Direct Observation of the Wetting Mode Transition during Evaporation of Water Droplets on Superhydrophobic Surfaces with Random Roughness Structure

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Abstract

Wetting mode and shape changes of ultrasmall water droplets (80 – 100 nL) were observed during evaporation on superhydrophobic surfaces with different random roughness sizes. Observation of droplets from a top view revealed that the nanometer-coating transition was from Cassie’s mode to air-containing Wenzel’s mode. For a sunny-side-up like state, flat liquid film formation around the droplet edge was observed on the superhydrophobic surface after the wetting mode transition. This state seems to depend on the relation of surface energy values between the solid surface and liquid.

Key-words: Superhydrophobic, Contact angle, Wetting mode transition

1. Introduction

A surface state for which the water contact angle is greater than 150° has commonly been designated as superhydrophobic. Chemical reactions and bonding formation through water are limited on such a surface because of the limited contact area between a solid and water. Accordingly, various functions such as snow removal, antifouling, anticorrosion, mold release, and electrical insulation have been expected on this surface.

Superhydrophobic state is not attainable merely by decreasing the surface energy of a solid. The combination of surface roughness with low surface energy is necessary to prepare superhydrophobic surfaces for enhancement of solid hydrophobicity. Wenzel modified Young’s equation and the described contact angle using roughness factor, which is defined as the ratio of the actual area of a rough surface to the geometrically projected area. This mode implies that surface roughness enhances the wettability of the solid because of the change of the interfacial free energies of solid-liquid and solid-gas interface. Therefore, a hydrophilic surface becomes more hydrophilic, and a hydrophobic surface becomes more hydrophobic.

Cassie proposed a model for a hydrophobic surface with large roughness. With increasing roughness scale of the surface, the air phase intrudes into the solid-liquid interface. Thus, the interface area is assumable as a composite surface of solid and air whose water contact angle is 180°. It has been demonstrated experimentally that the contribution of Cassie’s mode is dominant for a superhydrophobic surface with excellent water shedding properties. To date, various processing methods have been reported for superhydrophobic surfaces by combining surface roughness and low surface energy.

Cassie’s and Wenzel’s modes do not always appear as the most stable state. Cassie’s mode appears as a metastable state even when Wenzel’s mode is the most stable. The transformation phenomenon from Cassie’s mode (Fig. 1(a)) to Wenzel’s mode (Fig. 1(b)) is commonly defined as the wetting mode transition. It has been reported experimentally by evaporation, condensation, and vibration. This transition commonly accompanies an increase of contact angle hysteresis. The stability on each wetting mode has been evaluated from the perspective of surface structure and energy balance.

To date, most studies of wetting mode transition have been conducted using regular structures resembling pillars. Few investigations have examined this phenomenon using a surface with random roughness because of the difficulties in (1)
identifying the representative scale parameters of surface roughness, and (2) clear detection of the wetting mode transition because of insufficient resolution for detailed shape change in this phenomenon.

Very recently, we successfully detected the wetting mode transition of water during evaporation on two superhydrophobic surfaces with different random roughness sizes using nanoliter-scale droplets\(^\text{27}\). Moreover, in that study, we demonstrated that the wetting mode transition radii of a water droplet calculated from the model of Reyssat et al.\(^\text{25}\) using the relation between the average roughness distance \(R_{am}\) and the average roughness height \(R_s\) of the random structure on each surface were close to the experimental values. In this study, we used top and side views to observe evaporation or penetration behavior of ultrasmall water droplets (80 – 100 nL) on superhydrophobic surfaces with fine random roughness during evaporation. Then, the wetting state in this process was discussed.

### 2. Experimental

Transparent superhydrophobic surfaces were prepared using boehmite and a sublimation agent, as explained in our previous report\(^\text{28}\). A commercial boehmite powder (AlOOH, 50 mg, DISPAL 18N4; Contec Co. Ltd., Hamburg, Germany) and reagent-grade acetylacetonate (AACA, 0.915 g, Al(C5H7O2)), Tokyo Kasei Kogyo Co. Ltd., Tokyo, Japan) were mixed with ethanol (25 g). The suspensions were sonicated for 40 min. During sonication, AACA was dissolved into ethanol. The suspension was coated onto a Si (100) wafer (Aki Corp., Miyagi, Japan), which had been cut to 50 × 50 mm, by spin coating at 1000 rpm for 10 s. The coated wafers were dried at room temperature for 30 s. Then wafer heating was conducted at 460˚C for 20 s on a hot plate. Through this treatment, white smoke was produced from the coated surface through sublimation of AACA, and boehmite particles were deposited only on the Si wafer. These coating and heating procedures were repeated five times to yield a solid film with nanoscale roughness.

The plates coated with the roughened boehmite thin films were cleaned using vacuum ultraviolet light illumination (VUV, 172 nm wavelength, UER-20; Ushio Inc., Tokyo, Japan) for 15 min in air at room temperature. The pre-cleaned plate was coated with fluoroalkylsilanes using chemical vapor deposition by heating together with 20 µL of 1H,1H,2H,2H-perfluorodecyltrimethoxysilane (CF₃(CF₂)₇C₂H₆Si(OCH₃)), FAS17, TSL8233; GE Toshiba Silicones, Tokyo, Japan) in a Petri dish at 150˚C for 60 min with flowing N₂. Then, before drying, the sample surfaces were rinsed using acetone, toluene, and distilled water. Hereinafter, we designate this sample as ‘siv-coating’.

Additionally, using spin coating at 1000 rpm for 90 s, a commercial superhydrophobic coating liquid (Siv CLEAR; Car Mate Mfg. Co. Ltd., Tokyo, Japan) was coated onto the same Si (100) wafer, which had been cut to 30 × 30 mm. This coating procedure was repeated five times, producing a transparent superhydrophobic coating with nanoscale random roughness. The sample is designated as ‘siv-coating’.

The surface roughness of each coating was evaluated in 281 × 211 µm rectangular area (1024 × 768 pixel) using a 3D laser scanning microscope (VK-X200; Keyence Co., Osaka, Japan). The average roughness height \(R_s\) and the average roughness distance \(R_{am}\) were calculated from the observed coordinate data on each surface. The sessile drop method, using a contact-angle meter (Dropmaster DM-500; Kyowa Interface Science Co. Ltd., Saitama, Japan), was used to measure the contact angles. The water droplet volume for this measurement was 3.0 µL. Five points were measured for each sample. The values are described as (average) ± (standard deviation) in the text.

Observation of the evaporation behavior of nanoliter-scale water droplets (80 – 100 nL) was conducted using an automatic microscopic contact angle meter (MCA3; Kyowa Interface Science Co. Ltd., Saitama, Japan). Water droplets were placed on the surfaces and the shape change of water droplets were observed from the side view. Moreover, the evaporation was observed simultaneously from a top-view perspective using a charge-coupled device (CCD) camera. For this measurement, the focus was adjusted to the solid-liquid interface of the center part in the droplet (Fig. 2). Atmospheric conditions for these measurements were 22˚C and 22% relative humidity.

### 3. Results and Discussion

The average roughness height \(R_s\) and the average roughness distance \(R_{am}\) calculated from the obtained coordinate data on each surface were, respectively, 0.19 µm and 3.6 µm for the FAS17-coating, and 0.04 µm and 2.4 µm for the siv-coating. The static contact angles were, respectively, 163˚ ± 3˚ (FAS17) and 152˚ ± 2˚ (siv).

Fig. 3 presents sequential pictures of evaporation behavior for an ultrasmall water droplet on the FAS17-coating observed...
from the top view. As was described in the experimental section, the focus was adjusted sequentially to the solid-liquid interface with the droplet size (liquid phase thickness) change during evaporation.

Consequently, the magnifications of Fig. 3 differed for respective evaporation times. The inset pictures show corresponding images from the side view for each evaporation time. From side-view images, an increase of the contact radius was observed at around 171 s, suggesting the wetting mode transition, which corresponds to our previous study27). The colored region, showing the interference color from the air layer, was observable from the images at the solid-liquid interface. The thickness of the air layer varies with the roughness size of the random surface structure when Cassie’s mode is sustained. The different color (interference color) is appeared as a function of the thickness of the air layer. If there is no air layer at the solid-liquid interface, the interference color cannot be observed. The interference color remained even after wetting mode transition (after 171 s) at the solid-liquid interface. Moreover, the state of the center part differed from that of circumference in the image of the evaporation mark after completing evaporation (Fig. 3 (178 s)). The evaporation mark was homogeneous in terms of the circumference, but it was heterogeneous (generated around the salient part of the surface roughness) at the center part. These results suggest that the air layer remained at the solid-liquid interface after the wetting mode transition.

From these results, it was inferred that the wetting mode transition observed in this study was from Cassie’s mode (Fig. 1 (a)) and not to complete Wenzel’s mode (Fig. 1 (b)), but to air-containing Wenzel’s mode (Fig. 4 (a)) by water-phase penetration into the surface structure around the three-phase contact line with trapping air phase. It was deduced that the water phase penetration into the surface structure progressed...
The flat liquid film was observable around the droplet on the image \((t = 176 \text{ s})\) in Fig. 3. Ishino et al. compared the energetic stability for Cassie’s and Wenzel’s modes. It indicated the possibility of a “sunny-side-up state”\(^{26,29}\) (Fig. 4 (b)) as an additional wetting state, which is the droplet on the liquid film. They reported that the sunny-side-up state can appear as a quasi-static state when the droplet deposited on the liquid film is more stable than in Wenzel’s mode in the penetration process of liquid phase into surface structure. According to their report, the sunny-side-up state would appear during wetting mode transition, in which the liquid phase penetrates into the surface structure from the center part of the contact area between liquid and solid surface. However, no sunny-side-up state has been reported in the wetting mode transition from Cassie’s mode on the superhydrophobic coating during evaporation. The state of \((t = 176 \text{ s})\) resembles the sunny-side-up state, except for the contained air phase, which was trapped by the water-phase penetration into the surface structure around the three-phase contact line in the solid-liquid interface (Fig. 4 (c)).

A similar state was observed on the siv-coating in the evaporation of ultrasmall water droplets (Fig. 5). From side-view images, an increase of the contact radius was observed at around 164 s, suggesting the wetting mode transition. The interference color was apparent even after the wetting mode transition at the solid-liquid interface. Additionally, the liquid film, which resembles a sunny-side-up state, appeared around the edge of the droplet contact area in the image at \(t = 169 \text{ s}\) in Fig. 5. Moreover, multiple air bubbles were confirmed in the center part of the droplet from the top-view image on the state in the image at \(t = 171 \text{ s}\), although the state resembles completion of evaporation by observation from the side-view. Different homogeneity in evaporation between the circumference and the center part of the contact area was also observed after completion of evaporation (image at \(t = 172 \text{ s}\)). These results also suggest that the air layer remained in the solid-liquid interface after the wetting mode transition. In this study, the liquid film did not expand remarkably outward on the siv-coating after appearance of the sunny-side-up like state. This result revealed that the surface energy of solid phase was much less than that of the liquid phase: the surface energy gap separating the solid (FAS17) and liquid (water) phase was large.

However, when a small (10 nL) droplet of a liquid with a small surface energy is placed on a highly hydrophobic surface with surface energy greater than FAS17, the droplet penetrated into the surface structure. Fig. 6 presents sequential top-view pictures of such a case; an ultra-small ionic liquid droplet (1-hexyl-3-methyl-imidazolium/tetrafluoroborate (HMI; Sigma-Aldrich Corp., St. Louis, Missouri; surface energy 35.8 mJ·m\(^{-2}\), density 1.15 g·mL\(^{-1}\), viscosity 195 mm\(^2\)·s\(^{-1}\)) was put into the surface structure of the same boehmite films with nanoscale roughness coated with FAS3 (CF\(_3\)C\(_2\)H\(_4\)Si(OCH\(_3\))\(_3\), KBM-7103; Shin-Etsu Chemical Co. Ltd., Tokyo, Japan) instead of FAS17. The roughness of this coating was the same as that for the FAS17-coating, however its contact angle was 146˚ ± 2˚. In the image at \(t = 0.5 \text{ s}\), HMI had already penetrated into the surface structure of FAS3-coating, and the liquid film expands around the droplet. This state resembles the sunny-side-up state reported by Ishino et al.\(^{26}\).

Until around \(t = 4 \text{ s}\), the droplet part remained on the liquid film. After \(t = 5 \text{ s}\), the droplet part had combined with the liquid film, and the liquid phase was spreading into the surface structure. This result demonstrates that the droplet penetrated into the surface structure when the surface energy gap separating the solid and liquid phase was small.

Considering the effect of Laplace pressure from the droplet curvature, the wetting mode transition from Cassie’s to Wenzel’s mode is expected to occur from the center part of the droplet under a static or quasi-static state\(^{26}\). However, water droplet evaporation is not exactly a static state. The three-phase contact line position changes continuously with evaporation time. In the present research case, the wetting
mode transition initiated from the three-phase contact line, and the air phase was trapped on the center part of solid-liquid interface. Detailed discussion of the contact angle decrease under evaporation and the mixture of different wetting modes at the center and the circumference part of the droplet will be addressed in future studies.

4. Conclusion

Observation of droplet evaporation from the top view revealed that the wetting mode transition on this study for nanometer coating was from Cassie’s mode to air-containing Wenzel’s mode. The liquid film was observed for a nanometer coating around the circumference of the contact area of the droplet after the wetting mode transition, as in a sunny-side-up state.

References


ランダムな粗さをもつ超撥水表面上での水滴の蒸発過程での濡れ転移の直接観察

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要 旨

ランダムな粗さをもつ超撥水面上での、nLレベルの微小水滴の蒸発過程での濡れ転移を、水滴の上端と側面から高速度カメラを用いて連続的に観察した。蒸発は初期にはCassieモードで撥水をしていたが、蒸発が進むにつれてWenzelモードへ濡れ性が転移し、その際、蒸発の内部には完全に濡れずに気泡が残る様子が観察された。またその際、二重層の周辺に液膜が形成され、sunny-side-up stateに類似の状態がみられた。このような状態の実現には、液体と固体の表面エネルギーの大きさの相対関係が重要であることが示唆された。

キーワード：超撥水、接触角、濡れ転移

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