Superhydrophobic surface at low surface temperature

Min He, Huiling Li, Jianjun Wang, and Yanlin Song

Additional information on Appl. Phys. Lett.

Superhydrophobic surface at low surface temperature

Min He,[1,2] Huiling Li,[1] Jianjun Wang,[1,a)] and Yanlin Song[1,3,a)]

[1]*Beijing National Laboratory for Molecular Sciences (BNLMS), Laboratory of New Materials,
Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, People's Republic of China*
[2]*Graduate University of the Chinese Academy of Sciences, Beijing 100190, People's Republic of China*
[3]*Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190,
People's Republic of China*

Superhydrophobic surfaces have aroused great attention for promising applications, e.g., anti-ice/frost. However, most surfaces which are superhydrophobic at room temperature lose their superhydrophobicity at low surface temperatures. Here, surfaces with different area fractions of the solid surface in contact with the liquid (f_1) were designed. It is found that surfaces with f_1 equal to or smaller than 0.068 maintain the superhydrophobicity when the surface temperature approaches the dew-point. These results are crucial to understand the correlation between the surface morphology and the superhydrophobicity around the dew-point, and design effective surfaces with desired wettability. © *2011 American Institute of Physics.* [doi:10.1063/1.3558911]

Superhydrophobic materials that have water contact angles (CAs) in general larger than 150° have garnered much attention recently because of their wide applications in a rich variety of fields. In the processes of the heat transfer, for example, reports have shown that the heat transfer coefficient is enhanced by approximately one order of magnitude when the dropwise condensation occurs as compared with that of the film condensation.[1,2] It is well-known that the condensation mode of water is mainly determined by the surface wettability, e.g., superhydrophobic surfaces usually lead to the dropwise condensation. Thus, in order to have a permanent higher heat transfer coefficient it is highly desirable to maintain the surface superhydrophobic even when the surface temperature is lowered to the dew-point.

Up to date, many superhydrophobic materials have been fabricated[3–6] and the surface wettability was mainly investigated at the room temperature[7–9] based on the surface morphology and the surface chemical composition. Temperature has also recently been shown to affect the wettability of a surface,[10–14] it has been found that many materials lost the superhydrophobicity when the temperature changes. Liu *et al.*[15] reported that the surface wettability of "superhydrophobic" materials to hot water increased with the increase in the water temperature. Many experiments have also been carried out to investigate the wettability of natural water repellent surfaces[12,16] and artificial superhydrophobic surfaces[14,17] at the dew-point. Most of these surfaces are no longer superhydrophobic when the condensation occurs. However, little attention has been paid to the wettability evolution of different surfaces when the surface temperature changes from the room temperature to the dew-point,[18] and most importantly, no answer has been provided to the pending question: what kind of surface can maintain superhydrophobicity at the dew-point?

Here, several surfaces with different area fractions of the solid surface in contact with the liquid (f_1) were designed and the evolution of the wettability upon changing the surface temperature was investigated under the controlled relative humidity (RH) and the room temperature. A correlation is established between the surface morphology and the wettabilty at the dew-point and thus provides guidance for maintaining the superhydrophobicity when the surface temperature decreases. The experimental results show that the surfaces with f_1 equal to or smaller than 0.068 still has a water CA no less than 150° when the surface temperature approaches to the dew-point. A possible interpretation based on the water molecules adsorption was also proposed. These results will be beneficial to the design and fabrication of materials with optimal surface morphologies so that the superhydrophobicity could be retained even when the surface temperature varies.

Regular poly(dimethysiloxane) (PDMS) post arrays were fabricated using porous silicon wafers as the template. The porous silicon wafers were obtained by a lithographic etching process (see Ref. 19 for Fig. S1). The obtained porous silicon wafers consisted of pores with the diameter of around 2 μm (see Ref. 19 for Table S1). The PDMS post arrays were prepared by casting the PDMS precursor liquid mixed with the curing agent (10:1 by weight) onto the porous silicon wafers. After curing at 110 °C for 2 h, the porous silicon wafer was removed and the PDMS post arrays were obtained (Fig. 1).

It can be seen that the PDMS posts protrude perpendicularly out with a height of approximately 13.4 μm. The scanning electron microscopy (SEM) side-view images show that the PDMS post has a smooth spherical cap on the top. The

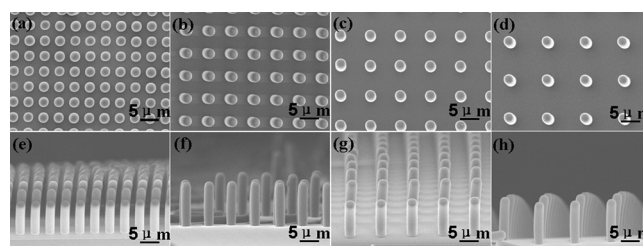FIG. 1. SEM images of arrayed PDMS posts with different spacing (a) 1.609 μm, (b) 3.648 μm, (c) 5.643 μm, (d) 7.666 μm, (e)–(h) corresponding side views of PDMS post arrays in (a)–(d).

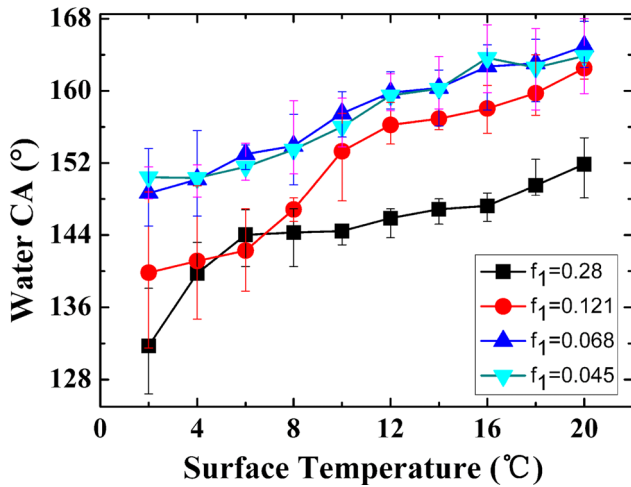a)Electronic addresses: wangj220@iccas.ac.cn and ylsong@iccas.ac.cn.

FIG. 2. (Color online) The evolution of water CA with different surface temperature on superhydrophobic PDMS surfaces with different f_1. The data are obtained at RH of 30% and the environmental temperature of 20 °C.
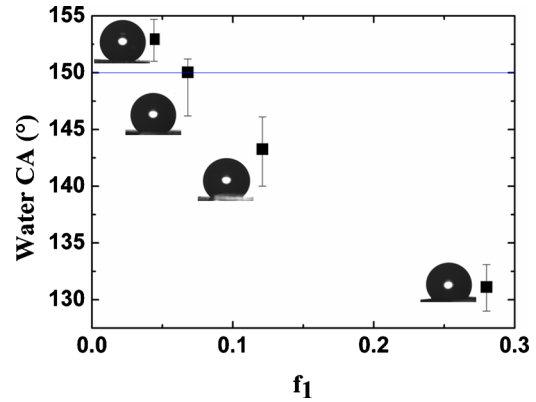

FIG. 3. (Color online) The water CA of superhydrophobic surfaces with PDMS post arrays (marked by black solid squares) at the dew-point. The data were obtained at surface temperature of approximately 2 °C, RH of 30%. The blue line is a guide for the CA of 150°.

average space between two neighboring circular PDMS posts is 7.666 μm, 5.643 μm, 3.648 μm, and 1.609 μm with the post diameter of 2.387 μm, 2.357 μm, 2.352 μm, and 2.391 μm, respectively (see Ref. 19 for Table S1). For these PDMS posts[20]

$$f_1 = \frac{\pi a^2}{4(a+b)^2}, \qquad (1)$$

where a is the diameter of the post and b is the space between two neighboring posts. According to the Eq. (1), the corresponding f_1 is 0.045, 0.068, 0.121, and 0.28, respectively. The static water CA measured at the room temperature is 163.9° standard deviation (SD 3.6), 164.4° (SD 2.5), 163.4° (SD 0.91), and 151.9° (SD 2.9) on the PDMS surface with f_1 of 0.045, 0.068, 0.121, and 0.28, respectively.

Based on the f_1, we used the Cassie equation to calculate the static CAs on these PDMS post array surfaces[21]

$$\cos \theta_c = f_1 \cos \theta_1 + f_2 \cos \theta_2, \qquad (2)$$

where f_1 and f_2 are the fractions of two different solid phases, respectively. θ_c is the apparent water CA at the Cassie state on roughness surface, θ_1 and θ_2 are the equilibrium water CAs on the two different solid phases. We obtained the static water CAs of 167°, 163.8°, 159.5°, and 149.4° on the PDMS surface with f_1 of 0.045, 0.068, 0.121, and 0.28, respectively. The experimentally measured water CAs agree very well with those calculated by the Cassie equation, which clearly indicates that droplets on these PDMS post array surfaces stay at the Cassie state at the room temperature.

In order to find out the evolution of the water CA with the surface temperature, the static water CAs were measured at different surface temperatures under the environmental condition of the RH of 30% and the room temperature of 20 °C. Under this experimental condition, the dew-point is about 2 °C. The results are shown in Fig. 2. The static water CA on the PDMS post arrays decreases with the decrease in the surface temperature when the surface temperature decreases to the dew-point. It is interesting to note that the static water CA on the PDMS post array surfaces with the f_1 smaller than 0.068 is greater than 150° at the dew-point, i.e., 2 °C. The trend of the evolution of the water CA with the

surface temperature is consolidated by that on the silicon post array surfaces (see Ref. 19 for Table S2, Figs. S2 and S3) and is similar to that reported recently by Nakajima and co-workers.[18]

The static water CAs on the PDMS post array surfaces at the dew-point are showed in Fig. 3. The blue line is the hallmark for water CAs equaling to 150°. The water CA at the dew-point increases with the decrease in f_1 on the PDMS post array surface. On the surfaces with f_1 of 0.28 and 0.121, the static water CAs are much smaller than 150° when the surface temperature is 2 °C, which is the dew-point under the experimental condition. When the f_1 is equal to 0.068, the static water CA on the PDMS posts surface is close to 150°. As the f_1 decreases to 0.045, the static water CA on the PDMS posts is above 150°. This obviously shows that the superhydrophobicity of PDMS post array surface is retained at the dew-point, when the f_1 is not more than 0.068.

The observations of the surface wettability evolution lead to the assumption that there are water molecules adsorption and condensation on the PDMS surfaces when the surface temperature approaches to the dew point. In order to test this hypothesis, the evolutions of the water CA on a smooth silicon wafer modified by heptadecafluoro-1, 1, 2, 2-tetradecyl trimethoxysilane (FAS-17) (see Ref. 19 for Fig. S4), and a PDMS surface at different surface temperature were investigated (Fig. 4). The values of the water CA on the smooth surfaces also decrease with the decrease in the sur-
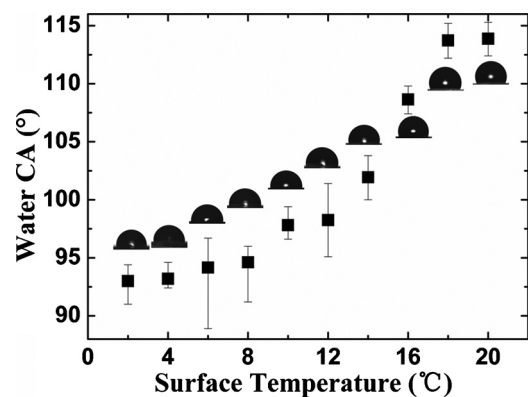

FIG. 4. The evolution of water CA on a flat PDMS surfaces with different surface temperature. The data are obtained at RH of 30% and the environmental temperature of 20 °C.

face temperature. This is due to the adsorption of water molecules on the cold surfaces. Water molecules adsorb on a cold surface when the surface temperature decreases, no matter the surface is hydrophobic or hydrophilic. This has already been proved by others.[22–25] According to the Young's equation [$\cos \theta = (\gamma_{sg} - \gamma_{sl}) / \gamma_{lg}$, γ_{sg}, γ_{lg}, and γ_{sl} are the surface tension of the solid-gas interface, liquid-gas interface and solid-liquid interface, respectively], when the water molecular adsorption is considered, the γ_{sg} is close to or even equal to the γ_{lg} (Refs. 26 and 27) and the static water CA decreases with the decreasing surface temperature, which agrees with our observations and confirms the adsorption of water molecules on the cool surfaces, including the patterned and smooth surfaces (if the water molecular adsorption is not considered, the static water CA increases due to the increase of γ_{lg} (Ref. 28) (in the present experiments, the γ_{sg} may not change so much with temperature), when the surface temperature decreases. This is in contrary to the experimental results).

Based on the water molecular adsorption on the surface, the evolution of the water CA on the structured silicon and PDMS surface at the dew-point is reliable according to the Cassie equation.[21] When water molecules are adsorbed on a cold surface, the solid-gas interfacial tension is considered to be close to the surface tension of water,[27] indicating a more hydrophilic solid surface. According to the Kelvin equation,

$$RT \ln \frac{P_r}{P_0} = \frac{2\gamma M}{\rho r}. \tag{3}$$

P_r is the saturated vapor of a droplet with the radius of r. P_0 is the saturated vapor of flat liquid surface. T is the temperature. M is the mole weight of water and ρ is the density of water. When a sessile water droplet approaches to a cold surface, the curved liquid-gas interface increases the humidity near the cold surface, which is useful to the water molecular adsorption and even leads to water condensation.[18] For an extreme case that adsorbed water molecules cover completely the local region under the water droplet when a sessile droplet approaches the solid surface [in this case, when a droplet sits on the top of the surface, it corresponds to water-on-water and the θ_1 is 0° (Ref. 29)]. The solid surface consists of two parts. One is the area covered by adsorbed water molecules and the other is entrapped air (the θ_2 is 180°). As a result, the Cassie equation can be written as below:

$$\cos \theta_c = f_1 - f_2. \tag{4}$$

Drops come into contact with a superhydrophobic material with the CAs in general larger than 150° (Ref. 30) and the f_1 should not be smaller than 0.067 according to the Eq. (4). This indicates that there should be the critical contact area fraction (f_c) at which a surface can be still superhydrophobic even when the surface temperature approaches to the dew-point. This result is in accordance with the results from the experiments that on the PDMS surface.

In summary, several superhydrophobic surfaces were fabricated to investigate the evolution of the wettability under controlled surface temperature. The wettability of all the surfaces is found to increase when the surface temperature decreases to approach the dew point. The water CA on these surfaces are still higher than 150° when the area fractions of solid surface in contact with liquid (f_1) are equal to or smaller than 0.068. According to the Cassie equation, there is the critical contact area fraction (f_c) equal to 0.067 for a superhydrophobic surface to maintain superhydrophobicity when the surface temperature approaches to the dew point of water, which is accordance with the results from the experiments. These results are important for the applications of superhydrophobic materials at natural conditions, and will be beneficial to design and optimize surface morphologies for solving the puzzles of wettability variation upon the change in temperature and RH.

[1]C. Dietz, K. Rykaczewski, A. G. Fedorov, and Y. Joshi, Appl. Phys. Lett. **97**, 033104 (2010).

[2]S. Daniel, M. K. Chaudhury, and J. C. Chen, Science **291**, 633 (2001).

[3]B. Bhushan, K. Koch, and Y. C. Jung, Appl. Phys. Lett. **93**, 093101 (2008).

[4]H. Y. Erbil, A. L. Demirel, Y. Avci, and O. Mert, Science **299**, 1377 (2003).

[5]K. Lau, J. Bico, K. Teo, M. Chhowalla, G. Amaratunga, W. I. Milne, G. H. McKinley, and K. K. Gleason, Nano Lett. **3**, 1701 (2003).

[6]B. Bhushan, K. Koch, and Y. C. Jung, Soft Matter **4**, 1799 (2008).

[7]C. W. Extrand, Langmuir **18**, 7991 (2002).

[8]L. C. Gao and T. J. McCarthy, Langmuir **22**, 2966 (2006).

[9]D. Quéré, Nature Mater. **3**, 79 (2004).

[10]F. Xia, H. Ge, Y. Hou, T. L. Sun, L. Chen, G. Z. Zhang, and L. Jiang, Adv. Mater. (Weinheim, Ger.) **19**, 2520 (2007).

[11]Y. M. Zheng, D. Han, J. Zhai, and L. Jiang, Appl. Phys. Lett. **92**, 084106 (2008).

[12]B. Mockenhaupt, H. J. Ensikat, M. Spaeth, and W. Barthlott, Langmuir **24**, 13591 (2008).

[13]D. Quéré, Annu. Rev. Mater. Res. **38**, 71 (2008).

[14]R. D. Narhe and D. A. Beysens, Phys. Rev. Lett. **93**, 076103 (2004).

[15]Y. Y. Liu, X. Q. Chen, and J. H. Xin, J. Mater. Chem. **19**, 5602 (2009).

[16]Y. T. Cheng and D. E. Rodak, Appl. Phys. Lett. **86**, 144101 (2005).

[17]K. A. Wier and T. J. McCarthy, Langmuir **22**, 2433 (2006).

[18]T. Furuta, M. Sakai, T. Isobe, and A. Nakajima, Langmuir **26**, 13305 (2010).

[19]See supplementary material at http://dx.doi.org/10.1063/1.3558911 for additional explanations, figures, and tables.

[20]N. A. Patankar, Langmuir **19**, 1249 (2003).

[21]A. Cassie and S. Baxter, Trans. Faraday Soc. **40**, 546 (1944).

[22]H. J. Wang, X. K. Xi, A. Kleinhammes, and Y. Wu, Science **322**, 80 (2008).

[23]C. A. Scholes, G. W. Stevens, and S. E. Kentish, J. Membr. Sci. **350**, 189 (2010).

[24]T. M. Roschina, N. K. Shoniya, M. S. Lagutova, A. B. Nikol'skaya, V. Y. Borovkov, and L. M. Kustov, Russian J. Phys. Chem. A **83**, 290 (2009).

[25]D. B. Asay and S. H. Kim, J. Phys. Chem. B **109**, 16760 (2005).

[26]C. A. Ward and K. Sefiane, Adv. Colloid Interface Sci. **161**, 171 (2010).

[27]H. Ghasemi and C. A. Ward, J. Phys. Chem. C **114**, 5088 (2010).

[28]E. H. Trinh and K. Ohsaka, Int. J. Thermophys. **16**, 545 (1995).

[29]M. Nosonovsky and B. Bhushan, Langmuir **24**, 1525 (2008).

[30]C. Dorrer and J. Rühe, Soft Matter **5**, 51 (2009).