Droplet Jumping on Superhydrophobic Copper Oxide Nanostructured Surfaces

Jonggyu Lee, Member, IEEE, Bowen Shao, Yoonjin Won, Member, IEEE

Abstract—Condensation has been widely explored because of its importance in numerous applications including water desalination, water harvesting, power generation, and thermal management. Previous studies have shown that the enhancement in condensation heat transfer can be achieved with the engineering of surface wettability by promoting dropwise condensation that has lower thermal resistances than film condensation. In this study, we explore microscopic-level droplet dynamics using various copper surfaces by employing a simple two-step chemical method. Nanostructured copper surfaces are prepared by a chemical immersion method using alkaline solution and are further functionalized by using dodecanoic acid that provides hydrophobicity. The wetting properties and corresponding condensation processes are examined using an optical microscope and environmental scanning electron microscope by capturing real-time phase change process. The measurements confirm that the surface morphology with the largest feature ratio promotes droplet jumping events. The understanding of condensation behaviors associated with nanostructured copper oxide surfaces can provide design rules for efficient surface structures for numerous condensation applications.

Index Terms—Copper oxide nanostructure, Droplet jumping, Dropwise condensation, Superhydrophobic surface

I. INTRODUCTION

In recent years, phase change heat transfer gains significant interest for its use in numerous industrial applications such as desalination [1], water harvesting [2], power generation [3], and thermal management [4, 5]. In particular, the thermal performance of passive heat transfer devices has been limited by condensing and evaporating processes through nanostructured surfaces in electronics thermal management system. Condensation heat transfer coefficients can significantly vary based on droplet dynamics on the condensation surfaces. Dropwise condensation has been shown to improve the condensation heat transfer coefficient by an order of magnitude over the typical film condensation surfaces by minimizing the thermal resistance of the liquid layer. Previous studies reported that hydrophobic nanostructured surfaces lead to dropwise condensation phenomena by promoting droplet removals [6-9]. Recently, efficient types of droplet removals through droplet ejection or “droplet jumping” from the superhydrophobic surfaces are reported [10]. During the coalescence of two or more droplets, the decrease in liquid-vapor interface results in an excess surface energy, which is subsequently transferred to the kinetic energy of droplet in a normal direction to the surface [11]. This kinetic energy makes droplet jumping possible with the installation of suitably-designed superhydrophobic surfaces containing nanoscale copper oxide features [12-17].

Surface wetting properties can be explained by three classic theories: the Young-Dupre model, Wenzel theory, and Cassie-Baxter theory. (1) The Young-Dupre model first explains that the droplet contact angle \( \theta \) on a flat surface is dictated by a force balance at all the three solid-vapor, solid liquid, and liquid-vapor interfaces: \( \cos \theta^V = (r_V - r_{SL})/r_{LV} \), where \( r \) is surface tension. The subscripts \( SV, SL, \) and \( LV \) represent solid-vapor, solid-liquid, and liquid-vapor, respectively. In order to explain the surface roughness \( r \) impacts on the droplet formation, (2) the Wenzel equation shows that contact angle on rough surfaces is defined by [18]: \( \cos \theta^W = r \cos \theta^V \), where \( r \) is the roughness that is the ratio of the total surface area to the projected area. This explains that hydrophobic surfaces become more hydrophobic or hydrophilic surfaces become more hydrophilic as the surface roughness increases. Once the Wenzel droplet is placed on a rough surface, it will completely wet the surface, resulting in the “Wenzel droplets” or “pinned droplets.” Considering the case where the droplet rests on the tip of nanostructures, (3) the Cassie-Baxter theory introduces air gap between droplets and the rough surface [19]: \( \cos \theta^CB = \phi_s (\cos \theta^V + 1) - 1 \), where \( \phi_s \) is a solid fraction. The trapped air underneath the liquid-vapor interface helps droplets be suspended from the substrate, leading to “Cassie-Baxter droplets” or “mobile droplets” [10, 20], which are suitable for droplet jumping. The superscripts \( Y, W, \) and \( CB \) represent Young-Dupre, Wenzel, and Cassie-Baxter, respectively.

Herein, we describe a novel method of improving the condensation performance by using self-assembled monolayers on various nanostructures to promote dropwise condensation.
for passive heat transfer devices. The hydrophobic nanostructured surfaces are prepared through a two-step chemical immersion technique that includes an aggressive oxidation treatment and additional surface functionalization. Then, the morphological details of structured surfaces will be correlated with surface properties (e.g., surface wettability) and droplet characteristics during condensation (e.g., droplet diameter, number density, distribution, surface coverages, and volume). Attaining hydrophobicity will benefit the droplet condensation heat transfer performance because of two facets: (1) The surface with a large ratio of two-level features makes it easy to remove droplets from the condensing surface by preventing pinning droplets; and (2) the droplets on a superhydrophobic surface maintain mobile mode, resulting in droplet jumping events.

II. METHOD

Nanostructured surfaces can be either hydrophobic or hydrophilic depending on chemical composition and surface roughness [21, 22]. Several techniques have been explored to modulate surface wettability, including hydrothermal methods, electrochemical process, chemical immersion methods, or a combination of two or more [23, 24]. Among different techniques, a chemical immersion method is considered a fast, cost-effective way to texture copper surfaces through an aggressive oxidation treatment. In this process, the detailed morphologies of copper oxide features can be engineered by modulating processing parameters, such as chemical choice, processing temperature, and immersion time. The nanostructured copper oxide surfaces are further functionalized to increase their hydrophobicity, enabling the dropwise condensation and droplet jumping phenomena.

A. Surface nanostructuring

We prepare various nanostructured copper surfaces by using a chemical immersion method, as shown in scanning electron microscope (SEM, Quanta 3D) images in Figs. 1(a–c). All the samples are prepared in a size of 10 mm×10 mm×0.5 mm. Before nanostructuring process, copper substrates (110 copper sheet, 99.9% pure, McMaster-Carr) are cleaned with acetone, methanol, and isopropanol and rinsed with 2M HCl and DI water. Then, the copper substrates are oxidized using the chemical solution of a 0.1M K2S2O8 and a 2M NaOH, creating

![Scanning electron microscope (SEM) images of nanostructured copper surfaces. Images show nanoneedles with nanoflowers for the (a) AR03, (b) AR10, and (c) AR47. Insets show the optical camera images of structured copper oxides, confirming various colors. The scale bar of insets is 0.5 mm. (d) Characteristic feature sizes of the AR03, AR10, and AR47 surfaces are plotted. The nanoflowers with a diameter of \(d_f\sim1.6\pm0.1\) \(\mu m\) (AR03) are formed and their sizes increase up to \(d_f\sim5.1\pm0.5\) \(\mu m\) (AR10) as the immersion time increases to 25 min. The nanoneedles oxidized at room temperature show a length of \(l_n\sim4.8\pm1.1\) \(\mu m\) and \(l_n\sim5.1\pm0.8\) \(\mu m\) for 5 min and 25 min immersion, respectively, which are longer than the nanoneedles oxidized at an elevated temperature possessing a length of \(l_n\sim0.7\pm0.03\) \(\mu m\). The red cross shows the ratio \(d_f/l_n\) of nanoflower diameter to nanoneedle length. Error bars represent standard deviation of the measured feature size. Inset illustrations show the schematics of each surface with different ratio of nanoflowers to nanoneedles.

Table 1. Feature sizes and aspect ratio of nanoflower diameter to nanoneedle length of the AR03, AR10, and AR47 surfaces.

<table>
<thead>
<tr>
<th>Feature Size</th>
<th>AR03</th>
<th>AR10</th>
<th>AR47</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanoflower Diameter (d_f, (\mu m))</td>
<td>1.68±0.14</td>
<td>5.09±0.44</td>
<td>3.34±0.8</td>
</tr>
<tr>
<td>Nanoneedle Length (l_n, (\mu m))</td>
<td>4.82±1.1</td>
<td>5.06±0.77</td>
<td>0.71±0.03</td>
</tr>
<tr>
<td>Apparent Ratio (AR)</td>
<td>0.3</td>
<td>1.0</td>
<td>4.7</td>
</tr>
</tbody>
</table>
copper oxide features. The resulting oxide morphology shows nanoneedle-like and/or nanoflowers-like features, depending on the immersion time and temperature where the roughness of the oxidized copper surface is reported up to 8 in our previous study [25]. The chemical process at room temperature (25°C) for 5 min provides the nanoneedles (l=4.8±1.1 µm) and small nanoflowers (d=1.6±0.1 µm) (Fig. 1a). As the immersion time increases up to 25 min, the nanoflower size increases to d=5.1±0.5 µm, whereas the nanoneedle size remains a constant (Fig. 1b). The chemical process at an elevated temperature of 60°C for 5 min provides a quick transition from long nanoneedle-like features to short nanograin-like features, resulting in the structured surface containing l=0.7±0.03 µm and d=3.3±0.8 µm (Fig. 1c). The feature size and shape of nanostuctures are listed in Table 1 and Fig. 1(d). Prepared samples are denoted as AR03, AR10, and AR47, where “AR” means the apparent size ratio of nanoflower diameter to nanoneedle length d/l. Each feature size is reported by averaging 30 samples using a commercial software, ImageJ.

### B. Surface wettability

The immersion to alkaline solution leads to form Cu(OH)\(_2\) (eq. (1)) and CuO (eq. (2) and eq. (3) in series) by following reactions:

\[
\begin{align*}
\text{Cu}^{2+} + 2\text{OH}^- &\rightarrow \text{Cu(OH)}_2 \quad (1) \\
2\text{Cu}^{2+} + 2\text{OH}^- &\rightarrow \text{Cu}_2\text{O} + \text{H}_2\text{O} \quad (2) \\
\text{Cu}_2\text{O} + 2\text{OH}^- &\rightarrow 2\text{CuO} + \text{H}_2\text{O} + 2\text{e}^- \quad (3)
\end{align*}
\]

The textured nanostructured surfaces consisting of Cu(OH)\(_2\) and CuO first become hydrophilic, as the contact angles (empty markers) are shown in Fig. 2 [25]. The hydrophilic surfaces are further functionalized by using 5 mM of dodecanoic acid for 30 min. This surface treatment greatly decreases the surface energy, resulting in surface hydrophobicity or superhydrophobicity, while it maintains the morphological details of copper oxides, as indicated in Fig. 2 (filled markers). The AR03 and AR10 show contact angles of 136° and 148°, respectively [26]. The AR47 surface presents superhydrophobicity by possessing a contact angle of 165°. The contact angle of the functionalized surfaces thereby increases as the AR increases. The contact angles are averaged from more than 5 measurements for each surface. The error bars representing the standard deviation of contact angles are relatively small.
C. Condensation measurements

Condensation behaviors are observed by using a custom-made condensation measurement setup, as illustrated in Fig. 3. The condensation setup consists of a chamber, a thermoelectric temperature controller with DC power supply, and a vapor generator. The condensation conditions are controlled by the different sets of relative humidity and surface temperature. The relative humidity in the condensing chamber can be modified by the vapor generator by flowing air through water and by mixing them. The surface temperature is modulated by using a thermoelectric cooling (TEC) module. Thermocouples are mounted between the sample and carbon tape to confirm a constant surface temperature during the condensation test with supersaturation level $S=1.09$ ($T_e=15^\circ$C and $P_v=1873$ Pa) in this work. The supersaturation $S$ is defined as $P_v/P_{sat}$, where $P_{sat}$ is saturation pressure at the surface temperature $T_e$. Corresponding droplet behaviors are recorded from the top view through a window using an optical microscope [27]. Image processing is further performed in order to quantify the droplet characteristics.

III. RESULTS AND DISCUSSION

The time-lapse microscopic images are recorded at $S=1.09$ for the AR03, AR10, and AR47 surfaces (225 $\mu$m x 160 $\mu$m) at different time frames, as shown in Fig. 5. The images allow us to evaluate the droplet characteristics (i.e., number density, diameter, and shape of droplets) as the condensation time increases.

A. Droplet shapes and corresponding modes

The identification of droplet shapes allows us to evaluate whether the surfaces favor pinning or mobile droplets, as illustrated in Fig. 4. Schematics show the detailed droplet status known as Wenzel (Fig. 4(a)) and Cassie-Baxter (Fig. 4(b)) model explaining pinned and mobile droplets on a rough surface, respectively. During the condensation, the droplets are pinned on a Wenzel surface as they are smaller than the characteristic lengths of nanoflowers and nanoneedles of the AR03 and AR10. Then, the droplets coalesce with other droplet in series, the liquid-solid contact area between droplets and the structured surface is maintained, causing droplets in random or mostly elliptical shapes (Fig. 4(c)). Conversely, the droplets on a Cassie-Baxter surface keep the spherical shape (Figs. 4(d-e)) due to both hydrophobicity and the trapped air underneath the liquid-vapor interface.

For the AR03 and AR10, the transition from sphere shape-dominated regime to elliptical shape-dominated regime occurs at 10 min and 70 min, respectively, as shown in Fig. 5(a). On the other hand, spherical-shaped droplets on the AR47 surface confirm the mobile mode and resulting droplet jumping events in the later stages. Once droplets jump, they provide extra spaces to enable new nucleation sites (see Fig. 5(b)), whereas it is difficult to observe new nucleation sites on other surfaces [12].

B. Droplet statistics

The details of droplet statistics (i.e., number design and distribution) are further analyzed and plotted in Fig. 6. In the early stage of condensation before 10 min, the droplet number
density of the AR03 (2.3×10³ µm⁻²) is larger than those of the AR10 and AR47 surfaces (5.2×10⁴ µm⁻² and 1.4×10³ µm⁻², respectively), as shown in Fig 6(a). This value increases first until 10 min and rapidly decays once droplets start to coalesce. A constant number density of the AR03 and AR10 is observed at the later stage of condensation after 10 min and 70 min, respectively, because of low condensation rates. The low number density of droplets leads to a small surface coverage by droplets during the condensation process lowering thermal resistance values [20].

The number density of the AR47 fluctuates due to droplet jumping and nucleation. The droplet jumping events enable continuous dropwise condensation by removing droplets from the surface and by providing additional nucleation sites, as shown in Fig 5(b). The droplet jumping events are governed by the adhesion force between droplet and surface, and extra surface energy determined by the droplets size. In this process, the minimum contact area between droplets and the surface, represented by a spherical shaped droplet, will also result in lower adhesion forces. The low adhesion force of the AR47 surface makes it favor droplet jumping events, which is also confirmed by the droplet distributions in Fig. 6(b) during the condensation. The droplet distribution confirms that we observe the droplet jumping events continuously during the entire period of the condensation for 90 min.

C. Droplet size changes

The changes in droplet sizes during the condensation are analyzed by using a power law of droplet growth \( R = at^\mu \), where \( R \) is the droplet radius, \( t \) is the time, \( a \) is a constant, and \( \mu \) is a power of exponent. The power of exponent \( \mu \) is known as 1/3 [28]. The values of \( a \) can be calculated by means of the least square of the droplet diameter in Fig. 7, where a large constant \( a \) value means that the fast increase rate of a droplet diameter. Error bars of the droplet diameter show the standard deviations of droplet diameters on the condensing surface. The droplet coalescences on the AR03 cause large droplet distributions, represented as large error bars. Most droplets on the AR10 are prone to grow with a minimum number of droplets coalescing.
event, leading to small error bars. The trend of droplet diameters of the AR47 fluctuates during the condensation because of the droplet jumping events.

D. Liquid-solid contact lines

We identify the surface coverage by droplets to determine whether the surface is favorable to dropwise condensation. The surface coverage is quantified by following equation:

$$R_c = R \cos(\theta - \frac{\pi}{2})$$

(4)

$$\epsilon = \frac{\pi R^2 N}{A_s}$$

(5)

where $N$ is the number of droplets, $\epsilon$ is the surface coverage, and $A_s$ is the total area tested. As shown in Fig 7(e), the droplets on the AR03 and AR10 cover a larger surface area (i.e., 17% and 10%, respectively) due to droplet pinning events. Inversely, the surface coverage of the AR47 surface is relatively small (i.e., 2%) due to the combination of large contact angles on the superhydrophobic surface and a smaller droplet number density because of droplet jumping events. The decrease in the surface coverage will significantly lower the overall thermal resistance by minimizing the water film. Note that the water film typically possesses a large thermal resistance due to the low thermal conductivity (0.6 W/m-K) and thick film layer (~30 µm).

We additionally calculate the total volume of the droplets for each surface:

$$V = \frac{\pi}{3} [(1 - \cos(\theta))^2(2 + \cos(\theta))R^3]$$

(6)

As shown in Fig. 7(f), the pinned droplets on the AR03 surface result in a smaller total volume of droplets than that of the AR10 despite a larger surface coverage in Fig. 7(e). However, the total volume of droplets of the AR47 is even smaller than other surfaces because the droplets are continuously removed from the surface through droplet jumping. In this process, the gravity effect is minimized by capturing droplets on a horizontal plate.

E. Droplet dynamics at a microscopic perspective

In order to examine droplet shapes at the smaller scale, we examine the environmental SEM (ESEM, Quanta 3D with GSED+GAD detector) images showing condensation process by modulating environmental temperature and pressure, as shown in Fig. 8. The surface temperature of the sample is controlled by using a Peltier cooling stage. In order to enable the condensation on surfaces, the temperature is set to 4°C first, and the chamber pressure is then increased to control the relative humidity over 100%. The pressure for each sample is recorded as 1333, 1095, and 1123 Pa, respectively. In this process, the presence of nanostructures has limited the direct observation of the droplet pinning on the surface. Instead, the changes in droplet shape and contact angle during droplet coalescence can be measured. The elliptical shape of droplets (i.e., pinned droplets) results in a large surface coverage and the decrease in contact angles of the AR03 surface. The AR10 surface first show small spherical droplets (< 20 µm) at the early stage, and they become elliptical shapes as droplet size increases. The droplets on the AR47 superhydrophobic surface exist as both suspended and partially wetted at the early stage, making it easy to be mobile on such surface. Such microscopic-level observations show a good agreement with the observation through optical images in the earlier section.

Based on the condensation performance obtained using the AR03, AR10, and AR47 surfaces, we understand the effects of hydrophobic surfaces’ morphology on droplet growth behavior. The hierarchy of copper oxide nanostructure provides the promising surface morphology in terms of desirable wetting properties and corresponding droplet status for dropwise condensation. It would be interesting for the future research to measure droplet jumping heights and velocity related to the excess kinetic energy of initial droplets.
IV. CONCLUSION

In summary, we study dynamic droplet behaviors under condensation by using various surface morphologies. The hierarchy of copper oxide nanostructures provides the promising surface morphology in terms of desirable wetting properties and droplet dynamics. For this, the copper substrates are prepared using the two-step chemical immersion method that oxides and further functionalizes the surface using a dodecanoic acid to offer hydrophobicity. Key findings from the study are as follows: (1) The combination of small feature size of nanoneedles and large aspect ratio of two-level features enhances the surface hydrophobicity. (2) Hydrophobic surfaces (i.e., AR03 and AR10) show both pinned and mobile droplets depending on condensation conditions. (3) Superhydrophobic surface through a large hierarchy of copper oxide nanostructures (i.e., AR47) facilitates the mobile droplets, enabling droplet jumping events, a small surface coverage, and thereby a minimum thermal resistance. We envision that condensation study of the nanostructured copper surface with different morphology broadens the design principle of hierarchical structures for applications ranging from condensation heat transfer to water collecting surfaces.

ACKNOWLEDGMENT

J.L. is thankful for the financial support from the UCI Mechanical and Aerospace Engineering Department Graduate Fellowship.

REFERENCES


