfaces with nanowires combined with pillars and with pyramids, the sliding angle remains low even at wet conditions, which implies large mobility of droplets during condensation. The slightly larger sliding angles for the case of nanowires on pillars is attributed to the larger resistance to movement due to more solid-liquid contact area (at the top of the pillars) as compared to the pyramidal structures. The presence of the nanowires in both cases avoid the direct contact of the droplet with the base surface of the structures and the transition to Wenzel state, also minimizing pinning effects. However, it is also possible to see that only a nano-scale level roughness (nanowires) is not enough to achieve super-repellency due to a larger contact angle hysteresis than the combined nano- and micro-structures during wet conditions.

In order to understand the difference in behaviour between the nanowires on pyramids and on pillars during wet conditions, visual characterization of the small droplets nucleated below a deposited Cassie state droplet was performed. The approach consisted in depositing a water droplet over the dry surface at ambient conditions and then reducing the temperature of the surface to promote condensation below the deposited droplet. The change with time of the apparent contact angle of the big droplet above the 5 types of surfaces is observed in Figure 4. A sudden decrease in contact angle for the surface with pillars and with pillars+nanowires can be observed both in the contact angle vs. time evolution plot as well as in the change in droplet profile with time. This indicates a transition from Cassie to partial Wenzel state. The profile of the droplet lying on the pyramids+nanowires surface does not show a significant difference in the droplet profile, which means that the droplet still maintains a Cassie-Baxter state during condensation.

Figure 5 shows images of the deposited droplet on the surface with pillars+nanowires and pyramids+nanowires. Corresponding images for the other three surfaces can be found in the Supporting Information S3. In Figure 5, one can see the deposited droplet on the surface and the nucleated droplets below by focusing the camera on the top of the droplet and on the bottom of the surface, respectively. In the case of the surface with pillars+nanowires, it is possible to observe that at the beginning the large droplet is in a Cassie-Baxter state, with some liquid penetrating within the pillars. After some time under condensation conditions, smaller droplets begin to nucleate between the pillars. The number of nucleated droplets grow with time and droplets start to connect laterally within the structures. These liquid pockets merge with the droplet lying on top, but since the liquid-to-surface area of the condensed liquid after coalescence within the structure is large, the adhesion force prevents the condensed liquid from moving upwards to a Cassie state and pulls the big droplet into a partial Cassie-Wenzel state. This is supported by the change of contact angle observed in Figure 4 after around 300 seconds into the experiment. This transition to partial Wenzel state also explains the decrease in droplet mobility in the sliding experiments.

A similar approach was followed with the surface with pyramidal structures and nanowires. However, in this case the growth in the number of nucleated droplets below the large droplet remains low compared to the previous case. Due to the lack of interconnectivity of lateral passages in the pyramidal structures as compared to the pillars, there is much less coalescence between the condensed droplets within the structure. In addition, the angle of the walls allows the nucleated droplets to rise and thus helps them to merge with the droplet above, avoiding the increase of surface adhesion of the larger droplet even under wet conditions.



Figure 4: (a) Change in contact angle of a deposited droplet with time during condensation for each of the five types of surfaces. (b) The morphology of the droplets from the side for the whole process is also shown, where the evolution of the perimeter of the droplet with time can be observed. A droplet of 5 μ L was placed on the surface. The temperature was then decreased at a rate of 10 °C/min from room temperature (22 °C) to 0 °C under open atmospheric conditions. The temperature was then kept at 0 °C for 9 minutes.



Figure 5: Condensation below a deposited droplet for (a) nanowires on pillars and (b) nanowires on pyramids. The experimental procedure is the same as for Figure 4. An optical microscope was used to take pictures from the top by placing the focal plane on the top of the droplet (top-row pictures) and on the surface (middle-row pictures) while looking through the droplet. The time between the two consecutive images during condensation is 620 seconds.

3.3 Droplet morphology and growth rate during condensation

Condensation experiments on the 5 types of surfaces were performed to analyze the condensed droplets characteristics. The condensation process was visualized with a digital video camera from the top. The results for the surfaces containing nanowires (nanowires, pillars+nanowires and pyramids+nanowires) are shown in Figure 6. Corresponding results for the single-micro roughness surfaces (pyramids and pillars) can be found in the Supporting Information S3.

As seen in Figure 6, there is a clear difference in droplet morphology during condensation on these surfaces. The surface with single nano-roughness nanowires (Figure 6a) gets wet within the structures after 30 minutes, with some small, round droplets remaining above the structures and showing some amount of droplet jumping. Droplets nucleating between the pillars+nanowires (Figure 6b) grow within the structure and coalesce with other neighbouring droplets. Thanks to the two-tier roughness, some of the droplets are pushed upward above the pillars, similar to the phenomenon that has been previously reported for similar surface structures.⁴⁹ Droplet jumping was also observed for this surface. In the case of the pyramids+nanowires (Figure 6c), a larger amount of smaller droplets above the structures can be observed. This can be explained by the lower coalescence rate between droplets within the structures, due to the less interconnectivity of the passages between the pyramids as compared to the pillars. Secondly, pyramids exert a larger upward capillary force on the droplets as compared to pillars, due to their inclined walls. This larger upward force forces the droplets to move above the structures before they can grow as large as in the case of the pillars-nanowires surface, where only the effect of the nanowires is driving the vertical movement. Droplet coalescence occurs mainly between droplets already lying on top of the pyramids for this type of surface. A large amount of droplet jumping was observed for this surface, indicating the low adhesion present for this type of structure.

The difference in droplet morphology and placement on the 2 two-tier roughness surfaces explains why when a large droplet is deposited on top of these surfaces, the droplet on the pillars+nanowires surface eventually shows a transition to Wenzel state while the droplet on the pyramids+nanowires surface remains in a Cassie-Baxter state. In the case of the surface with pillars+nanowires, not all the larger droplets trapped between the pillars acquire the necessary kinetic energy during coalescence with the droplet on top and remain within the structures, causing the wetting transition and affecting the droplet mobility during wet conditions.

As condensation continues (surfaces were subject to condensation conditions for a total of 3 hours, without any deposited droplet on top), droplet jumping caused by droplet-droplet coalescence above the structures is observed for the nanowires, pillars+nanowires and pyramids+nanowires surfaces. The frequency of droplet jumping was determined visually from the obtained videos (see Supporting Information) and is shown in Figure 7. Although observed on the three kinds of surfaces, droplet jumping is weaker for the surface with only nanowires than for the other two surfaces. Based on the observation in Figure 6a, liquid fills the space between the structures and only a small amount of droplets remain free for jumping. As for the other two surfaces, during the first hour of condensation the jumping droplet phenomenon is weaker (down to 20%) for the pillars+nanowires surface than for the pyramids+nanowires surface. After 2 hours of condensation, more liquid is present on both surfaces. It is observed that the jumping frequency increases for the pyramids while it decreases significantly for the pillars surface. Since the samples were placed horizontally, a large number of the jumping droplets fall down back to the surfaces again, and thus the diameter of the droplets increases during the whole process. When the droplets grow larger, much more energy is needed for them to jump away after coalescence with another droplet. This effect is more pronounced on the surface with pillars, due to the larger adhesion on the pillars top than on the tip of the pyramids. With droplets becoming larger due to lack of a removal mechanism from the surface, droplet growth by condensation and coalescence becomes faster and the jumping droplet regime is almost completely suppressed for the pillars+nanowires surface after 3 hours of condensation. The surface with pyramids+nanowires could sustain the droplet jumping regime without flooding for the entire testing period.

Although droplet removal by jumping mechanism could be increased by a vertical-oriented surface, these results still show that the surface adhesion during wet conditions increases significantly for the surface with pillars+nanowires while the surface with pyramids+nanowires maintains a high droplet mobility even under these conditions.



Figure 6: Condensation process on surfaces with (a) nanowires, (b) pillars with nanowires and (c) pyramids with nanowires. Surfaces were placed on a cooling stage, decreasing the temperature from $22^{\circ}C$ to $0-1^{\circ}C$ at a rate of $10^{\circ}C/\text{min}$. The temperature was then kept constant at that value. The relative humidity was maintained at 38%.



Figure 7: Number of jumping droplets per mm^2 per minute after 1, 2 and 3 hours of condensation The frequency of droplet jumping was determined visually from the obtained videos (see Supporting Information).

4 Conclusions

In summary, we have shown that micro-pyramidal structures combined with a second level of roughness consisting of nanowires can maintain droplet mobility and low sliding angles even during wet conditions. The surface shows superhydrophobic properties during dry conditions, and shows almost zero sliding angle for deposited droplets under both dry and wet conditions. The pyramidal shape of the structures minimise the interconnectivity of the channels within the structure, thus avoiding the coalescence among the condensed droplets. Smaller droplets within the structure present lower lateral adhesion to the pyramids sides and can therefore be lifted by coalescence toward a larger Cassie droplet over the structures. Thus, a Cassie-Wenzel state transition is avoided and the droplet mobility is not affected. Surfaces with nanowires on cylindrical pillars show similar properties, although the extra lateral adhesion due to the larger solid-liquid contact area at the top of the pillars increases the sliding angle with respect to the pyramids, especially during wet conditions. It is shown that a singlelevel roughness such as nanowires is not enough to maintain super-repellent properties in humid environments. Furthermore, we showed that all surfaces show a serious deterioration of wetting properties after condensation. This highlights the fact that characterising the wetting and repelling properties of a surface only during dry conditions is not representative of the surface behaviour when subjected to a humid environment.

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Supporting Information Available

The following files are available free of charge.

- Figures S1-S5 (PDF)
- Video S1 (AVI)
- Video S2 (AVI)

References

- Wisdom, K. M.; Watson, J. A.; Qu, X.; Liu, F.; Watson, G. S.; Chen, C.-H. Self-Cleaning of Superhydrophobic Surfaces by Self-Propelled Jumping Condensate. *Proceedings of the National Academy of Sciences* **2013**, *110*, 7992–7997.
- (2) Lu, Y.; Sathasivan, S.; Song, J.; Crick, C.; Carmalt, C.; Parkin, I. Robust Self-Cleaning Surfaces that Function when Exposed to either Air or Oil. *Science (New York, N.Y.)* 2015, 347, 1132–1133.
- (3) Jang, N. S.; Ha, S. H.; Kim, K. H.; Kim, J. M. Facile One-Step Photopatterning of Hierarchical Polymer Structures for Highly Transparent, Flexible Superhydrophobic Films. *Progress in Organic Coatings* **2019**, *130*, 24–30.
- (4) Liu, K.; Jiang, L. Bio-Inspired Self-Cleaning Surfaces. Annual Review of Materials Research 2012, 42, 231–263.
- (5) Zheng, Y.; Bai, H.; Huang, Z.; Tian, X.; Nie, F. Q.; Zhao, Y.; Zhai, J.; Jiang, L. Directional Water Collection on Wetted Spider Silk. *Nature* **2010**, *463*, 640–643.
- (6) Lee, A.; Moon, M. W.; Lim, H.; Kim, W. D.; Kim, H. Y. Water Harvest via Dewing. Langmuir 2012, 28, 10183–10191.
- (7) Bai, H.; Wang, L.; Ju, J.; Sun, R.; Zheng, Y.; Jiang, L. Efficient Water Collection on Integrative Bioinspired Surfaces with Star-Shaped Wettability Patterns. Advanced Materials 2014, 26, 5025–5030.

- (8) Zhu, H.; Guo, Z.; Liu, W. Biomimetic Water-Collecting Materials Inspired by Nature. Chemical Communications 2016, 52, 3863–3879.
- (9) Zhang, S.; Huang, J.; Chen, Z.; Lai, Y. Bioinspired Special Wettability Surfaces: From Fundamental Research to Water Harvesting Applications. *Small* 2017, 13, 1–28.
- (10) Hou, Y.; Shang, Y.; Yu, M.; Feng, C.; Yu, H.; Yao, S. Tunable Water Harvesting Surfaces Consisting of Biphilic Nanoscale Topography. ACS Nano 2018, 12, 11022– 11030.
- (11) Mu, C.; Pang, J.; Lu, Q.; Liu, T. Effects of Surface Topography of Material on Nucleation Site Density of Dropwise Condensation. *Chemical Engineering Science* 2008, 63, 874–880.
- (12) Lv, C.; Hao, P.; Yao, Z.; Song, Y.; Zhang, X.; He, F. Condensation and Jumping Relay of Droplets on Lotus Leaf. *Applied Physics Letters* **2013**, *103*.
- (13) Wang, L.; Gong, Q.; Zhan, S.; Jiang, L.; Zheng, Y. Robust Anti-Icing Performance of a Flexible Superhydrophobic Surface. *Advanced Materials* **2016**, *28*, 7729–7735.
- (14) Meuler, A. J.; McKinley, G. H.; Cohen, R. E. Exploiting Topographical Texture To Impart Icephobicity. ACS Nano 2010, 4, 7048–7052.
- (15) Xu, Q.; Li, J.; Tian, J.; Zhu, J.; Gao, X. Energy-Effective Frost-Free Coatings Based on Superhydrophobic Aligned Nanocones. ACS Applied Materials and Interfaces 2014, 6, 8976–8980.
- (16) Wang, N.; Xiong, D.; Pan, S.; Wang, K.; Shi, Y.; Deng, Y. Robust Superhydrophobic Coating and the Anti-Icing Properties of its Lubricants-Infused-Composite Surface under Condensing Condition. New Journal of Chemistry 2017, 41, 1846–1853.
- (17) Shen, Y.; Xie, X.; Xie, Y.; Tao, J.; Jiang, J.; Chen, H.; Lu, Y.; Xu, Y. Statistically Understanding the Roles of Nanostructure Features in Interfacial Ice Nucleation for

Enhancing Icing Delay Performance. *Physical Chemistry Chemical Physics* **2019**, *21*, 19785–19794.

- (18) Barthwal, S.; Lim, S.-H. Rapid Fabrication of a Dual-Scale Micro-Nanostructured Superhydrophobic Aluminum Surface with Delayed Condensation and Ice Formation Properties. Soft Matter 2019, 39, 7945–7955.
- (19) Cao, L.; Jones, A. K.; Sikka, V. K.; Wu, J.; Gao, D. Anti-Icing Superhydrophobic Coatings. Langmuir 2009, 25, 12444–12448.
- (20) Spencer, N. D.; Spori, D. M.; Drobek, T.; Zurcher, S.; Ochsner, M.; Sprecher, C.; Muehlebach, A. Beyond the Lotus Effect: Roughness, Influences on Wetting Over a Wide Surface-Energy Range. *Langmuir* 2008, 24, 5411–5417.
- (21) Lai, Y.; Gao, X.; Zhuang, H.; Huang, J.; Lin, C.; Jiang, L. Designing Superhydrophobic Porous Nanostructures with Tunable Water Adhesion. Advanced Materials 2009, 21, 3799–3803.
- (22) Liu, K.; Cao, M.; Fujishima, A.; Jiang, L. Bio-Inspired Titanium Dioxide Materials with Special Wettability and Their Applications. *Chemical Reviews* **2014**, *114*, 10044–10094.
- (23) Zhang, W.; Lin, G.; Li, J.; Xue, H.; Luo, Y.; Gao, X. Fabrication of Biomimetic Polymer Nanocone Films with Condensate Microdrop SelfåÅŘRemoval Function. Advanced Materials Interfaces 2015, 2, 1500238.
- (24) Xiao, L.; Li, J.; Mieszkin, S.; Di Fino, A.; Clare, A. S.; Callow, M. E.; Callow, J. A.; Grunze, M.; Rosenhahn, A.; Levkin, P. A. Slippery Liquid-Infused Porous Surfaces Showing Marine Antibiofouling Properties. ACS Applied Materials and Interfaces 2013, 5, 10074–10080.
- (25) Li, J.; Kleintschek, T.; Rieder, A.; Cheng, Y.; Baumbach, T.; Obst, U.; Schwartz, T.;

Levkin, P. A. Hydrophobic Liquid-Infused Porous Polymer Surfaces for Antibacterial Applications. ACS Applied Materials and Interfaces **2013**, 5, 6704–6711.

- (26) King, W. P.; Qian, H.; Weisensee, P. B.; Schultz, D.; Miljkovic, N.; Wang, Y. Condensate Droplet Size Distribution on Lubricant-Infused Surfaces. *International Journal of Heat and Mass Transfer* **2017**, *109*, 187–199.
- (27) Celestini, F.; Kofman, R. Vibration of Submillimeter-Size Supported Droplets. *Physical Review E* 2006, 73, 041602.
- (28) Luo, M.; Gupta, R.; Frechette, J. Modulating Contact Angle Hysteresis To Direct Fluid Droplets along a Homogenous Surface. ACS Applied Materials & Interfaces 2012, 4, 890–896.
- (29) Hao, P.; Lv, C.; Yao, Z.; He, F. Sliding Behavior of Water Droplet on Superhydrophobic Surface. *EPL* 2010, *90*, 66003.
- (30) Im, H.; Ji, S.; Moon, D.-I.; Lim, H.; Choi, Y.-K. Enhanced Water Droplet Mobility on Superhydrophobic Rippled Nanoshell Array. *Applied Physics Letters* 2016, 109, 151601.
- (31) Sun, M.; Watson, G. S.; Zheng, Y.; Watson, J. A.; Liang, A. Wetting Properties on Nanostructured Surfaces of Cicada Wings. *Journal of Experimental Biology* 2009, 212, 3148–3155.
- (32) Avramescu, R. E.; Ghica, M. V.; Dinu-Pîrvu, C.; Prisada, R.; Popa, L. Superhydrophobic Natural and Artificial Surfaces - A Structural Approach. *Materials* 2018, 11, 866.
- (33) Zhao, H.; Park, S. J.; Solomon, B. R.; Kim, S.; Soto, D.; Paxson, A. T.; Varanasi, K. K.; Hart, A. J. Synthetic Butterfly Scale Surfaces with Compliance-Tailored Anisotropic Drop Adhesion. Advanced Materials 2019, 31, 1–6.

- (34) Marmur A, The Lotus Effect: Superhydrophobicity and Metastability. Langmuir 2004, 20, 3517–3519.
- (35) Ensikat, H. J.; Ditsche-Kuru, P.; Neinhuis, C.; Barthlott, W. Superhydrophobicity in Perfection: The Outstanding Properties of the Lotus Leaf. *Beilstein Journal of Nanotechnology* **2011**, *2*, 152–161.
- (36) Boreyko, J. B.; Chen, C. H. Restoring Superhydrophobicity of Lotus Leaves with Vibration-Induced Dewetting. *Physical Review Letters* **2009**, *103*, 1–4.
- (37) Teisala, H.; Butt, H. J. Hierarchical Structures for Superhydrophobic and Superoleophobic Surfaces. *Langmuir* 2019, 35, 10689 – 10703.
- (38) Zhang, S.; Huang, J.; Chen, Z.; Yang, S.; Lai, Y. Liquid Mobility on Superwettable Surfaces for Applications in Energy and the Environment. *Journal of Materials Chemistry A* 2019, 7, 38–63.
- (39) Whyman, G.; Bormashenko, E. How to Make the Cassie Wetting State Stable? Langmuir 2011, 27, 8171–8176.
- (40) Tuvshindorj, U.; Yildirim, A.; Ozturk, F. E.; Bayindir, M. Robust Cassie State of Wetting in Transparent Superhydrophobic Coatings. ACS Applied Materials and Interfaces 2014, 6, 9680–9688.
- (41) Spori, D. M.; Drobek, T.; Zürcher, S.; Spencer, N. D. Cassie-State Wetting Investigated by Means of a Hole-to-Pillar Density Gradient. *Langmuir* 2010, 26, 9465–9473.
- (42) Ding, W.; Fernandino, M.; Dorao, C. A. Conical Micro-Structures as a Route for Achieving Super-Repellency in Surfaces with Intrinsic Hydrophobic Properties. *Applied Physics Letters* 2019, 115, 053703.
- (43) Cheng, Y. T.; Rodak, D. E. Is the Lotus Leaf Superhydrophobic? Applied Physics Letters 2005, 86, 144101.

- (44) Dorrer, C.; Rühe, J. Condensation and Wetting Transitions on Microstructured Ultrahydrophobic Surfaces. *Langmuir* 2007, 23, 3820–3824.
- (45) Mouterde, T.; Lehoucq, G.; Xavier, S.; Checco, A.; Black, C. T.; Rahman, A.; Midavaine, T.; Clanet, C.; Quéré, D. Antifogging Abilities of Model Nanotextures. *Nature Materials* 2017, 16, 658–663.
- (46) Wilke, K. L.; Preston, D. J.; Lu, Z.; Wang, E. N. Toward Condensation-Resistant Omniphobic Surfaces. ACS Nano 2018, 12, 11013–11021.
- (47) Park, I.; Fernandino, M.; Dorao, C. Wetting State Transitions over Hierarchical Conical Microstructures. Advanced Materials Interfaces 2018, 5, 1701039.
- (48) Frankiewicz, C.; Attinger, D. Texture and Wettability of Metallic Lotus Leaves. Nanoscale 2016, 8, 3982–3990.
- (49) Lv, C.; Hao, P.; Zhang, X.; He, F. Dewetting Transitions of Dropwise Condensation on Nanotexture-Enhanced Superhydrophobic Surfaces. ACS Nano 2015, 9, 12311–12319.
- (50) Yan, X.; Chen, F.; Sett, S.; Chavan, S.; Li, H.; Feng, L.; Li, L.; Zhao, F.; Zhao, C.;
 Huang, Z.; Miljkovic, N. Hierarchical Condensation. ACS Nano 2019, 13, 8169–8184.

Graphical TOC Entry

