DROPLET TRANSPORT ON FLAT CHEMICALLY HETEROGENEOUS SURFACES VIA PERIODIC WETTING BARRIERS AND VIBRATION

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ABSTRACT

We report on a Flat Surface Ratchet, capable of achieving droplet transport using curved hydrophilic rungs patterned onto a hydrophobic surface. These periodic asymmetric wetting barriers can be fabricated easily on a wide variety of surfaces. Transport of a 10 µl droplet is achieved by an electromagnetic speaker with vertical sinusoidal vibrational amplitudes as low as 37 µm at 82 Hz, making this technology implementable for a wide range of discrete microfluidic applications.

INTRODUCTION

Discrete microfluidic droplet transport technologies are advantageous for developing reliable and reusable lab-on-a-chip devices due to their prevention of cross contamination between samples. Today, droplet transport technology is dominated by devices which move droplets via local gradients controlled by a stimulus (active transport). Darhuber et al. [1] built a thermocapillary microfluidic device, transporting droplets by engaging micro-heaters, driving the liquid towards the colder surface. Cho et al. [2] used electro-wetting on dielectric (EWOD) to control droplet motion via an electric stimulus. Active droplet transport devices have excellent controllability, but require precise fabrication and power intensive actuation mechanisms.

In contrast to active transport, Chaudry and Whitesides [3] made water run uphill by varying the chemical composition of a surface. Shastry et al. [4] reported droplet transport on a vibrating surface with a roughness gradient. These are passive droplet transport technologies, driven by pre-determined asymmetry and actuated by non-droplet specific mechanisms. Passive transport is usually less controllable than active transport, but more simply fabricated and actuated. A limitation of these initial passive transport technologies was that they could only transport droplets over short distances, as the length of a gradient is limited. This limitation was overcome with the implementation of a ratchet.

Ratchets have a periodic asymmetric structure, a pawl, and an agitation which drives transport along the pawl. Previously reported microfluidic ratchet designs have achieved transport using a periodic saw-tooth surface asymmetry and various agitations including superparamagnetism and vibration [5, 6]. In our previous work we reported the Surface Ratchet (SR) [7, 8, 9], which implemented a new pawl asymmetry, using periodic curved rungs on a rough hydrophobic surface. The result was highly predictable droplet transport actuated with vibration. SRs have been previously realized on a hydrophobic silicon wafer, polydimethylsiloxane (PDMS), and parylene [10].

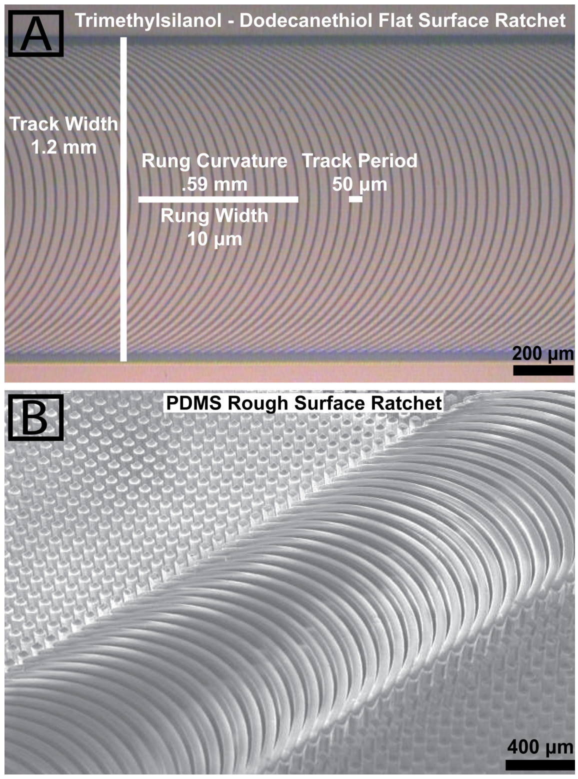

Figure 1: A comparison between flat SRs and the previously reported rough SRs. (A) TMS - dodecanethiol flat SR. Dark regions correspond to the hydrophilic TMS rungs and lighter areas to the hydrophobic dodecanethiol coated Au. (B) A scanning electron microscope image of a previously reported polydimethylsiloxane (PDMS) rough SR.

We report a novel implementation of SRs on flat chemically heterogeneous surfaces. Flat SRs are fabricated using both oxide and gold adhering self-assembled monolayers (SAMs) to pattern the wettability of a surface. Two flat SRs are reported: a trimethylsilanol–perfluorooctyltrichlorosilane flat SR and a trimethylsilanol–dodecanethiol flat SR (figure 1A).

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THEORY AND DESIGN

Previously reported SRs had rough, chemically homogeneous hydrophobic surfaces (water contact angle ~125º) designed with periodic curved rung features delimited by circular pillars (figure 1B). Vertical vibrations triggered droplet transport by initiating expansion and contraction of the droplet's footprint. An asymmetric drag force from the droplet pinning to the curved rungs' edges is the active force in droplet transport. The pinning force at either edge of the droplet can be quantified by the pinning interval of the leading and trailing edge. The force on a liquid at a three-phase sharp edge was first considered by Gibbs [11], and was experimentally confirmed by Oliver et al. [12]. The pinning interval, demonstrated in figure 2A, is the difference in contact angle between the maximum angle an interface can sustain ($\theta_{Critical}$) and the characteristic contact angle of the surface ($\theta_{Surface}$):

$$\theta_{Pinning\ Interval} = \theta_{Critical} - \theta_{Surface} \quad (1)$$

Due to the alignment of the droplet's leading edge with the curvature of the rungs, the pinning interval is larger for the leading edge than the trailing edge; this asymmetry is the underlying cause of droplet transport.

Flat SRs take advantage of a similar pinning phenomenon, the wetting barrier at a four-phase interface. A water-vapor-hydrophilic surface-hydrophobic surface interface has a wetting barrier when the liquid spreads from a hydrophilic surface to a more hydrophobic one. As seen in figure 2B, the maximum contact angle this four-phase interface can sustain corresponds to the characteristic contact angle for the hydrophobic surface. Flat SRs are realized by creating the same periodic curved rung design, by patterning the wettability on a flat surface.

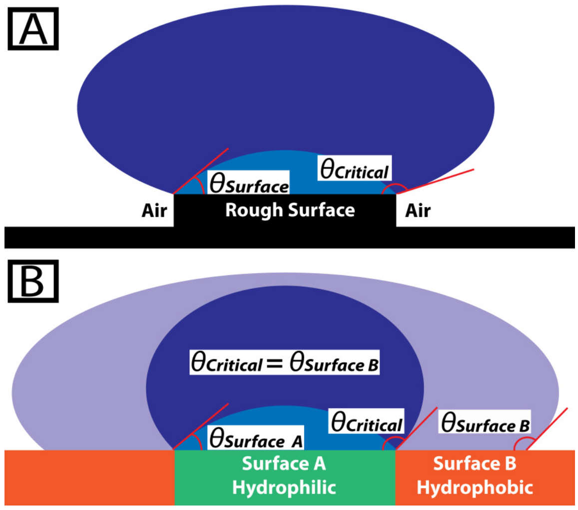

Figure 2: A comparison of how water pins to a sharp edge and to a wetting barrier. (A) Water's strong pinning to sharp edges is a well known phenomenon; it is commonly demonstrated by the ability of a drinking glass with sharp rims to hold more water than its volume. The edge sustains much larger contact angles than the characteristic wetting contact angle of the surface ($\theta_{Surface}$). At some critical angle ($\theta_{Critical}$) the droplet will collapse outwards [12]. (B) Pinning also occurs at wetting barriers, when water spreads from a hydrophilic ($\theta_{Surface\ A}$) to a more hydrophobic surface ($\theta_{Surface\ B}$). In this case, the critical angle at wetting barriers corresponds to the characteristic wetting contact angle of the hydrophobic surface.

FABRICATION

We present two novel flat SRs designed on smooth chemically patterned surfaces with trimethylsilanol (TMS, 53° water contact angle) as the more hydrophilic surface and dodecanethiol SAM (104° water contact angle) or perfluorooctyltrichlorosilane (FOTS, 108° water contact angle) as the hydrophobic surface.

For both processes, a cleaned silicon wafer is coated with a liquid film of hexamethyldisilazane (HMDS) adhesion primer and allowed to react for 20 seconds before it is spun off. The result is a monolayer of TMS on the wafer surface. Photolithography is then performed. After development, the remaining photoresist forms the pattern of the SRs rungs. An oxygen plasma at 40 W for 5 minutes removes the exposed TMS (the area not covered with photoresist), revealing a bare oxide layer.

At this point the fabrication sequences of the two devices diverge. For the FOTS flat SR, the next step is Chemical Vapor Deposition (CVD) of FOTS. After the CVD the photoresist is removed with acetone and the FOTS is annealed by placing the device on a hot plate for 1 hour at 150 °C to create covalent siloxane bonds between FOTS and the oxide. For the dodecanethiol flat SR, the next step is to evaporate 50 nm Au onto the surface, with a 10 nm Cr adhesion layer. Liftoff is performed and then the device is immersed into a 1:4 dodecanethiol:ethanol (by volume) bath for 1 hour to allow the dodecanethiol to assemble on the Au surface.

RESULTS

To demonstrate the ratcheting effect of a moving droplet, a side view video was taken with a high-speed camera (1000 fps). Several frames from one period of oscillation are displayed in figure 3A; the contact angle was measured for each frame and plotted in figure 3B. At 0 ms the droplet's footprint is at its maximum expansion just prior to recession. Initially, the droplet's edges recede symmetrically from 0 to 6 ms. Asymmetric pinning is clear from 6 to 8 ms, where the droplet's leading right edge pins to the surface while its contact angle decreases;

simultaneously, the trailing left edge's contact angle increases as it recedes, leaving a faint residue of water behind.

Actuation Amplitude

To achieve droplet transport, the agitation must be significant enough to overcome the leading edge's pinning interval so the edge can advance at least one rung. The pinning interval at a geometric sharp edge is larger than at a flat wetting barrier, therefore a flat SR will have a smaller pinning interval for its leading edge. We predicted that the actuation amplitude for droplet transport would be reduced for flat SRs due to their smaller pinning interval. Figure 4 displays the results of actuation amplitude experiments of a rough SR versus the two new flat SRs with identical rung designs. Figure 4 shows that the actuation amplitude for both flat SRs is significantly less than for the previously reported rough SRs. The most significant decrease was observed with the 10 μl droplet, with a reduction of actuation amplitude from 133 μm on the rough SR to 37 μm on the FOTS flat SR.

Invisible Surface Ratchet

When a droplet is placed on the optically flat TMS-FOTS design (figure 5A), the strong pinning is easily observed by an oblong stretching along the hydrophilic track. In figure 5B images of the leading and trailing edges were taken and overlaid with the mask of the track design, demonstrating how the observed pinning compares directly with the patterned rungs. This invisible ratchet demonstrates that a fully transparent SR could realistically be built and seamlessly integrated onto a naturally vibrating transparent surface, such as a car's windshield.

DISCUSSION

SRs on an optically flat surface are easily cleaned and integrated with sensors directly fabricated onto the same substrate. The simplicity of a hydrophilic-hydrophobic patterned surface drastically increases the fabrication options, including one-step processes such as patterning a surface with photo-responsive wettability (for example, ZnO_2) by exposing it to UV light through a mask or potentially inexpensive and quick fabrication methods, for example, printing the hydrophilic pattern directly onto a hydrophobic sheet.

Flat SRs have significantly reduced the actuation amplitude for SRs to just 37 μm. Future flat SR optimization could potentially reduce the actuation amplitude to the range where alternative actuators could be considered, such as surface acoustic wave or piezoelectric technologies.

Through the realization of flat SRs we have demonstrated that the ratcheting mechanism derived from periodic curved rungs is simply a function of the asymmetric pinning interval, which we have created

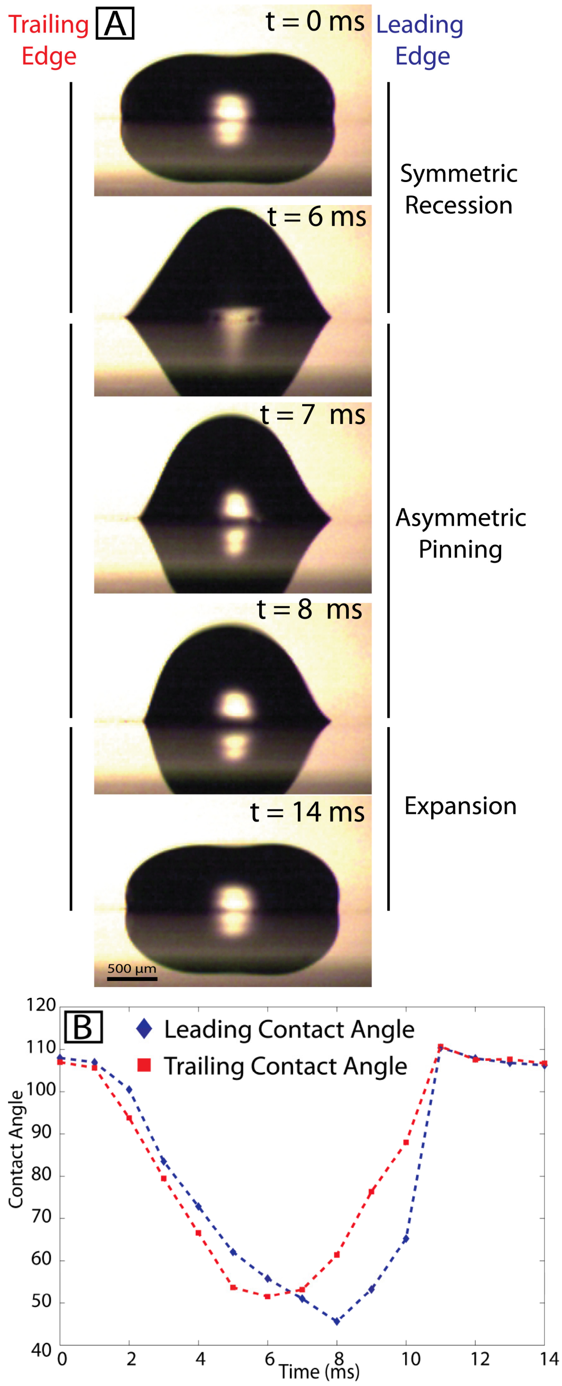

Figure 3: A 12.5 μl droplet transported on a TMS-FOTS Flat Surface Ratchet is captured using a high speed camera (1000 fps) as it moves from left to right at an average velocity of 5.4 mm/s. Transport is accomplished with a vibrational amplitude of 100 μm at 72 Hz. (A) Five frames from one period of oscillation are displayed and (B) the contact angles for this period are measured and plotted vs. time. The chosen frames highlight the asymmetric pinning that occurs between 6 and 8 ms. This is also clearly observable in the contact angle plot, as the slopes of the leading and trailing contact angles temporarily diverge.

using both the pinning at a geometric sharp edge, and at a wetting barrier. Future SR devices will take advantage of novel implementations of the pinning interval. For example, an EWOD device may be able to drastically reduce actuation voltages by taking advantage of the ratcheting phenomenon.

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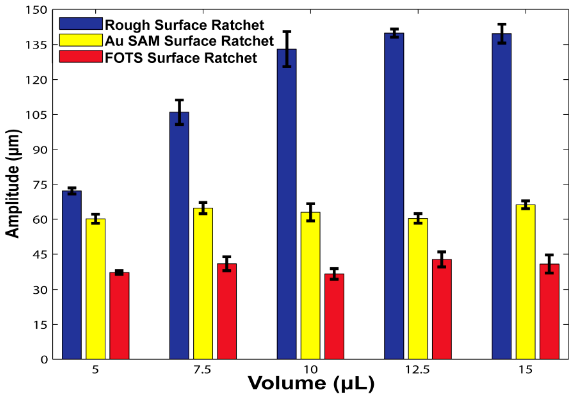

Figure 4: Actuation amplitude comparison between a rough SR and the dodecanethiol and FOTS flat SR designs. Each device had identical rung designs and was actuated at its resonant frequency for the given ratchet and droplet volume. The FOTS design clearly outperformed both the rough SR and the dodecanethiol design. The advantage of the FOTS over the dodecanethiol design can be explained by the small roughness due to the deposited Au pattern (~60 nm). Error bars indicate the standard deviation of each set of measurements.

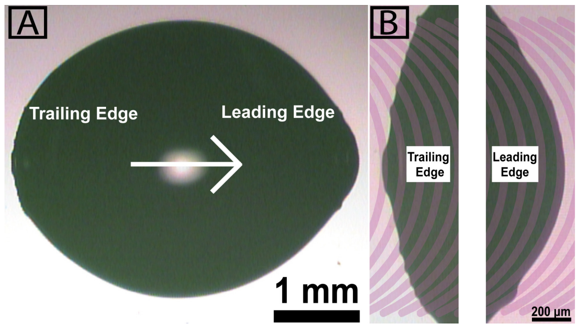

Figure 5: TMS-FOTS Flat SRt. (A) A 10 μl droplet with an oblong shape on the invisible ratchet. (B) Close-up images of the deformities at the leading and trailing edges were taken and overlaid with the mask for the track designs to demonstrate that the tight curvature at the leading edge aligns with the rung curvatures while the bumps on the trailing edge correspond with its intersection of hydrophilic rungs.

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