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Self-Propelling and Positioning of Droplets Using Continuous Topography Gradient Surface

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A radial pattern with continuous topography gradient is presented, which induces a continuous inward wettability gradient and enables self-propelling and accurate positioning of droplets to the pattern center. The effect of droplet size and wettability gradient of the pattern on the self-mobility of droplets is investigated. The wettability gradient is found to increase towards the pattern center, enhancing the self-motion of droplets at the inner area of the pattern. Moreover, larger droplets give rise to a larger solid-liquid contact diameter, which helps to satisfy the self-motion criteria that the advancing contact angle at front edge is smaller than the receding contact angle at rear edge. Consequently, a larger droplet size favors self-motion initiated from the outer area of the pattern. The continuous topography gradient employed here allows the flexible dispensing of droplets at any place within a certain range, and avoids potential pinning defects to droplets at geometrical discontinuities. An average self-motion velocity up to 4.0 cm/s for microliter-sized droplets is achieved on the resultant patterned surface.

1. Introduction

Directional transportation and/or positioning of droplets has promising applications in micro-chemical synthesis^[1], biomedical research^[2], condensation heat transfer^[3], and separation technology^[4]. Another specific application is to develop advanced sample handling system in instrumental analysis. For example, in mass spectrometric analytical devices^[5], sample plates capable of lossless droplet transportation and positioning can effectively avoid the sample drift and cross contamination, thus enabling more convenient and reliable analyses. External stimuli, including light^[6], electric field^[7], magnetic field^[8], or vibrations^[9] provides feasible routes to drive directional droplet transportation. However, these routes require complex operation and power consumption to induce droplet motion. Hence, self-propelling surface, i.e., a surface that can induce self-motion of droplets by itself, provides an easy-to-operate and energy-efficient way to realize directional droplet transportation.

Self-propelling surfaces generally can be created by exploiting a wettability gradient^[10], on which a liquid droplet can move spontaneously in the direction of increasing wettability. So far, construction of chemical gradient^[11] or topography gradient^[12] are two feasible routes to create self-propelling surfaces. However, chemical gradient surfaces involve reactive formation of molecular gradient of alkanethiolate^[13] or alkylsilane^[3, 14], which may deteriorate due to migration or degradation of organic molecules and result in decay of chemical gradient in the long term. Construction of surfaces with topography gradient thus provides a desirable advantage by addressing this problem. Several surfaces with a roughness gradient that could guide spontaneous movement of a droplet have been reported very recently. However, the reported surfaces were based on discrete groups of parallel or radial stripe structures^[12a-c], which resulted in a discontinuous contact line when droplets moved from one group of stripes to the other. Discontinuities can cause contact line pinning and reduce the droplet transportation efficacy. Furthermore, the discrete structures gave rise to a discontinuous wettability gradient, which in turn limited the available area on the patterned

surface for droplet self-motion. Here, we employ a radial pattern design to create a continuous topography gradient on a surface. Self-propelling droplet motion is successfully achieved on the surface and consequently gives rise to the accurate positioning of droplets at the central point of the patterned area. Benefiting from the continuous gradient, droplets can be dispensed at any location within a certain range of the pattern center to initiate their self-motion. In addition, our pattern provides a continuous pathway for droplet motion and avoids contact line pinning at geometrical discontinuity, thus enabling a high self-motion velocity of up to 4.0 cm/s for a 3.0 μL droplet.

2. Results and Discussion

To prepare a surface with an inward wettability gradient, we designed a pattern composed of regular, radial directed stripes (**Figure 1**). This pattern creates an inward gradient wettability for directional droplet transportation to the center and also provides a continuous pathway that minimizes contact line pinning during droplet motion. The droplet transportation is also enabled by the Cassie-Baxter state, which minimizes the contact angle hysteresis and drag on the droplet.

For this radial pattern, we can theoretically calculate its static contact angle according to Cassie-Baxter formula. The contact angle for a Cassie surface is described as:

$\cos \theta = f_1 \cos \theta_0 - (1 - f_1)^{[16]}$. Here f_1 is the solid fraction of the textured surface, and θ_0 is the equilibrium contact angle on a flat surface of the same material. In our case, the solid

fraction at an arbitrary point $f_1(l)$ can be calculated as: $f_1(l) = \frac{s_1}{s_2} = \frac{r\varphi}{l\varphi} = r/l$. Here r is the

radius of the inner circle area, and l is the distance of the location to the center point.

Therefore, the contact angle at the gradient surface satisfies:

$$\cos \theta(l) = r \cos \theta_0 / l - (1 - r/l) = r(1 + \cos \theta_0) / l - 1 \quad (r < l) \quad (1)$$

$$\text{and } \theta(l) = \arccos[r(1 + \cos \theta_0) / l - 1] \quad (r < l) \quad (2)$$

For a given textured surface, r and θ_0 are constant, and it is clear from equation (1), $\cos\theta(l)$ decreases with the increase of l . Accordingly, $\theta(l)$ increases with l , indicating a radially inward wettability gradient.

The fabrication process of our radial pattern surface is shown in **Figure 2**. First, a 400 nm SiO₂ layer was created on a silicon wafer using plasma enhanced chemical vapor deposition (PECVD). The oxide mask was patterned by optical lithography and etched by a CHF₃/Ar based reactive ion etching (RIE). After photoresist removal, silicon etching was done by deep reactive ion etching (DRIE). The etching depth of the pattern is about 20 μ m, which is considered high enough to form a Cassie-Baxter state. Atomic layer deposition (ALD) was used to coat a 100 nm TiO₂ layer on the pattern in order to enhance the wettability properties. Finally, the pattern was coated with a 45 nm thick hydrophobic fluoropolymer layer to obtain a Cassie-Baxter surface. The fluoropolymer was deposited by PECVD from CHF₃ precursor gas^[15].

Figure 3 shows the detailed structure of the as-prepared radial pattern surface. The patterned area has an outer diameter of 8 mm. The magnifying images show that it is composed of highly regular, radial stripes. The central circle is formed by the intersection of these stripes and has a diameter of ~ 1.2 mm. Each strip has a width of 10 μ m and height of ~ 22 μ m, and the angle between the neighboring stripes is 1.25 degrees. Moving from the edge to the center, the gas fraction continuously decreases as the stripes get closer, and as a result the patterned surface has a maximum wettability at its center. Note that the central circle's diameter is only 1.2 mm, while the contact diameter of a droplet (1-5 μ L) on the as-prepared gradient surface is generally larger than this size, thus enabling droplets to be exactly positioned at the center. By comparison, a previously reported surface had a large central area with diameter of 8 mm, which makes it more difficult to exactly position a droplet of several microlitres to the center as the central area lacks a wettability gradient^[12c].

The self-motion of the droplet is driven by the wettability gradient due to the different contact angles acting on the solid-liquid contact lines at the advancing and receding edges of the droplet. It should be emphasized that a wettability gradient on a surface does not necessarily ensure spontaneous droplet motion due to the effect of hysteresis, which can be caused by surface defect sites or geometrical/chemical heterogeneity. This effect leads to the occurrence of advancing and receding contact angles (ACAs and RCAs), which quantify respectively the minimum and maximum contact angles that are required to activate the motion of solid-liquid-air three-phase contact line at each point on a surface. Consequently, for a droplet to move spontaneously toward the region of higher wettability, the receding contact angle at the rear edge (θ_{rA}) should be higher than the advancing angle at the front edge (θ_{aB}). Otherwise, the droplet will stick to the surface due to surface hysteresis effect. This criterion for self-motion of droplet is illustrated in **Figure 4**.

The measured ACAs and RCAs on our gradient surface are shown in **Figure 5a**. The larger the distance to the central point (i.e., d) is, the larger the ACA and RCAs are. This fact clearly indicates that an inward wettability gradient is successfully created through the construction of a radial pattern on the surface. The surface appears to be in Cassie-Baxter state, as notable reflection can be observed beneath the droplet due to the existence of air-cushion (**Figure S1**). We calculated the theoretical Cassie-Baxter contact angles (CCAs) of the patterned surface. The equilibrium contact angle θ_0 on the flat inner circle area is measured to be 98° (**Figure S2 a**), and the radius of the inner circle is 0.6 mm, so according to equation (2), we can get: $\theta(l) = \arccos[0.6 \times (1 + \cos 98^\circ) / l - 1]$ ($r < l$). The solid curve in Figure 5a gives the theoretical CCAs, which shows a similar variation trend to experimental ACAs and RCAs. The calculated CCAs locate between the measured ACAs and RCAs, and are very close to the ACAs. These facts indicate that the experimental results are well in accordance with the theoretical model. In addition, the fluoropolymer coatings

used in our study is highly stable over time. We found that the contact angles of the radial patterned surface showed no observable change even after six months of storage in ambient conditions.

The contact angle hysteresis (CAH), i.e., the difference between the advancing and receding contact angle at the same point ranged from $\sim 24^\circ$ (close to the center) to $\sim 9^\circ$ (close to the edge) on our radial pattern. Due to the effect of CAH, the droplet size (related to the contact diameters of the test droplets) and gradient steepness are crucial to activate the self-motion of droplets. If a tiny droplet touches an area with less gradient steepness, the receding contact angle of the rear edge may become smaller than the advancing angle of the front edge ($\theta_{rA} \leq \theta_{aB}$) due to the smaller diameter of the solid-liquid contact area, making self-motion impossible. According to Figure 5a, to meet the criterion of $\theta_{rA} > \theta_{aB}$, the solid-liquid contact diameter needs to be larger than $\sim 1\text{ mm}$ when the droplet is located within $\sim 2.5\text{ mm}$ of the center and larger than $\sim 1.5\text{ mm}$ when the droplet is located outside a 2.5 mm radius range. In short, in order to initiate self-motion, smaller droplets should be placed closer to the center while bigger droplets can be placed farther away from the center point on the less wettable area (as illustrated in Figure 5b). It should be noted that even though CAH is higher at region close to the pattern center, the droplets are still easily self-propelled due to a steeper wettability gradient there which more than compensates for increased CAH. It was found, droplets hardly move spontaneously on the patterned surface without introducing the TiO_2 layer, as the non- TiO_2 coated surface has a much less steep wettability gradient (Figure S3c). The possible role of TiO_2 layer on the wetting property is briefly discussed in the Supporting Information.

To confirm the above analysis, we examined the effect of different droplet sizes ($1\text{--}5\text{ }\mu\text{L}$), which showed remarked effect on its mobility on the radial pattern. We found that small droplets ($1\text{--}2\text{ }\mu\text{L}$) are fairly difficult to be self-propelled on the less wettable outer part,

whereas if placed within ~ 1.5 mm of the center the droplets can easily move to the center as shown in **Figure 6a**. When increasing the droplet size, the solid-liquid contact diameter increases accordingly, and this favors the self-propelled droplet motion from the outer area of the textured surface. Figure 6b-d evidence that the relatively larger droplets (3-5 μL) can spontaneously move to the center from less wettable outer area. A droplet of 3 μL can propel itself within 2 mm of the center, whereas droplets of 4 or 5 μL can propel itself within 2.5 mm of the center.

The Cassie-Baxter air cushion and the continuous pathway for droplet motion of the radial pattern surface reduces the pinning effect to contact line effectively, and therefore favors rapid transportation of droplets. As a result, the droplets acquire self-propelling velocities to the order of several cm/s, and an average velocity of up to 4.0 cm/s for a 3.0 μL droplet can be obtained on our continuous topography gradient surface (Figure 6). For comparison, a surface with discrete topography gradient as reported by Bardaweel et al. showed an average velocity of 5 mm/s for a ~ 2 μL droplet^[12c].

The self-propelling and positioning feature of our radially patterned surface makes it particularly useful for developing intelligent sample plates in various micro-sample analysis systems (e.g., mass spectrometric analysis), where even if the sample droplet is initially not accurately dispensed at the detected area it can adjust its own position to the central desirable point, thus being of possible assistance for high spatial precision detection and analysis.

Although a small droplet tends to stick to the surface when being placed on the outer area of the gradient surface, we found another way to activate its directional motion towards the center by adding tiny droplets to it. To demonstrate this phenomenon, a 2 μL droplet was first placed near the outer edge of the patterns and stuck to the surface. Tiny droplets were then continuously dispensed to the first droplet at a speed of 0.2 $\mu\text{L/s}$ from a fixed dispenser until they touched and coalesced into the first droplet on the surface. Consequently, the coalesced

drop would be able to overcome the hysteresis effect and move towards the center of the pattern. **Figure 7** shows the coalescence-induced directional moving of droplets when tiny droplets were added from three different relative positions (upper left, right above and upper right) to the first droplet. It can be seen in all three cases the coalesced droplets moved towards the central point irrespective of the initial relative position of the dispenser to the first droplet. This coalescence-induced directional motion is driven by the cooperative effects of droplet coalescence and surface wettability gradient. First, upon droplet coalescence, excessive surface energy is released due to the reduction of total liquid-air interface area, which provides additional energy to overcome the surface hysteresis and drive droplet motion^[3, 17]. Then the directional inward wettability of the radially patterned surface directs the preferential motion of droplets towards the center point. The coalescence-induced directional motion of our radially patterned surface is distinct from previous report^[3] which was based on chemical gradient induced directional motion whereas ours is based on surface topography gradient. Furthermore the droplets move towards the central point in our case compared to outwards motion in the previous study.

3. Conclusion

In summary, we demonstrated a surface with a continuous radial wettability gradient for accurate transportation and positioning of droplets. We also reveal the effect of droplet size and wettability gradient steepness on the self-mobility of droplets. The research provides a new route for spontaneous and continuous driving of water droplets in a rapid and directional manner. The self-propelling and positioning of droplets could bring out potential applications in a range of applications, including bio-/chemical analysis, sensors, water collection^[10f, 18] and micro-chemical reaction^[19]. Ongoing work includes optimizing the fabrication methods to further decrease the surface hysteresis and tuning the surface property for transporting droplets of various liquids.

Experimental Section

Pattern Fabrication. The pattern was fabricated on a 525 μm thick p-type $\langle 1\ 0\ 0 \rangle$ silicon wafer that had resistivity of 30–50 $\Omega\ \text{cm}$. A 400 nm SiO_2 mask was prepared by PECVD, photolithography, and RIE (Oxford Instruments, Plasmalab 80, etching time 11.8 min, pressure 30 mTorr, power 200 W, CHF_3 25 sccm, Ar 25 sccm). After removal of the photoresist, DRIE was employed for patterning the silicon wafer (Oxford Instruments, Plasmalab System 100, etching time 15 min, pressure 10 mTorr, power: 1000 W, temperature -120°C , SF_6 50 sccm, O_2 6.5 sccm). A 100 nm TiO_2 layer was deposited by ALD (Beneq, TFS-500, temperature 200°C , rate: 0.0426 nm/cycle, precursors: TiCl_4 and H_2O). Final fluoropolymer layer^[15] was grown by PECVD (Oxford Instruments, Plasmalab 80, growth time 10 min, pressure 250 mTorr, RF power 50 W, CHF_3 100 sccm). The thickness of the fluoropolymer coating was measured by profilometry and was 45 nm for the 10 minutes deposition time.

Morphological characterization of pattern. Optical micrographs were obtained with a Nikon ECLIPSE TE300 microscope (Nikon Instruments, Badhoevedorp, the Netherlands) and a CoolSNAPPro color CCD camera (Cheos, Espoo, Finland). SEM image was taken by a Supra 40 field emission scanning electron microscope (Zeiss, Oberkochen, Germany). Roughness and film thickness was characterized by Profilometer (DekTak, veeco).

Contact angles and droplet motion measurements. Contact angles and droplet motion were measured using a Goniometer (Theta from Attension). A 30-gauge flat-tipped needle was used to dispense water droplets. To determine the advancing and receding contact angles on different position of the pattern, a 2 μL droplet was first applied to the center of the patterns. Subsequently, the needle tip was lowered and embedded in the droplet for reducing the distortion of the droplet shape in the following measurements. The advancing contact angles were measured while gradually increasing the volume of liquid at a speed of $0.2\ \mu\text{L}\ \text{s}^{-1}$ and

pictures were taken with 333 ms (3 frames in 1 s) intervals. One minute after measuring the advancing contact angles, the receding contact angles were measured while gradually decreasing the volume of liquid at a speed of $0.2 \mu\text{L s}^{-1}$ with pictures also taken at 333 ms intervals.

During the initial period, the contact angle changed with the volume of the droplet, while the baselines of the droplets remained the same value. Advancing contact angles and receding contact angles were recorded after the baselines began to change. When determining the advancing contact angles at different positions, the larger of the two contact angles (left and right) was chosen. While for determining the receding contact angles, the smaller of the two angles was used. All measurements were carried out at room temperature. (The advancing and receding angles were difficult to measure reliably once the baseline exceeded 3 mm, as the large droplet deformed heavily.) The motion of water droplets on this gradient surface was examined with different droplet size (volume: 1-5 μL) with pictures taken with ~ 17 ms intervals (60 frames in 1 s).

Supporting Information

Supporting Information is available online from the Wiley Online Library or from the author.

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Figure 1. The schematic of the radial wettability gradient pattern and the parameter relationships on this surface.

Figure 2. Schematic of the fabrication procedure of radial pattern.

Figure 3. a) Optical image of the whole pattern taken by a digital camera. b, c) Enlargement of inside sections of the pattern. d) Scanning electron microscopy (SEM) image of the pattern's outside section. e) Typical profilometer image shows the height of representative strips is about $\sim 22\text{ }\mu\text{m}$.

Figure 4. Schematic illustrating the criterion for self-propelling of droplets on the radial patterned surface with wettability gradient. To initiate the self-motion of a droplet, the receding contact angle at the rear edge (θ_{rA}) should be higher than the advancing angle at the front edge (θ_{aB}).

Figure 5. a) Wettability on the radial patterned surface. The closed and open circles represent the measured advancing and receding contact angles, respectively. The solid curve represents the calculated Cassie-Baxter contact angles of the gradient surface. b) Schematic illustrating the self-motion capability of droplets of different sizes on the gradient surface. Larger droplets can initiate the self-motion from outer region whereas smaller droplets can initiate the self-motion within inner region.

Figure 6. The moving behavior of droplet of different sizes on the gradient surface. a) a 1.5 μL droplet moves with an average speed of 3.0 cm/s within 1.5 mm of the center; b) a 3.0 μL droplet moves with an average speed of 4.0 cm/s within 2.0 mm of the center; c) a 4.0 μL droplet moves with an average speed of 2.5 cm/s within 2.5 mm of the center; d) a 5.0 μL droplet moves with an average speed of 2.5 cm/s within 2.5 mm of the center. See video V1-4.

Figure 7. The coalescence-induced motion of a droplet on the gradient surface. A 2 μL droplet was first placed near the outer edge of the textured surface, then tiny droplets were added to the first droplet from different directions: L1---L3 left, M1-M3 middle and R1-R3 right. See video