DROPLET EVAPORATION ON NANOSTRUCTURED SUPERHYDROPHOBIC SURFACES

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ABSTRACT

We report the evaporative processes of droplets of pure water and a protein solution on superhydrophobic surfaces made of sharp-tip nanostructures having a submicron pitch and varying heights.

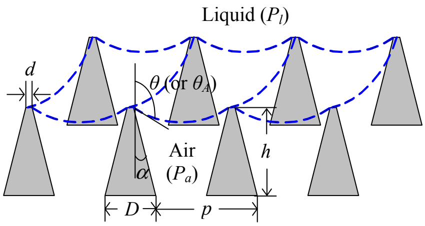
KEYWORDS: Droplet, Evaporation, Nanostructure, Superhydrophobic surface

INTRODUCTION

Droplet evaporation on solid surfaces is important for many applications such as ink-jet printing, DNA chip, and protein crystallization. Although studies on planar hydrophilic or hydrophobic surfaces have been extensive, investigations on patterned surfaces have started only recently with the advent of superhydrophobic surfaces. So far, the tested surfaces had structures in micrometers [1, 2] or with random roughness [3], limiting the meaningful range of a droplet size to above ~50 μm. And the examined liquids were simple water [1-3]. In this paper, the surfaces had a precisely-defined nanometer-scale pattern, capable of extending the range of study, and two different types of liquids were tested -- pure water and a protein solution.

THEORY

Surface parameters such as a structural pitch, height, and sidewall profile affect surface superhydrophobicity. For the sharp-tip nanopost structures (Fig. 1), the criterion to maintain a de-wetted state can be reduced to following equations:



$$p < \sqrt{\frac{\pi d^2}{4} - \frac{\pi \gamma d \cos(\theta_A - \alpha)}{\Delta P}}, \qquad (1)$$

$$h > \frac{1 - \sin(\theta_A - \alpha)}{-2\cos(\theta_A - \alpha)} \cdot \left(\sqrt{2}p - d\right) \qquad (2)$$

Figure 1. Liquid meniscus expected over hydrophobic post structures of a cone shape. In case of d<<p, a liquid meniscus is assumed to have a spherical shape forming a contact angle of θ (or an advancing contact angle of θ_A) with a post side.

where p denotes a structural pitch, d a tip diameter, γ the interfacial tension of the liquid-air interface, θ_A an advancing contact angle, α a cone angle, ΔP a liquid pressure over than of an air (i.e., $P_l - P_a$), and h a structural height, respectively. While a hydrostatic pressure due to a droplet's weight is typically negligible, a Laplace pressure due to a droplet curvature significantly increases as the size of a

978-0-9798064-1-4/µTAS2008/$20©2008CBMS

droplet decreases in evaporation. The key requirement to maintain the de-wetted superhydrophobic state is to have tall and slender, dense-array (e.g., submicron-pitch) nanostructures with a high advancing angle.

EXPERIMENTAL

A well-ordered square-array of nanopost structures was fabricated on a silicon substrate (2×2 cm^2) by interference lithography and deep reactive ion etch (DRIE) (Fig. 2) [4]. Maintaining the pattern periodicity at 230 nm and keeping the structural tips sharp (less than 10 nm in the apex radius of curvature), only structural heights were varied from ‘Low’ (~100 nm), ‘Mid’ (~300 nm), to ‘High’ (~500 nm). The evaporative processes of water and a protein solution (Dulbecco′s Modified Eagle Medium: DMEM) were examined on a planar control surface (Smooth) and nanopost samples both coated with Teflon (~10 nm thick). While a droplet (initial volume of ~25 μL) was evaporated in a room environment, a contact angle and a contact diameter were measured with a goniometer at every 15 minutes (Fig. 3).

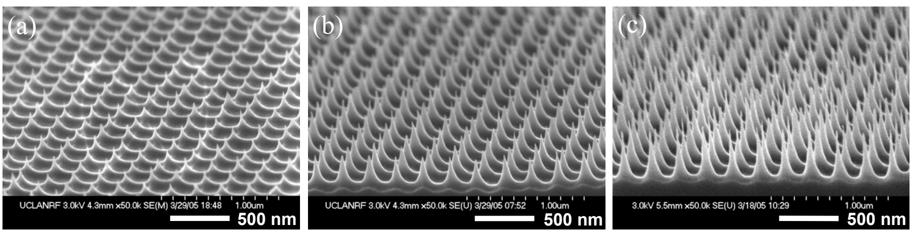


Figure 2. Scanning electron microscopy images of sharp-tip nanopost structures: (a) Nanopost-Low;(b)Nanopost-Mid;(c)Nanopost-High.

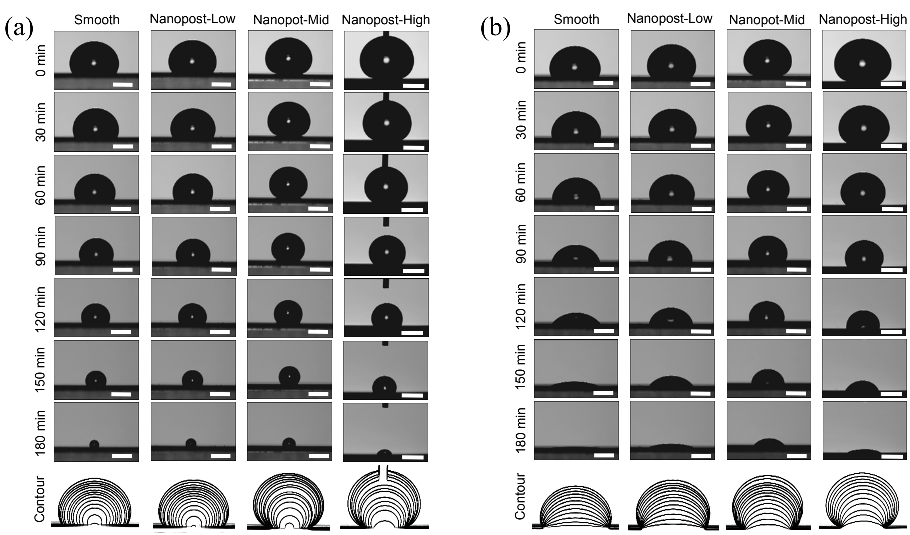


Figure 3. Optical micrograph images and contours of evaporating droplets: (a) Water droplets; (b) DMEM droplets. (Scale bar in each image: 1 mm)

RESULTS AND DISCUSSION

Initially, for both water and DMEM droplets, High and Mid provided a great superhydrophobicity (contact angle > 170°) while Low did not (contact angle < 130°, similar to ~120° of Smooth). During the evaporation of water on High and Mid (Figs. 3a and 4a), the contact angles initially decreased rapidly from 170° with a slow decrease in the contact diameter, suggesting a contact-line pinning on the tips. Once the receding contact angles reached ~130°, the contact angles decreased slowly with a rapid decrease in the contact diameter, suggesting the contact-line jumping from posts to posts with the de-wetted state maintained. During the evaporation of DMEM (Figs. 3b and 4b), a noticeable increase of a contact diameter was observed on High and Mid for the starting 30 minutes, suggesting an adsorption of proteins onto the surface and a consequent loss of superhydrophobicity. Afterward, a contact angle decreased continuously with a minuscule decrease in the contact diameter, suggesting that the contact line was pinned throughout the evaporation.

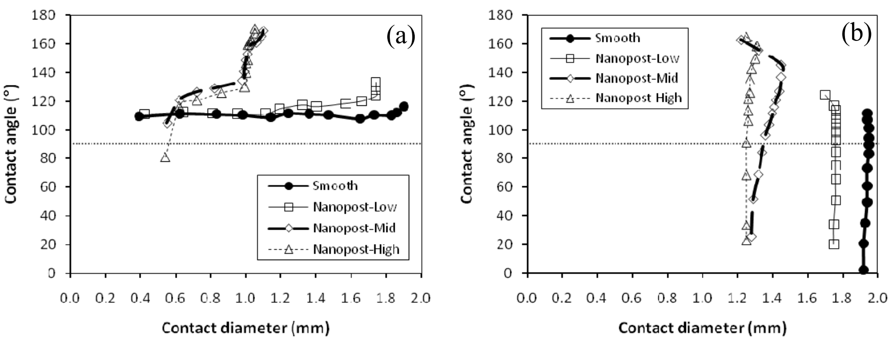


Figure 4. A change of a contact angle with a contact diameter: (a) Water droplets; (b) DMEM droplets.

CONCLUSIONS

We showed that the nanometric structures of superhydrophobic surfaces significantly affect the evaporation processes of droplets. The evaporation processes were different depending on a liquid type and the structural heights, suggesting that such effects should be considered in design and application of droplet-based micro-devices involving evaporation.

REFERENCES

[1] G. McHale, S. Aqil, N. J. Shirtcliffe, M. I. Newton, H. Y. Erbil, *Analysis of droplet evaporation on a superhydrophobic surface*, Langmuir, **21**, 11053, (2005).

[2] M. Reyssat, J. M. Yeomans, D. Quere, *Impalement of fakir drops*, Europhysics Letter, **81**, 26006, (2008).

[3] X. Zhang, S. Tan, N. Zhao, X. Guo, X. Zhang, Y. Zhang, J. Xu, *Evaporation of sessile water droplets on superhydrophobic natural lotus and biomimetic polymer surfaces*, ChemPhysChem, **7**, 2067, (2006).

[4] C.-H. Choi, C.-J. Kim, *Fabrication of dense array of tall nanostructures over a large sample area with sidewall profile and tip sharpness control*, Nanotechnology, **17**, 5326, (2006).