Influence of geometric patterns of microstructured superhydrophobic surfaces on water harvesting performance via dewing

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Abstract. We investigate how the wetting state of microstructured SHPo surfaces influences water harvesting performance via dewing by testing two different patterns including posts and grates with varying structural parameters. On grates, the observed Cassie wetting state during condensation is well described by the thermodynamic energy criteria, and small condensates can be efficiently detached from the surfaces due to the small contact line pinning force of Cassie droplets. Meanwhile, on posts, the observed wetting state is dominantly the Wenzel state regardless of the thermodynamic energy of each state, and the condensates are shed only after they grow to a sufficiently large size to overcome much larger pinning force of the Wenzel state. Based on mechanical force balance model and energy barrier consideration, we attribute the difference in the droplet shedding characteristics to the different dynamic pathway from the Wenzel state to the Cassie state between posts and grates. Overall, the faster droplet shedding helps enhance the water harvesting performance of the SHPo surfaces by facilitating the condensation on the droplet-free area, as evidenced by the best water harvesting performance of grates on the Cassie state amongst the tested surfaces.

1. Introduction

Recently, water harvesting from air-borne moisture has received the renewed interest as the promising way to address the global water shortage problem[1]. Many previous researches have studied the effects of surface wettability on the water harvesting performance employing the macroscopic properties such as apparent contact angle and contact angle hysteresis for the calculations[2]. But the effects of microscale geometries have not been well-understood. In this work, to clarify the influence of microscopic structural features on the dew harvest performance, we fabricated microposts and microgratings with varying structural parameters. And we investigated the condensates mobility and resulting water harvesting performances by used the microscopic geometric information in modeling.

2. Experimental method

Table 1 shows the investigated designs. Considering the equilibrium energy criteria $E^*$, we designed samples with Cassie ($E^*<1$) and Wenzel ($E^*>1$) wetting morphologies for posts and gratings[3] samples were fabricated with DRIE techniques followed by TFTS vapor deposition. The condensation
experiments were conducted within the environmental chamber fixing the supersaturation level at 2.21 as shown in figure 1.

Table 1. Geometric parameters of test samples for experiments. The C and W indicate the Cassie and Wenzel states, respectively. The $r$ is the roughness factor and $\varphi_s$ is the solid fraction.

| Surface | Grate width or post radius (µm) | Pitch (µm) | Height (µm) | $r$   | $\varphi_s$ | $E^*$ |
|---------|---------------------------------|------------|-------------|-------|------------|-------|
| Grating |                                 |            |             |       |            |       |
| C I     | 20                              | 60         | 60          | 3.00  | 0.33       | 0.76  |
| C II    | 20                              | 80         | 60          | 2.50  | 0.25       | 0.91  |
| W I     | 20                              | 60         | 20          | 1.67  | 0.33       | 1.36  |
| W II    | 20                              | 80         | 20          | 1.50  | 0.25       | 1.51  |
| Post    |                                 |            |             |       |            |       |
| C I     | 20                              | 60         | 60          | 3.09  | 0.35       | 0.74  |
| C II    | 22                              | 80         | 60          | 2.30  | 0.24       | 0.99  |
| W I     | 20                              | 60         | 20          | 1.70  | 0.35       | 1.34  |
| W II    | 22                              | 80         | 20          | 1.43  | 0.24       | 1.59  |

3. Results and discussion

3.1. Sliding behaviors of condensed droplets

Figure 2 shows the behavior of water condensation on each test surface, captured using a CCD camera on the macro scale. Because of the hydrophobic nature, all surfaces exhibit high contact angles (> 130°) as well as dropwise condensation. The condensation behavior appears to be clear difference in the sizes of the pinned droplets which might be attributed to the different pinning force on each surface\(^2,4\). On Grating C I, most of the surface area is clear of droplets, and the average size of pinned droplets is smaller than those on Grating W I since the mobility of droplets on the Cassie state is higher than the Wenzel state. Interestingly, we do not observe any difference in condensation behavior between Post C I and Post W I in contrast with gratings. Furthermore, the size of remaining droplets on posts is generally larger than those on gratings. To understand this difference, a microscopic force analysis is applied to calculate the pinning force at the contact line using the geometric details of surface patterns.

Figure 1. Experimental setup for harvesting water.

Figure 2. Time-lapse images of the water condensation until the most condensed droplets are removed. (scale bar: 10mm)
Figure 3(a-f) shows a schematic illustration of the contact line force when the droplet begins to slide on each surface. To slide on the surface, the droplet should overcome the maximum pinning force imparted by surface structures, which is dependent on the structure shape and wetting state, as detailed in the following. And for simplicity, we only consider the complete Cassie or Wenzel state.

\[
F_{C, \text{Grating}} = w \gamma (\cos \theta_r - \cos \theta_a) / L ,
\]

\[
F_{W, \text{Grating}} = \gamma (2H + L)(\cos \theta_r - \cos \theta_a) / L ,
\]

\[
F_{C, \text{Post}} = \pi D \gamma \cos \theta_r / L ,
\]

\[
F_{W, \text{Post}} = \{ \pi D \gamma \cos \theta_r + 2H\gamma (1 + \sin \theta_r) + L\gamma (\cos \theta_r - \cos \theta_a) \} / L ,
\]

where \( w \) is the width of the grates, \( \gamma \) is the surface tension of the liquid-air interface, \( L \) is the center to center distance of structures (i.e., defined as pitch), \( H \) is the height of the structures, and \( D \) is the diameter of the post. The diameter of a sliding droplet can be calculated by comparing pinning force and gravitational force, \( \rho g V = b F_{\text{pinning}} \) where \( \rho \) is the water density, \( g \) is the gravitational acceleration, \( V \) is the volume of a droplet, and \( b \) is the contact diameter of the droplet[5].

Figure 3(b) compares the predicted sliding droplet diameters by the above calculation with those actually observed in the experiments, which shows a good agreement between the prediction and the experiment for gratings. However, for posts, the actual sliding droplet size on Post C surfaces is much larger than the prediction and is comparable to that on Post W surfaces, which imply that the droplets are not on the Cassie state on Post C surfaces and the wetting criteria based on \( E^* \) might be inapplicable to posts.

Figure 3. (a-f) Contact line force between a droplet and structures when the droplet begins to slide on the (a) Cassie grating, (b-c) Wenzel grating, (d) Cassie post, and (e-f) Wenzel post surfaces. (g) Droplet diameters calculated by modelling and observed by experiments.

3.2. Wetting states during condensation
To further understand the condensation behavior and the resultant wetting state on each surface, optical microscopy was employed to determine the actual wetting state on micro-scale by focusing on the top of surface structures[3]. As shown in figure 4(a), the droplets on most surfaces initially show satisfactory agreement with the expectation of the wetting state by the \( E^* \) criteria. However, the droplet on Post C I surface begins to irregularly spread out at 50 min, and become to take a similar morphology with that on Post W I surface after 70 min, indicating that the droplet is no longer on the Cassie state.
Figure 4(b) shows time-lapse images of droplets coalescence motion. When two large droplets merge on the surfaces, some parts of the droplet can penetrate into structures, as surface energy released during merging is converted to fluctuations or kinetic energy, which provide the sufficient energy for the transition from the Cassie state to the Wenzel state if the structures are not tall enough compared to the merged droplet. On Grating C I surface, the liquid-solid interface elongates along the direction of the grates during merging, and the droplet vibrates along the same direction because of the difference in the energy barrier along and across gratings. Later, the pinned interface returns to the top of gratings and the droplet relaxes to a more spherical shape, implying occurrence of de-wetting transition from the Wenzel state to the Cassie state. Meanwhile, on the post C I surface, the liquid-solid interface does not return to the top of posts after penetrating into the structures with no sign of the transition from the Wenzel state to the Cassie state on posts, even when the Cassie state is energetically more stable state. This difference was attributed to the different dynamic pathway from the Wenzel state to the Cassie state between posts and grates. It has been suggested that a large energy barrier prevents the transition from the Wenzel to the Cassie state on posts, while it is absent or is negligibly small on grates.

Figure 4. (a) Time-lapse images of water condensation motion in micro scale. (b) Time-lapse images of droplets coalescence motion. (scale bar: 0.6 mm)

3.3. Water harvesting performance

We investigate how the difference in droplet mobility and wetting state (i.e., the Cassie and Wenzel state) of SHPo surfaces affect the water harvesting performance. To compare the harvesting characteristics, the average mass and falling frequency of droplets detached from each surface were measured, as shown in figure 5(a). With the smaller pinning force of droplets on gratings than on posts, the harvesting falling frequency is noticeably higher on grates. In addition, the Cassie state grating surfaces exhibit higher falling frequency and smaller droplet mass ranges compared to the Wenzel state grating surfaces due to the smaller pinning forces on the Cassie state compared to the Wenzel state. On posts, all the tested samples similarly exhibit the low falling frequency and large mass ranges, as the condensed droplets are on the Wenzel state, which is associated with the strong pinning force.

The harvesting performance is calculated by multiplying the average droplet mass and falling frequency for a unit time. Figure 5(b) shows our main results about water harvesting performance of each SHPo surface. Despite the similar surface wettability and surface area, the performance of the grating surfaces is noticeably better than the post surfaces. Also, on graters, the Cassie state is better in
water harvesting performance than the Wenzel state except for Grating C II surface, which exhibits a partial Wenzel state with $E^*$ close to a unity. The reason that the Cassie state surface with the small pinning force and the high droplet mobility is associated with the better water harvesting performance can be explained by the consideration that the droplets resting on the surfaces act as the thermal resistance against heat transfer between the surface and vapor in air, thus delaying the water condensation. It agree with our experimental results that the water harvesting performance was the best on Cassie gratings where the droplet mobility was the highest or the critical falling mass of droplets was the smallest amongst the tested surfaces.

Figure 5. (a) Average mass and frequency of falling condensate on each test surface. (b) Water harvesting performance.

4. Conclusion
We experimentally studied the dew harvesting performance of SHPo surfaces with two different patterns (posts and gratings) and varying geometric parameters. It was found that thermodynamic energy criterion could be applied to determine the observed wetting state between the Cassie and Wenzel states on gratings during condensation, while it failed to predict the actual wetting state on posts. To characterize the dew harvesting performance, we measured both the mass and frequency of each fallen droplet in a temperature/humidity controlled environment to clarify the relationship between the droplet dynamics and water harvesting performance. Our results show that the different wetting state imparts the different pinning force against the droplet movement and thus affects average mass and falling frequency of collected droplets, which are the crucial factors in harvesting the water from dew. In the present study, the grates on the Cassie state with the highest droplet mobility exhibited the best harvesting performance amongst the tested surfaces, which was attributed to the enhanced heat transfer between the surface and vapor with the facilitated removal of smaller droplets from the surface.

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