Observation of hydrophobic-like behavior in geometrically patterned hydrophilic microchannels

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We present our observation of meta-hydrophobicity, where geometrically patterned surfaces make *hydrophilic* microchannels exhibit *hydrophobic-like* behaviors. We analyze the wetting-induced energy decrease that results from the surface geometries and experimentally demonstrate how those geometries can modulate the dynamics of capillary-driven wetting and evaporation-driven drying of microfluidic systems. Our results also show that the modulated wetting dynamics can be employed to generate regulated patterns of microbubbles. © 2010 American Institute of Physics. [doi:10.1063/1.3499416]

The phenomenon of wetting is central in many processes in nature (e.g., the rise of sap in plants and the transport of ground water in porous soils) and in artificial systems (e.g., the wicking in tissue papers and the filling of capillary tubes).¹ The classical models proposed by Wenzel² and Cassie–Baxter,³ based on their investigations on textiles, are commonly used to explain the hydrophilic/hydrophobic behavior of various surfaces, which in turn determine the resulting wetting processes at such surfaces.^{4–6} Recently, the phenomenon of wetting forms a significant interconnection with the fast growing field of microfluidics.⁷ On one hand, as surface effects significantly influence the microscopic flows, microfluidics can benefit from chemically or geometrically patterned channel surfaces that allow for an efficient control of the flows.⁸ On the other hand, investigations performed in microfluidics provide deeper insight on the rich physics involved in wetting phenomena. One recent example is the investigation by Kusumaatmaja *et al.*,⁹ which highlighted the mechanism of liquid-front pinning at sharp corners and demonstrated how it can modulate the capillarity-driven filling dynamics inside microfluidic channels. Here we further expand on their analysis, particularly presenting our observations that geometrically patterned surfaces can make *hydrophilic* channels exhibit *hydrophobic-like* behaviors, which is in stark contrast with previously reported phenomena where geometrically patterned surfaces can only enhance the hydrophobicity of hydrophobic surfaces (or the hydrophilicity of hydrophilic surfaces).^{2–5}

Our analysis employs grooves, rather than posts/ridges,⁹ because grooves are more straightforward to fabricate (and hence more suitable for experimental comparison), for example, by isotropic etching on a monolithic microfluidic substrate. Figure 1(a) shows schematics of the liquid front dynamics during capillarity-driven wetting in a two-dimensional grooved microchannel (θ_a =advancing contact angle): while the liquid front at the upper wall will proceed normally, the liquid front at the lower wall will be pinned at the sharp corner,⁹ where the contact angle expands gradually from θ_a to $\theta_a' = 90^\circ + \theta_a$.¹ Even though Kusumaatmaja *et al.*⁹ correctly con-

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FIG. 1. Schematics of the liquid front dynamics during capillarity-driven wetting [in (a) two-dimensional (2D) (Ref. 9) and (b) three-dimensional (3D) top views] and evaporation-driven drying [in (c) 2D and (d) 3D top views]. For detailed dimensions, see supplementary information (Ref. 12).

cluded that this pinning will become permanent only when the equilibrium contact angle is $\theta_e > 45^\circ$, their conclusion is only valid for two-dimensional systems without sidewalls, which is rarely found in both natural and artificial systems. When such sidewalls exist, we need to extend the analysis into three dimensions, as shown in Fig. 1(b). Here we focus on low-aspect-ratio (i.e., height $\ll$ width) channels commonly fabricated in microfluidics, where capillary wetting at the sidewalls is relatively faster than at the channel center,^{10,11} mainly because the sidewalls allow for

larger liquid-solid interface area (and hence experience larger wetting-induced energy decrease) than the channel center. Interestingly, the capillarity-induced flows at the sidewalls will allow the liquid front to *circumvent* the grooves, effectively altering the condition for pinning: as long as capillary filling still occurs through the sidewalls, the liquid front will rather go around the grooves (through the sidewalls, where the contact angle is θ_a) than through the grooves (with sharp edges, where the contact angle has to expand from θ_a to θ_a'). This dynamics will result in several interesting phenomena. First of all, as the liquid front can be prevented from spontaneously wetting the grooves [even for an equilibrium contact angle of $\theta_e < 45^\circ$ (Ref. 9)], the hydrophilic grooved microchannel can exhibit hydrophobic-like behavior during the capillary filling. On top of that, the liquid front that goes around the grooves can end up enclosing and trapping air bubbles, possibly allowing us to generate *regulated patterns* of air bubbles that depend mainly on the groove dimensions.

Expanding our analysis to the evaporation-driven drying process, Fig. 1(c) shows the schematics of the liquid front dynamics that will occur in a two-dimensional grooved microchannel (θ_r =receding contact angle): while the liquid front at the upper wall will proceed normally, the liquid front at the lower wall will experience a sudden change of contact angle at the sharp corner, i.e., from θ_r into $\theta_r' = 90^\circ + \theta_r$. Because the energy required to maintain wetting at θ_r' is higher than for θ_r , at this point the liquid front will spontaneously relocate to allow the contact angle to return to θ_r . Here we have two possibilities for the liquid front at the lower wall: either it moves toward the gas phase or toward the liquid phase. The second option is more favorable energetically, because evaporation will induce a liquid-to-gas phase transition and hence push the liquid front toward the liquid phase. When this happens, the liquid front will swiftly relocate from one sharp edge of the groove into the other edge. Interestingly, this will mean that the hydrophilic grooved microchannel will experience a relatively quicker drying, which is usually associated as a hydrophobic-like behavior. This analysis can be further expanded into three dimensions [Fig. 1(d)]. During the drying process, the larger wetting-induced energy decrease at the sidewalls dictates that the wet condition at the sidewalls is maintained longer than at the channel center. Upon touching the nearest edge of a groove, the liquid front will swiftly relocate to the furthest edge, resulting in a quicker drying particularly at the grooves. The liquid front will then gradually reshape to follow the evaporation rate, until it arrives at another groove and repeat the process.

Our analysis indicates that geometrically patterned hydrophilic microchannels can exhibit hydrophobic-like behaviors (a phenomenon we call as meta-hydrophobicity) during both the wetting and drying processes. Here we should emphasize the difference between meta-hydrophobicity and superhydrophobicity:⁵ while meta-hydrophobicity is a result from a nonequilibrium process (i.e., either wetting or drying), superhydrophobicity is a result from a metastable configuration where the surface energy is in a (local) minimum.

We experimentally investigate this phenomenon of meta-hydrophobicity using monolithically hydrophilic microfluidic chips made from D263 borosilicate glass wafers (Schott AG, Mainz, Germany). Channels were isotropically etched (height $H=1\ \mu\text{m}$, width $W=100\ \mu\text{m}$, see Fig. 1) into the top wafer using hydrofluoric acid, while the inlet and outlet were made using powder blasting. Periodic grooves, with a total length of $600\ \mu\text{m}$, were isotropically etched into the bottom wafer. Different sets of grooves with varying periods ($P=5, 10$, and $15\ \mu\text{m}$) and depths ($D=0.2, 0.5$, and $0.8\ \mu\text{m}$) were used.¹² After cleaning, the wafers were thermally fused. For each experiment, a 5 ml droplet of distilled water spontaneously filled the channel from the inlet, and afterward experienced spontaneous drying due to evaporation at 293 K. The wetting and drying processes were captured using a Nikon Ti-E microscope (Nikon Instruments Europe B.V., Amstelveen, The Netherlands) with a $10\times$ lens ($\text{NA}=0.3$) (NA denotes numerical aperture) and a digital camera (Sensicam QE, PCO AG, Kelheim, Germany) with a 1376×1040 pixel charged-coupled device format ($6.45\times 6.45\ \mu\text{m}^2$ pixel size). These images were acquired by means of the DAVIS software (LaVision GmbH, Goettingen, Germany, 2×2 binning, 20 Hz) and were processed and analyzed using ImageJ (<http://rsbweb.nih.gov/ij/index.html>).

Figures 2(a) and 2(b) show snapshots of the wetting process in the microchannels, without and with the grooves, respectively. Without the grooves, faster wetting at the sidewalls leads to air

FIG. 2. Typical dynamics observed experimentally: (a) wetting without the grooves; (b) wetting with the grooves; (c) drying without the grooves; (d) drying with the grooves. Also shown are the liquid front propagation for different groove periodicity: (e) without grooves, (f) with groove period of $P=15 \mu\text{m}$; (g) with groove period of $P=10 \mu\text{m}$.

bubble enclosure by the liquid front at the channel center.¹⁰ On one hand, bubble formations in microfluidic systems can have negative consequences, e.g., if they lead to slower filling rates of channels¹¹ or when they disrupt the flow.¹³ On the other hand, these bubbles can also be useful, particularly if their sizes and locations can be regulated, such that they can serve as bubble-based

platforms^{14,15} for various lab-on-a-chip applications, e.g., to produce optofluidic elements¹⁶ or to study the structure and dynamics of foam.¹⁷ Figure 2(b) demonstrates this possibility, where the wetting dynamics modulation by the grooves led to generation of regulated patterns of bubbles. The observed filling dynamics also match our analysis in Fig. 1(b): faster wetting at the sidewalls is followed by “zipping” of the liquid fronts on the ridges, thus somehow similar to the phenomenon reported earlier,^{4,5} except that we use “closed channels” rather than “open surfaces.” Furthermore, Fig. 2(b) also shows that the liquid fronts are somehow prevented from spontaneously wetting the grooves, which agrees well with our analysis above on meta-hydrophobicity. Because $\theta_e \cong 25^\circ$ at water-glass interfaces,¹⁸ our data confirm that, as long as the capillary filling process still occurs at the sidewalls, the liquid front is prevented from wetting the grooves, even for $\theta_e < 45^\circ$.⁹ Repeated experiments using ethanol, with $\theta \cong 0^\circ$ on glass surfaces,¹⁸ show qualitatively similar bubble patterns.¹²

Figures 2(c) and 2(d) show snapshots of the drying process in our channels, without and with the grooves, respectively. Drying without the grooves resulted in monotonous propagation of the liquid front, while drying with the grooves led to a more complex dynamics that matches our analysis in Fig. 1(d), where varying the groove periodicity led to different modulation of the liquid front propagation. Figures 2(e)–2(g) show the measured liquid front dynamics for (e) without grooves, (f) $P = 15 \mu\text{m}$; (g) $P = 10 \mu\text{m}$, where the red and green curves correspond to the distances illustrated in the inset. From the data shown in Figs. 2(e)–2(g), we can draw several interesting conclusions. First, comparison of the red curves demonstrates that the grooves indeed modulate the liquid front propagation along the channel center. Second, comparison of the green curves shows that, while for (e) drying without grooves and (f) drying with $P = 15 \mu\text{m}$ the green curves eventually reach a similar saturated value of ~ 450 pixels (corresponding to the channel’s full width), it is a different situation for (g) drying with $P = 10 \mu\text{m}$, where the increased modulation frequency prevents the green curve from reaching the channel’s full width.

Our analysis also predicted that the groove dimension variation results in various classes of bubble patterns during the wetting process. The data in Fig. 3(a) demonstrate this: inside the red box we have “one lump” of bubbles; inside the green box we have “individual” bubbles on most of the grooves; and inside the blue box we have “many fractions” of bubbles. Meanwhile, the numbers η_{NE} and η_{E} shown below the patterns of Fig. 3 are the number of formed bubbles divided by the number of available grooves. The mean and standard deviation of η were obtained from five repeated measurements for each combination of P and D using two types of grooves [see Figs. 3(b)–3(d)]: nonextended (NE) grooves (groove width is $W' = W - 10 \mu\text{m} = 90 \mu\text{m}$) and extended (E) grooves (groove width is $W' = W + 10 \mu\text{m} = 110 \mu\text{m}$);¹² the cases with nonzero standard deviations indicate situations where different numbers of formed bubbles were observed at the same set of grooves. While η_{NE} and η_{E} in Fig. 3 are identical (between NE and E) inside the red box, they differ inside the blue and green boxes: η_{E} are systematically higher than η_{NE} , indicating that the E grooves are more easily wetted (and, consequently, result in a higher number of bubbles) than the NE grooves. This can be explained by the difference between the wetting flows at the sidewalls in the NE and E grooves: while the sidewall flows at the NE grooves occur only *around* the grooves, the sidewall flows at the E grooves have to cross *on top of* the ends of the grooves,¹² hence increasing the probability of the liquid front penetration at the E grooves.

These results demonstrate the rich physics involved in wetting phenomena at microfluidics, with possible further investigations may involve nanoparticle image velocimetry¹⁹ to study the effects of periodical grooves fabricated on *both* the lower and upper walls, which can lead to more complex wetting and drying processes⁹ and three-dimensional bubble arrays.¹⁵ A full understanding of meta-hydrophobicity requires further investigations, but our present analysis observes new possibilities to make hydrophilic materials exhibit hydrophobic-like behaviors, which is strikingly similar with Wenzel’s seminal observations on duck feathers,² except that our investigations involve closed channels rather than open textured surfaces. In the field of Biomicrofluidics, we envision that geometrically patterned microchannels can be used to provide modulation for capillarity-based pumping in point-of-care diagnostic devices^{7,20} or to provide higher flexibility of

FIG. 3. (a) Typical bubble patterns obtained for different values of the period P and the groove depth D , with the corresponding η , i.e., the number of bubbles formed normalized by the number of available grooves. Also shown in (b)–(d) are the schematics of the microchannels' cross sections at (b) the nongrooved part, (c) the NE grooves, and (d) the E grooves, respectively.

device designs in evaporation-driven DNA combing,²¹ hence complementing on other relevant works published in Biomicrofluidics.^{22–25}

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