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Confined wetting of water on CNT web patterned surfaces

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We report the formation of a thin liquid film of pre-determined shape that is achieved through wetting of water on a silicon surface patterned with aligned carbon nanotube arrays or CNT webs. We measured the profiles of liquid films on two types of silicon substrate surfaces (namely, with and without a patterned CNT web) using monochrome interferometry. We found that the CNT web patterned surface produces a much thinner liquid film with a well-controlled shape due to the roughness-induced wetting enhancement on the CNT web and the anchoring effect of contact lines at morphological edges. We further used a thermodynamic surface energy based model to interpret our experimental observations and to elucidate the underlying mechanism of wetting enhancement induced by the CNT web. Our study provides a promising approach for forming thin liquid films of controllable pre-determined shape that has numerous potential applications. *Published by AIP Publishing.*

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Wetting is a phenomenon that widely occurs in natural and many technological processes. Understanding the wetting dynamics and predicting the wetting state of liquids on the surfaces of interest are of great importance due to the significance from both fundamental^{1–3} and application^{4–8} viewpoints. Surface wettability can be modified by tailoring surface energy and/or inducing topological asperities. Owing to advances in micro- and nano-fabrication technologies, study of wetting on solid surfaces of well-controlled structures has gained intensive attention in the past decade. The surfaces with 1D directional patterns,^{9,10} asperity arrays,^{11–15} and morphological/chemical gradients^{16,17} are notable examples.

A special case, where the equilibrium state of wetting forms a thin liquid film of a well-controlled shape, is required in diverse applications, such as thin film fabrication,^{18,19} liquid delivery,^{20,21} and lab-on-chip devices.^{21,22} Such kind of wetting usually exhibits confined wetting behavior, which is attributed to liquid contact lines encountering chemical heterogeneity or physical discontinuity on solid surfaces. It was shown recently that smooth chemically patterned surfaces are capable of confining the liquid within pre-determined shapes.²³ For most common materials, however, the complete wetting state cannot be achieved by solely tailoring the surface energy. Thus, the thickness of liquid films cannot be reduced sufficiently. By contrast, morphologically patterned surfaces can effectively promote wetting within pre-determined shapes and induce strong pinning at morphological edges, thus promising formation of ultra-thin liquid films with well-controlled shapes.^{24,25} However, there is still lack of quantitative characterization of the liquid film on morphologically patterned surfaces. Conventional optical approaches, such as interferometry, cannot be applied to the case of those morphologically patterned surfaces due to two reasons.^{26–28} First, the optical distortion of the liquid/air interface becomes inevitable when the asperity dimension is comparable with the liquid film thickness.²⁹ Second,

diffusive reflection occurs at the rough substrate instead of mirror reflection. Hence, coaxial reflection, which is essential to the formation of stable interference fringe patterns, is disturbed by the curve liquid/air interface and the substrate asperities.

This study presents a unique thin wetting film that has the same shape as the surface patterned with aligned carbon nanotube arrays or CNT webs. We compare the wetting behaviours of a water droplet on an unpatterned smooth silicon surface and a CNT web patterned silicon surface. The fabricated CNT web, unlike other morphological asperities, has two important features. First, the CNT web comprises asperities with both height and pitch on the nanometer scale, possessing relatively large roughness. Second, between the periodic structures (fibers) is the exposed atomically smooth substrate base, which allows the occurrence of coaxial reflection. Thanks to these two features, we are able to use monochrome interferometry to quantitatively determine the local height and thus the profile of the liquid film near the wetting edge on the CNT web patterned surface. Our results show that the CNT web patterned surface produces a much thinner liquid film. We also use a thermodynamic surface energy based model to explain the wetting enhancement and to explore the physical mechanism of such confined wetting of water on the CNT web patterned surface.

We used atomically smooth silicon wafers as the substrates and fabricated two types of surfaces, i.e., an unpatterned smooth surface and a CNT web patterned surface. We cleaned the silicon substrates using a standard protocol, which involves rinsing with acetone, isopropyl alcohol (IPA), ethanol, and deionized water subsequently and then drying in nitrogen gas flow. After that, we fabricated each type of surface through different protocols. A schematic illustration of the fabrication details is provided in [supplementary material](#), Fig. S1.

Figure 1(a) schematically illustrates the smooth surface that was treated in an oxygen plasma chamber to promote hydrophilicity. The treated surface exhibits superhydrophilic

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FIG. 1. Characteristics of the two types of the silicon wafer surfaces and their typical wetting behaviors: (a) schematic of the unpatterned smooth surface; (b) an optical image showing the fabricated CNT web patterned surface; (c) a scanning electron microscopy image of the CNT web structure; (d) wetting of a water droplet on the smooth surface; (e) wetting of a water droplet on the CNT web patterned surface. (d) and (e) were obtained by gently depositing a deionized water droplet with a fixed volume of $2 \pm 0.1 \mu\text{l}$ on the surfaces shown in (a) and (b), respectively.

with a typical equilibrium contact angle of $\theta^* < 5^\circ$. The CNT web patterned surface was fabricated through bonding a vertically aligned carbon nanotube array on the cleaned silicon substrate. We grew the spinnable CNT arrays using thermo-chemical vapor deposition, as described in our previous paper.³⁰ The CNT web was drawn out from the array by a tweezer directly and aligned on a cleaned silicon substrate. Acetone was used to wet the CNT film and increase the adhesion between the CNT web and the substrate. The morphological features of CNT array and individual CNT were characterized using field emission scanning electron microscopy (FESEM, JEOL7600) and transmission electron microscopy (TEM, JEOL 2010), as shown in [supplementary material](#), Fig. S2. Figure 1(b) shows an optical image of the CNT web patterned surface (width $w = 2 \pm 0.1 \text{ mm}$). Figure 1(c) depicts the morphological structure of a CNT web under FESEM (other FESEM images at two lower magnification ratios are provided in [supplementary material](#), Fig. S3). A typical CNT web has a thickness of about 50 nm and comprises mainly well-aligned parallel CNTs with some occasionally cross fibers.^{31,32}

Figures 1(d) and 1(e) show the wetting behaviors of a water droplet on the unpatterned smooth and the CNT web patterned silicon surfaces, respectively. Prior to experiments, each surface was rinsed with deionized water and dried in nitrogen gas flow. A degassed deionized water droplet of a fixed volume of $2 \pm 0.2 \mu\text{l}$ was gently deposited onto the surfaces through a micropipette. For the unpatterned smooth

surface [Fig. 1(d)], the water droplet spontaneously spreads quite evenly in all directions, leading to the formation of a circular wetting film with the tiny zig-zag contact line due to the pinning at fabrication defects or possible dust from the air. In contrast, for the CNT web patterned surface [Fig. 1(e)], the water droplet only spreads on the area with the patterned CNT web, yielding a typical confined wetting. The contact line is pinned along the microscopically continuous morphological edges, forming a wetting film having the same shape as that of the CNT web patterned surface. This shows that the wetting film on such a CNT web patterned surface can form a pre-determined and well-controlled shape. Furthermore, it appears clearly that the liquid film on the CNT web patterned surface is much thinner than that on the unpatterned smooth surface.

We carried out a quantitative evaluation of the liquid film thickness. Figure 2 shows the schematic of our experimental setup to determine the local height and thus profiles of the liquid thin films near the wetting edge using monochrome interferometry. We used a white light source with a monochromatic filter (green, $\lambda \approx 532 \text{ nm}$) to produce monochromatic light. A CCD camera with a microscopic objective lens was focused on the wetting edge of the liquid film. For the unpatterned smooth surface, both the air/water interface

FIG. 2. Experimental measurement of the liquid film profile using monochrome interferometry: (a) schematic of the monochrome interferometry setup. (b) Schematic of the coaxial reflection at the air/water interface and the substrate base. δ is the thickness of the liquid film, varying as a function of the distance from the wetting edge. (c) An example of an interference fringe pattern obtained by using a Matlab-based image processing approach as described in [supplementary material](#), Fig. S4.

and the water/substrate interface are smooth, resulting in the coaxial reflection of the monochromatic light. For the CNT web patterned surface, the coaxial reflection comprises the reflections from the air/water interface and the light from exposed substrate areas among CNT fibers. Stable interference fringe patterns are thus formed. Using a Matlab-based image processing approach, we obtained the liquid film profile near the wetting edge. This image processing approach consists of inverting greyscale, background subtraction, noise suppression, and intensity evaluation. An example is provided in [supplementary material](#), Figs. S4–S6 to show how the profile of a liquid thin film is extracted from the direct capture of an interference fringe pattern.

Figure 3 shows the interference fringe patterns [Figs. 3(a) and 3(b)] and correspondingly the profiles of the liquid films [Fig. 3(c)]. The density of fringes represents how fast the liquid film thickness changes, from which one can obtain the profile of the wetting film. Based on the quantitative results shown in Fig. 3(c), we found that the liquid film thickness on the CNT web patterned surface is only about 40% of that on the smooth surface. Our experimental findings demonstrate that the CNT web patterned surface can not only confine the wetting fluid in the pre-determined shape but also promote wetting, thereby producing a much thinner liquid film.

To explain our experimentally observed wetting phenomena, we use a surface thermodynamic based approach to analyze the equilibrium contact angles on both the unpatterned smooth surface and the CNT web patterned surface. With a negligible gravitational effect, the surface energy variation

FIG. 3. Interference patterns and profiles of the wetting edge of the liquid film on two types of surfaces shown in Fig. 1: (a) and (b) the interference fringe patterns on the unpatterned smooth surface and the CNT web patterned surface, respectively; (c) the profiles of the liquid film near the wetting edge, determined by using the fringe density along the dashed line in (a) and (b). Error bars were obtained by analyzing 38 samples.

for a small contact line displacement is $dE = \gamma_{S,L}dA_{S,L} + \gamma_{S,G}dA_{S,G} + \gamma dA_{L,G}$, where γ is the interfacial energy of liquid and vapour, and A is the area of the individual interface. The subscripts S , L , and G denote the substrate, liquid, and air, respectively. The liquid wetting is favorable if $dE < 0$, and an equilibrium state is obtained when $dE = 0$. We use θ_1 and θ_2 to denote the contact angles on the smooth surface and the CNT web patterned surface, respectively.

For the smooth surface, the variation of surface energy per unit length of the contact line caused by an apparent displacement dx can be written as, $dE_1 = (\gamma_{Si,L} - \gamma_{Si,G})dx + \gamma dx \cos\theta_1$. The contact angle in the equilibrium state is expressed as $\cos\theta_1^* = (\gamma_{Si,G} - \gamma_{Si,L})/\gamma$, which is actually the classic Young equation.

For the CNT web patterned surface, its structure shown in Fig. 4(a) is considered in our model. For simplicity, here we assume: (1) the CNT web is treated as a group of parallel cylindrical fibers having the same diameter D , aligned with a uniform pitch P ; (2) the effect of across fibers is neglected; (3) all the surface structures are completely wetted in Wenzel's mode; and (4) the effect of evaporation is negligible. As confined wetting occurs on the CNT web patterned surface, we need to analyze two equilibrium contact angles along the parallel (x) and the vertical (y) directions. For the wetting along the parallel direction of the CNT web by a quantity of dx , the surface energy variation is

$$dE_{2||} = (\gamma_{Si,L} - \gamma_{Si,G})dx + (\gamma_{CNT,L} - \gamma_{CNT,G})\frac{1}{P}\pi D dx + \gamma dx \cos\theta_{2||}.$$

The contact angle in the equilibrium state is thus obtained as

$$\cos\theta_{2||}^* = \frac{(\gamma_{Si,G} - \gamma_{Si,L}) + (\gamma_{CNT,G} - \gamma_{CNT,L})\frac{1}{P}\pi D}{\gamma}.$$

Because of the same surface treatment used via oxygen plasma, we further assume the same interfacial energy for the smooth Si and CNT fibers, i.e., $\gamma_{CNT,L} = \gamma_{Si,L}$ and $\gamma_{CNT,G} = \gamma_{Si,G}$. The equilibrium contact angle along the parallel direction is thus written as

$$\cos\theta_{2||}^* = \cos\theta_1^* \left(1 + \frac{\pi D}{P}\right).$$

Similarly, for the wetting along the vertical direction of the CNT web by a quantity of dy [as shown in Fig. 4(b)], the surface energy change is

$$dE_{2\perp} = (\gamma_{Si,L} - \gamma_{Si,G})dy + (\gamma_{CNT,L} - \gamma_{CNT,G})\frac{dy}{P}\pi D + \gamma dy \cos\theta_{2\perp},$$

and the equilibrium contact angle is given by

$$\cos\theta_{2\perp}^* = \cos\theta_1^* \left(1 + \frac{\pi D}{P}\right).$$

Our analytical model shows that as long as the liquid wetting occurs within the CNT web covered region, the two equilibrium contact angles along the parallel and vertical directions

FIG. 4. (a) Schematic illustration of the CNT web structure proposed in this work, where x and y , respectively, denote the parallel and the vertical directions. (b) Schematic of the liquid wetting along the vertical direction. (c) The calculated $\cos \theta_2^*$ varying with θ_1^* at different ratios of D/P .

are the same, i.e., $\theta_{2H}^* = \theta_{2\perp}^* \equiv \theta_2^*$, which is validated experimentally as shown in [supplementary material](#), Fig. S7. This conclusion is also consistent with a recent literature study which shows that the liquid has no preferential wetting direction unless the pattern dimension (groove/stripe width) is comparable with the droplet size.³³ In this work, the confined wetting behavior occurs due to the anchoring of contact lines along the patterned CNT web edge (see [supplementary material](#), Fig. S8). The apparent contact angle at the chemical/morphological edges can vary between the equilibrium contact angles on the two adjacent regions.^{34,35} Thus, we have the smaller contact angle on the CNT web patterned surface, $\theta_2^* < \theta_1^*$. This explains why water only wets the CNT web patterned region and the resultant wetting film has a much smaller thickness.

Using our model, we calculated $\cos \theta_2^*$ as a function of θ_1^* for different D/P ratios, and the results are shown in Fig. 4(c). The figure shows that for a given θ_1^* , the wetting behavior can be altered by judicious control of the CNT fiber

diameter and pitch, allowing for achieving a tunable liquid film thickness. Also, for a given D/P ratio, the complete wetting state with $\cos \theta_2^* = 1$ on the CNT web patterned region can be readily achieved when θ_1^* is smaller than a certain value given by $\theta_{1-cr}^* \equiv \arccos(1 + \frac{\pi D}{P})^{-1}$. This can lead to an ultra-thin liquid film. Therefore, the model is valid only when $\theta_1^* > \theta_{1-cr}^*$. Particularly, corresponding to our experimental conditions, we can evaluate the ratio of $D/P \approx 0.2$, based on the surface morphology characterization result shown in Fig. 1(e) (note: approximately 30 fibers are present in a window width of $2 \mu\text{m}$, and each fiber comprises 4–10 CNTs, thereby giving the CNT fiber diameter around 15 nm). Clearly, also from our experiment we have $\theta_1^* < 5^\circ$, which is smaller than the critical contact angle of θ_{1-cr}^* given by the model. Therefore, our model, though is able to provide an explanation of our experimental results, cannot directly give a quantitative comparison with our experimental contact angle and profile of the film.

In summary, we have experimentally and analytically investigated the wetting behavior on the CNT web patterned surface. We observed that water wetting only occurs on the CNT web patterned region, leading to the formation of a wetting film having the same shape as the pre-determined CNT web patterned surface. Also, we found that the CNT web patterned surface can enhance wetting and anchoring the contact line at the morphological edges, thus producing a much thinner liquid film. Moreover, taking advantage of the unique features of the CNT web patterned surface, we were able to quantify the profiles of the wetting films on both the unpatterned smooth surface and the CNT web patterned surface, and the results showed that the wetting film on the CNT web patterned surface is about 60% thinner than that on the unpatterned smooth silicon surface. Additionally, our surface energy based analytical model shows that the equilibrium contact angles along the parallel and vertical directions of CNT fibers are the same, and they both are smaller than the contact angle on the smooth silicon surface, thereby giving rise to a thinner wetting film on the CNT web patterned surface.

Also, this type of CNT web patterned surface is inexpensive, with a robust synthetic approach, and capable of modifying a large area. Further studies can be explored by combining structural and chemical patterns, e.g., chemically patterned CNT webs, leading to unique heterogeneous wetting.

See [supplementary material](#) for surface fabrication processes, characterization of the CNT web, the Matlab-based image processing approach, and the dynamic wetting and pinning of the patterned CNT web behaviours.

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