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Sliding droplets on hydrophilic/superhydrophobic patterned surfaces for liquid deposition

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A facile gravity-induced sliding droplets method is reported for deposition of nanoliter sized droplets on hydrophilic/superhydrophobic patterned surface. The deposition process is parallel where multiple different liquids can be deposited simultaneously. The process is also high-throughput, having a great potential to be scaled up by increasing the size of the substrate. *Published by AIP Publishing.*
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Nanoliter sized droplet deposition is essential in many biomedical, chemical, and microfluidic applications, including droplet based microfluidic systems,^{1,2} delivery of DNA,³ DNA microarrays,⁴ cell screening,⁵ protein chips,⁶ and material synthesis.⁷ There are several techniques for droplet deposition, including contact⁸ and non-contact dispensing technique,⁹ dip-pen nanolithography,^{10–13} and liquid deposition using patterned hydrophilic/hydrophobic surfaces^{14,15} including dip-coating.^{16–19} Dip-coating is a high-throughput method, depositing massive number of droplets in a short time,¹⁷ though does not allow deposition of different liquids on individual deposition sites. On the other hand, all other methods allow deposition of different liquids on desired deposition sites. However, they are based on direct deposition of liquid on substrates,^{9,11} which requires each deposition site being addressed by individual heads of the dispensing device, where the deposition throughput is linear to the speed of the device. By increasing the number of operating dispensing heads, the speed can be increased linearly at the expense of associated device complexity and fabrication costs.⁹

In this paper, we introduce a facile gravity-induced sliding droplets method for rapid and high-throughput deposition of droplets which can break this linear relation between the deposition throughput and the speed of dispensing device. The deposition throughput can be scaled linearly by the size of substrate without increasing the dispensing speed. We employ sliding droplets on an inclined patterned hydrophilic/superhydrophobic surface, where a nanoliter-range liquid volume is deposited on the hydrophilic pads. The motion of droplet has been extensively studied on superhydrophobic surfaces in general,^{20–25} and a few studies also report on droplet motion on patterned hydrophilic/hydrophobic surfaces.^{15,26–30} However, the motion of a droplet moving on patterned hydrophilic/superhydrophobic surfaces remains unexplored. We characterize the motion of a droplet sliding on a patterned hydrophilic/superhydrophobic surface by investigating the speed of the droplet and the deposited

volume on hydrophilic pads. We also demonstrate that the method can be used for parallel nanoliter deposition using different liquids. The proposed method is simple to apply and scalable, where the system only involves droplets and patterned hydrophilic/superhydrophobic surfaces.

A sketch of the proposed deposition method is presented in Fig. 1. A substrate containing a matrix of hydrophilic pads with superhydrophobic background is placed on a motorized rotational stage; different kinds of liquids are dispensed on the first row of the hydrophilic pads as shown in Fig. 1(a). The details of the deposition process are zoomed in Fig. 1(b). The substrate is then tilted and droplets start sliding by gravity. Each droplet follows the path of its corresponding column of hydrophilic pads, which are coated by the corresponding liquid due to large wetting contrast between hydrophilic pad and superhydrophobic background. During the sliding process, the rear edge of the droplet is repeatedly pinned and depinned (see Fig. 1(c)) from the hydrophilic pads. As the rear edge of the droplet transforms from the pinning state (zoomed view in Fig. 1(d)) to the depinned, part of the droplet is deposited on the hydrophilic pad.

When a droplet is moving on an inclined hydrophilic/superhydrophobic patterned surface, the major forces acting on the droplet include contact line pinning force, gravitational force, and viscous force. According to Macdougall and Ockrent,³¹ the pinning force preventing the droplet sliding down is caused by contact angle hysteresis and unbalanced Young's force, which can be described as $F_Y = L \cdot \gamma_{LV} \cdot (\cos \theta_r - \cos \theta_a)$, where L is the width of the droplet and it is perpendicular to the droplet moving direction, γ_{LV} is the surface tension of the liquid, and θ_a and θ_r are the advancing and receding contact angle at the downhill and uphill edges of the contact line. In our analysis, viscous forces are negligible, because the droplet is mainly sliding on the surface and there is no obvious viscous flow observed within the droplet in our experiments, in agreement with the previous report.³² The movement of a droplet on a hydrophilic/superhydrophobic surface was simulated using Matlab Simulink.

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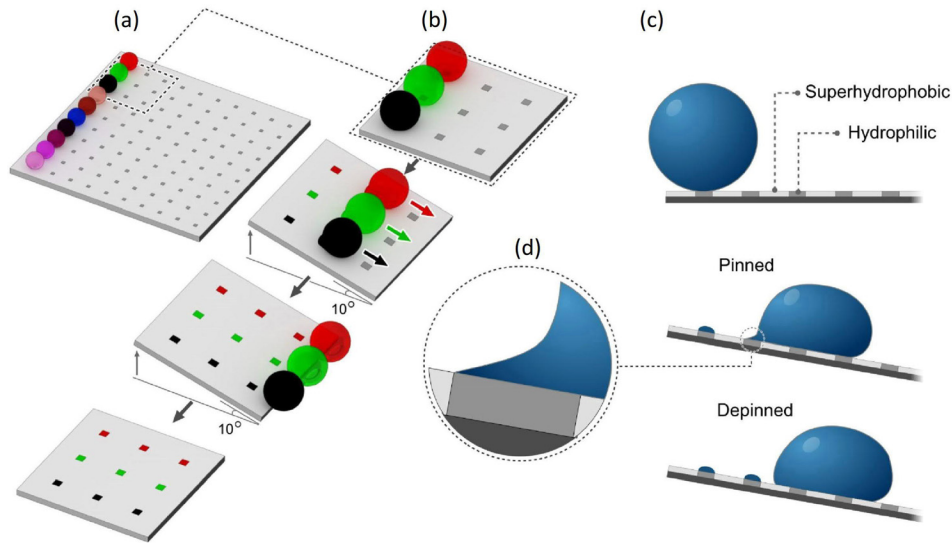


FIG. 1. Sketch and illustration of deposition by sliding droplets on patterned hydrophilic/superhydrophobic surface: (a) different kinds of liquids are placed on the first row of a 10×10 matrix of hydrophilic pads surrounded by superhydrophobic substrate; (b) zoomed view of sliding droplets deposition process; (c) side view of a droplet sliding on a patterned surface; (d) zoomed view of the rear edge of the contact line pinned on the hydrophilic pad.

As shown in Figs. 2(a) and 2(b), when the rear edge of the contact line is pinned on the hydrophilic pad, the contact line starts to elongate and a small tail forms. At this state, the pinning force includes two parts: one part is the pinning force on superhydrophobic surface F_{Y1} and another is the pinning force on the pad F_{Y2} . The total pinning force is the sum of two

$$F_{Y1} + F_{Y2} = L\gamma_{LV}(\cos \theta_r - \cos \theta_a) + l\gamma_{LV}(\cos \theta_p - \cos \theta_r), \quad (1)$$

where $F_{Y1} = (L - l)\gamma_{LV}(\cos \theta_r - \cos \theta_a)$, $F_{Y2} = l\gamma_{LV}(\cos \theta_p - \cos \theta_a)$, L and l are the width of the droplet and

hydrophilic pad, respectively, θ_p is the rear contact angle on the hydrophilic pad, varying between the advancing contact angle and the receding contact angle of the pad.

Based on the gravitational force and the varying pinning force, the total force acting on the droplet can be calculated, and the acceleration and velocity of the droplet can be derived. We simulated the motion of a 0.15 ml droplet sliding on a 10° tilted hydrophilic/superhydrophobic substrate, having a column of $0.5 \text{ mm} \times 0.5 \text{ mm}$ pads with 0.2 mm and 0.5 mm gaps. The simulated velocity of the droplet is shown in Fig. 2(c). The results show that the droplet periodically speeds up and down according to the size of the hydrophilic pad and the distance between two pads. When the rear edge of the contact line is pinned on the hydrophilic pad, the velocity drops, and as the edge of the droplet is depinned from the pad, the velocity increases. The gap size has an obvious influence on the velocity, with a smaller gap size leading to more frequent fluctuations in velocity.

Experimental tests were carried out on a hydrophilic/superhydrophobic patterned surface, which consists of $0.5 \text{ mm} (L) \times 0.5 \text{ mm} (W)$ hydrophilic black silicon pads and black silicon substrate coated with fluorocarbon polymer. The measured advancing contact angle on the substrate and the pad is 170° and 30° , respectively. The details of the fabrication process are reported in the supplementary material.³³ The sliding droplet deposition process was characterized with a high-speed video camera (Phantom Miro M-310), and images were analyzed by image processing algorithms in MATLAB, see Figs. 3(a) and 3(b). The velocity of the droplet was estimated based on the trajectory of the contact line center (Fig. 3(b)), and the amount of the deposition was estimated using the same images.

The sliding droplet deposition in Fig. 3 is on a substrate with gaps between hydrophilic pads of 0.2 mm. The rear edge of the droplet was pinned on one pad for about 4 ms (see multimedia view of Figs. 3(a) and 3(b)). The velocity of the sliding droplet was observed to fluctuate periodically, where an average of five sets of the experimental data is compared with the simulation in Fig. 3(c), following well the trend of the theoretical estimation. The average speed of droplet was also analyzed for tilt angle a of 10° , 20° , 30° , 40° , and 50° . The

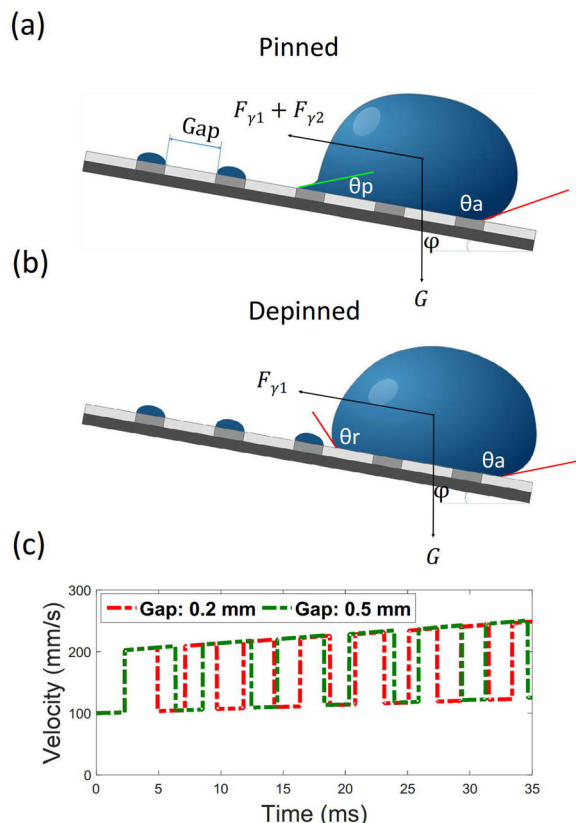


FIG. 2. Force configuration and simulation: (a) and (b) force configuration of a pinned and depinned droplet on a hydrophilic/superhydrophobic patterned surface; (c) calculated velocity as a function of time.

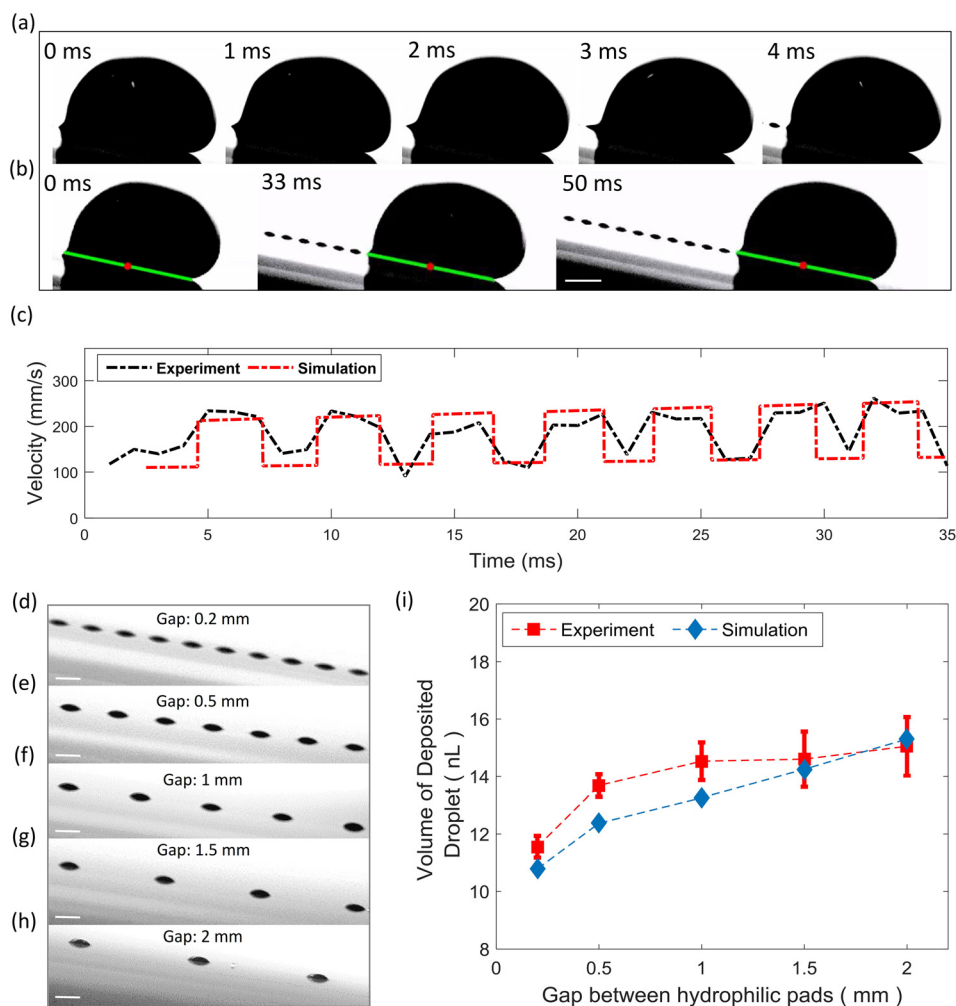


FIG. 3. Characterization of a droplet sliding on a patterned hydrophilic/superhydrophobic surface tilted at 10° : (a) and (b) side view images of a sliding droplet on patterned surface with detected contact line (green line) and center (red dot), scale bar 2 mm; (c) comparison of the simulated velocity with the average of experimental data; (d)–(h) deposited droplets on pads of $0.5 \text{ mm} \times 0.5 \text{ mm}$ and with gap of 0.2 mm, 0.5 mm, 1 mm, 1.5 mm, and 2 mm, scale bars 0.5 mm; (i) volume of deposited droplet as a function of gap between pads. (Multimedia view) [URL: <http://dx.doi.org/10.1063/1.4947008.1>]

calculated capillary number Ca has linear relationship with $Bo \sin(\alpha)$ as shown in Fig. S2 of supplementary material,³³ which is in consistent with an earlier report.³⁰

We varied the gap from 0.2 mm to 2 mm to investigate its influence on the deposited volume. Figs. 3(d)–3(h) show the images of the deposited droplets on hydrophilic pads with different gaps. The relationship between the volume of deposited droplet and the size of the gap between the pads is presented in Fig. 3(i), where each test was repeated 6 times. The results show that 11–16 nl deposition with a standard deviation of 0.5–1.5 nl can be achieved on patterned hydrophilic/superhydrophobic surfaces. When the gap is 0.2 mm, the deposition is $11.5 \pm 0.5 \text{ nl}$. The deposited volume increases slightly with larger gap sizes, and the standard deviation increases to 1.5 nl.

The results agree reasonable well with the simulation using HyDro,³⁴ as indicated in Fig. 3(i). In the simulation, we noticed that the neck between the small and the large droplet is longer with larger gaps, and the breaking point of the neck is further away from the hydrophilic pad, leading to greater volume of the deposition on the pad.

The sliding droplet deposition was demonstrated by liquid patterning and parallel deposition. Samples with different shapes of hydrophilic pads have been fabricated, where the results are highlighted in Fig. 4. Figs. 4(a) and 4(b) show the detailed features in the logo of Uppsala

University and a flower-shaped pad visualized by the sliding droplet. The possibility of parallel deposition was also tested. Water droplets dyed in different colors were dispensed (see multimedia view of Fig. 4(c)) and deposited (Fig. 4(d)) on the sample. Additionally, the proposed deposition method is scalable. Taking the parameters used in the experiments (pad size: $500 \mu\text{m}$, gap size: $200 \mu\text{m}$, average speed of the sliding droplet: 200 mm/s , size of the sliding droplet: 0.15 ml, deposited volume on each pad: 15 nl), a single sliding droplet can deposit 1000 pads in just 3.5 s. The throughput can be further scaled up using the parallel deposition method proposed in the paper, which leads to 10 000 deposition with 10 simultaneously sliding droplets in 3.5 s. This shows the great potential of the proposed method for large scale and high-density liquid deposition.

In summary, a simple deposition method was presented, utilizing moving droplets on patterned hydrophilic/superhydrophobic surface to achieve parallel deposition. The combination of a good wetting property of the pads and superhydrophobicity of the substrate, as well as reasonable gaps between the pads, can lead to deposition with uniformity better than 5%. The proposed method should also be applicable to other substrates such as glass or polymer, provided hydrophilic/superhydrophobic patterns can be produced on the substrate. Additionally, the method can be used for parallel deposition using multiple different liquids.

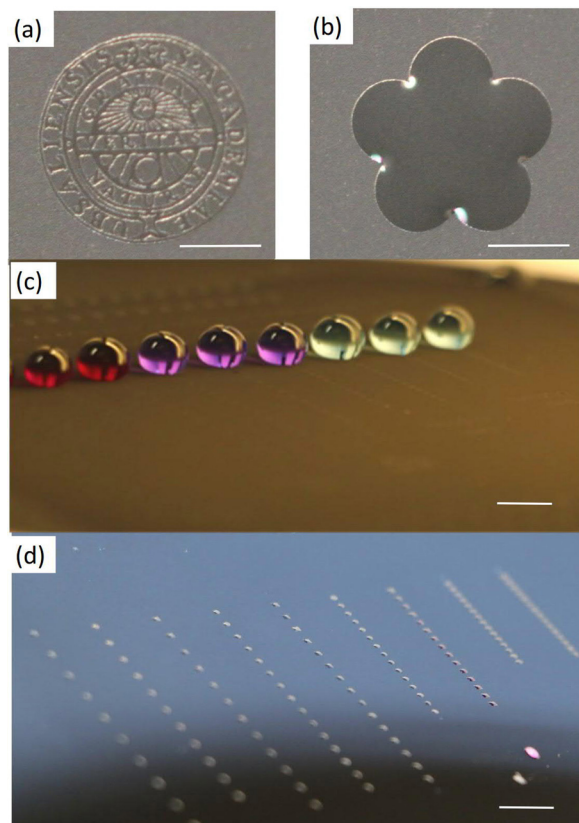


FIG. 4. Liquid patterning and parallel droplets deposition: (a) a logo of Uppsala University visualized with water, scale bar 1 mm; (b) a flower-shaped pad filled with water, scale bar 1 mm; (c) and (d) parallel deposition using different colored liquids on 0.5×0.5 mm pads, scale bars 1 cm. (Multimedia view) [URL: <http://dx.doi.org/10.1063/1.4947008.2>]

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