A Novel Bioinspired Continuous Unidirectional Liquid Spreading Surface Structure from the Peristome Surface of *Nepenthes alata*

Huawei Chen,* Liwen Zhang, Pengfei Zhang, Deyuan Zhang, Zhiwu Han, and Lei Jiang

Directional liquid spreading has gradually attracted worldwide attention owing to its potential applications in various fields, such as fog harvesting,[1–3] filtration,[4] and microfluidic devices.[5–9] Several anisotropic liquid spreading phenomena have been discovered on 1D thread-shaped natural systems, including water harvesting on spider silk[12,10] and fog collection on cactus needles.[3] However, all these cases of liquid spreading occur at the micronanoscale, with gradients in surface energy[8,11–14] and gradients in the Laplace pressure,[15–17] in which the spreading speed is slow and the spreading distance is short. We have discovered a unique multiscale structure involving duck-billed microcavities with arch-shaped open sharp edges and gradient wedge corners of the peristome surface of *Nepenthes alata*. This unique structure generates a top-closed capillary rise and liquid pinning effect and leads to 2D unidirectional liquid spreading on the surface with fast speed and long distance properties.[18,19] To broaden its applications, bioinspired continuous unidirectional liquid spreading surfaces were here proposed by a combination of an arch-shaped open sharp edge and a microgroove, which were extracted from the peristome surface as structural features. These bioinspired surfaces were fabricated via two-step UV lithography, and their unidirectional liquid spreading capabilities were experimentally compared. The inclined arc pitted groove was found to have superior unidirectional liquid spreading effects to those of other cases. Finally, the mechanism of the unidirectional liquid spreading was investigated by the microgroove-induced capillary effect, and inclined arc pits induced a strong liquid-pinning effect.

As a carnivorous plant, the peristome of *N. alata* possesses a marvelous function of unidirectional liquid spreading to form a wet slippery surface for capturing insects.[20,21] The structural characterization demonstrated that the unidirectional liquid spreading mainly results from its unique structural features, i.e., a sharp edge with an arch-shaped outline aligning at the bottom of the microgroove. Under the inspiration from *N. alata*, a microgroove with a pit array aligned at its bottom is critical for the unidirectional liquid spreading surface. To make clear the impact of the sharp edge and its arch-shaped outline, various pit shapes at the bottom of microgroove should be built for comparison, including an inclined square pitted groove, arc pitted groove, and inclined arc pitted groove. Here, we define the inclined pit extension direction and arc protruding direction as the front direction of the pitted groove surface structure, and its opposite direction as the rear direction. All these complicated surface structures were fabricated by the use of two-step UV lithography.

The fabrication of the inclined pitted groove is composed of two successive steps of UV lithography. The first step is the inclined pit array fabrication. SU-8 photoresist was chosen for the construction of the thick structure and spin coated on the glass substrate. Mask-a with arc patterns \( \odot \) and square patterns \( \odot \) was used to expose the arc pit array and square pit array, as shown in Figure 1a. An inclined UV source with an angle \( \Omega \) of 45° was shot from the rear to the front of the arc patterns to build the inclined pit array.\(^{[22]}\) The second step is the fabrication of the overlaid microgrooves on the pit array. After the development of the photoresist, the inclined pit array was spin coated again with the same thickness of SU-8 as in the first step. A straight strip pattern with the same width as the pit array was used as Mask-b, as shown in Figure 1b. During the exposure, strips of Mask-b were carefully aligned to cover the inclined pit array, ensuring that the microgroove was well overlaid upon the pit array, and UV exposure was performed perpendicularly to Mask-b. After the second development, the inclined arc pitted groove and inclined square pitted groove were finally obtained. The arc pitted groove was built with an angle \( \Omega \) of 0°, and a smooth groove was fabricated by the use of Mask-b with common UV lithography.
Scanning electron microscope (SEM, Model JSM-6010LA, JEOL, Ltd.) images of these four surface structures are shown in **Figure 2**. After the second exposure, microgrooves are overlaid precisely upon each row of pits. The front rims of pits are formed with $\approx 45^\circ$ sharp edges (Figure 2b,d, section view). The width of each microgroove $w$ in all four types of surface structure is $\approx 120 \mu$m. The depths of the overlaid microgrooves $h_1$ and pits $h_2$ are both $\approx 30 \mu$m. The length of each stage $d_1$ between pits in the inclined square pitted groove, arc pitted groove and inclined arc pitted groove is 40, 60, and 60 $\mu$m, respectively, and the length of each pit $d_2$ is 140, 160, and 160 $\mu$m, respectively (see Figure S1, Supporting Information).

To test the liquid spreading on these surface structures, a volume of $\approx 0.1 \mu$L ethanol was dropped at the center of these microgrooves, as the surface can be totally wet by ethanol. A high-speed video recorder (I-speed LT, Olympus, Japan) was used to record the liquid spreading process. The liquid spreads symmetrically along both sides of the smooth groove (Figure 2a right, see also Video S1, Supporting Information), but in both the inclined square pitted groove and arc pitted groove, the liquid spreading appears asymmetrical, being much quicker in the front direction than in the rear direction (Figure 2b right, see also Video S2, Supporting Information).

Here, a factor $\xi_d$ describing the level of anisotropy of the liquid spreading is defined as

$$
\xi_d = \frac{|d_l - d_f|}{\max(d_f, d_l)}
$$

where $d_f$ and $d_l$ are the spreading distances of the liquid in the front and rear directions during the same period.

By measuring the distance of the liquid spreading using high-speed video, the factor $\xi_d$ of the smooth groove, inclined square pitted groove, arc pitted groove, and inclined arc pitted groove are determined to be 0, 0.2 $\pm$ 0.1, 0.6 $\pm$ 0.1, and 1, respectively. When $\xi_d = 0$, the liquid spreads symmetrically, while $\xi_d = 1$ means that the liquid spread is completely unidirectional. Hereafter, with respect to the asymmetrical liquid spreading, the faster direction of liquid spreading is defined...
Figure 2. SEM images of surface structures and liquid spreading high-speed images. A volume of ≈0.1 \( \mu \)L ethanol was dropped into the center of these microgrooves, as marked by the dashed lines. The left parts show the top view and section view of the surface structure, and the right parts show the liquid spreading procedure after the dropping of an ethanol droplet. a) Liquid symmetrically spreads along a smooth groove. The liquid spreading speed in the front direction is greater than that in the rear direction in both the b) inclined square pitted groove and c) arc pitted groove. d) In the inclined arc pitted groove, unidirectional liquid spreading occurs, with liquid spreading only in the front direction. The section views of (b,d) demonstrate distinct sharp edges with an ≈45° inclination on the front rims of these pits. Arrow lines indicate the liquid spreading status in the microgrooves. See Videos S1–S4 (Supporting Information).
as forward spreading and the slower direction is defined as backward spreading.

In a smooth groove, the liquid spreads symmetrically as both sides form the same half-open square tube capillary.\cite{23}

The leading edge of the spreading liquid usually appears at the two intersected bottom corners because they form a strong capillary rise effect (Figure 3e).\cite{24-26}

For the forward asymmetrical liquid spreading along the three types of pitted groove, the leading edge of the spreading liquid generally appears along corner A (CA) formed between the microgroove wall and the top of the pit stages (Figure 3a, i-iii). Different from along the smooth grooves, the liquid spreading along the three types of pitted groove needs to bypass the front edge (FE) of the stage to continue filling the pit along corner B (CB), which is formed by the microgroove wall and the front wall of the stage. The opening angle of CB in both the arc pitted groove and the inclined arc pitted groove are smaller than that of the inclined square pitted groove, so that with a smaller $\alpha$, the capillary rise effect is much greater to make the liquid spreading easier in the first two cases than in the last.

During the continuous filling of the pits, the liquid initially spreads along the three types of pitted groove with a wedge corner formed between the inclined front pit wall and the bottom of the pit. This wedge corner can provide a higher capillary rise effect, but its influence on the liquid spreading is not distinct because the inclination of the wedge is not so large as that of the wedge corner of \textit{N. alata}. After the liquid level rises up to the front rim of the pit, the liquid will climb onto the stage to continue filling. This filling-climbing process will continue until the liquid amount is not sufficient to fully fill the next pit. The liquid spreading process in an inclined arc pitted groove (Figure 3c, see also

![Schematics of liquid spreading](image)

**Figure 3.** Schematics of liquid spreading a) forward and b) backward in inclined square pitted groove, arc pitted groove and inclined arc pitted groove. CA, CB, CC, FE, and RE represent corner A, corner B, corner C, front edge, and rear edge of stages, respectively. $\theta_1$ and $\theta_3$ are the equilibrium contact angles of the liquid at the center of RE. $\theta_2$ and $\theta_4$ are the equilibrium contact angles of the liquid at the intersection of RE and CA. $d$ is the distance between CA and arc RE. c) In the inclined arc pitted groove, high-speed images show that the liquid is spreading in the forward direction and is pinned in backward direction. Dashed lines describe the outline of the liquid. Scale bar is 50 $\mu$m. d) Pinning structure in backward spreading. $\beta$ is the arc tangent angle formed by RE and CA at their intersection. $\gamma$ is the solid edge angle of RE. e) Schematics of liquid spreading in half-open square tube induced by capillary force, and liquid capillary rise in sharp corner formed by two plates. $\alpha$ is the angle formed by two plates. f) Liquid pinning at sharp edge. $\theta_0$ is the natural contact angle of the liquid on the surface. $\theta_c$ is the critical contact angle at the moment that the liquid spreads spontaneously down the edge. $\phi$ is the angle of the solid edge.
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Video S5, Supporting Information) is identical to that on *N. alata*’s peristome.

In the backward direction, the liquid pinning effect plays a great role in asymmetrical liquid spreading. This is known as the Gibbs inequality condition. The equilibrium contact angle \( \theta \) of a liquid at a solid edge has a range of (Figure 3f)

\[
\theta_0 \leq \theta \leq \theta_c
\]

\( \theta_0 \) is the natural contact angle of a liquid on the surface. \( \theta_c \) is the critical value of \( \theta \) at the moment that a liquid spreads spontaneously down the edge and is equal to \( 180^\circ - \varphi + \theta_0 \), where \( \varphi \) is the angle of the solid edge.\(^{[27]} \) Using this pinning method, Liimatainen et al. fabricated a line stage with sharp edges to restrict the liquid spreading.\(^{[28]} \)

In the backward spreading within an inclined square pitted groove, the liquid initially spreads along the CA corner and then gradually gathers at the rear edge (RE) of the stage (Figure 3b, iv). As liquid tends to aggregate at the corner, the equilibrium contact angle at the intersection of RE and CA, \( \theta_0 \), is larger than that at the center of RE, \( \theta_c \) (Figure 3b, iv). This would weaken the pinning effect of RE at its intersection with CA and would result in liquid easily spreading into the pit along corner C (CC) formed by the microgroove wall and the rear wall of the stage. Because the edge angle of RE is smaller than that of FE, asymmetrical liquid spreading occurs in the microgrooves with a factor \( \xi \) larger than zero. Different from the straight RE in the inclined square pitted groove, the arc RE in the arc pitted groove creates a smaller arc tangent angle \( \beta \) at the intersection of RE and CA (Figure 3d) and makes the liquid volume in CA gradually decline along RE as the distance \( d \) between CA and arc RE decreases. Consequently, the equilibrium contact angle at the intersection of arc RE and CA, \( \theta_0 \), is smaller than that at the center of arc RE, \( \theta_c \) (Figure 3b, v). The liquid pinning in the arc pitted groove becomes much stronger with a higher \( \xi \) than that in the square pitted groove. This also indicates that the arch-shaped outline of *N. alata*’s sharp edge can help pin liquid to increase the asymmetrical liquid spreading.

Especially in the inclined arc pitted groove, the inclination of the sharp arc RE also contributes to the liquid pinning of the backward spreading (Figure 3b, vi). With dual liquid pinning effects from both the sharp edge (smaller angle \( \gamma \)) and its arch-shaped outline (smaller angle \( \beta \)) on RE (Figure 3d), the liquid spreading stops at the rear rim (Figure 3c, backward case, see also Video S6, Supporting Information), and then a remarkable unidirectional liquid spreading appears in the inclined arc pitted groove with the highest factor \( \xi \) of 1.

Since the width and depth of inclined arc pitted groove are constant, the spreading distance linearly increases with liquid volume as shown in Figure S2a,b (Supporting Information). For certain volume of liquid, its spreading speed decreases at approximately linear manner with spreading distance (see Figure S2c and Video S7, Supporting Information). Compared to previous directional liquid spreading surface, the spreading speed in inclined arc pitted groove is much faster and the spreading distance is longer.\(^{[8,29]} \) By modifying the surface wettability with oxygen plasma treatment, water can also unidirectionally spread on inclined arc pitted groove (see Figure S3 and Videos S8 and S9, Supporting Information). Such a unidirectional liquid spreading surface bioinspired from the peristome surface of *N. alata* must have potential applications in MEMS (micro-electro-mechanical Systems) and mechanical engineering.

In conclusion, inspired by the unique multiscale surface structures on the peristome of *N. alata*, novel microgrooves with a pit array at their bottom have been proposed and fabricated by two-step UV lithography. Pits with a sharp edge and an arc-shaped outline were investigated to test the impact of the outline of the pit on asymmetrical liquid spreading. Liquid spreading tests demonstrated that the arch-shaped outline and sharp edge on the pit rim play a great role in the directional liquid spreading. The mechanism of asymmetrical liquid spreading was particularly explored, and a bioinspired inclined arc pitted groove exhibited unique unidirectional liquid spreading. This novel bioinspired surface structure with fast and long-distance unidirectional spreading properties might find potential applications in various fields such as drip irrigation in agriculture, nonpowered delivery of medicine, and self-lubrication in mechanical engineering.

Supporting Information

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

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