Fabrication of extreme wettability surface for controllable droplet manipulation over a wide temperature range

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Abstract
Droplet controllable manipulation over a wide temperature range has promising applications in microelectronic heat dissipation, inkjet printing, and high temperature microfluidic system. However, the fabrication of a platform for controllable droplet manipulation using the methods commonly used in industry remains a tremendously challenge. The popular method of controlling droplets is highly dependent on external energy input and has relatively poor controllability in terms of droplet motion behaviors and manipulation environment, such as distance, velocity, direction and a wide temperature range. Here, we report a facile and industrially applicable method for preparing Al superhydrophobic (S-phobic) surfaces, which enables controlled droplet bouncing, evaporation, and transport over a wide temperature range. Systematic mechanic studies are also investigated. Extreme wettability surfaces were prepared on Al substrate by a composite process of electrochemical mask etching and micro-milling. To investigate the evaporation process and thermal coupling characteristics, controlled evaporation and controlled bouncing of droplet in a wide temperature range were conducted. Based on the evaporation regulation and bouncing mechanism of droplets on an extreme wettability surface, by using Laplace pressure gradients and temperature gradients, we realized controlled transport of droplets with confluence, split-flow, and gravity-resistant transport over a wide temperature range, offering a potential platform for a series of applications, such as new drug candidates and water collection.

Keywords: extreme, wettability surface, superhydrophobic, controlled evaporation, controlled bouncing, controlled transport

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1. Introduction

Beetles in the desert can obtain drinking water from the air, and this water harvesting process relies on alternating hydrophobic–hydrophilic patterns on their dorsal surfaces. Inspired by such natural phenomena, scholars are strongly interested in the manipulation of droplets on extreme wettability surfaces, that is S-phobic-hydrophilic or superhydrophilic (S-philic) surfaces. In particular well-controlled liquid droplet manipulation on extreme wettability surfaces is essential to various practical fields, such as biochemistry [1], microfluidic systems [2, 3], cell culture [4, 5] and energy harvesting and utilization [6]. Despite remarkable significance, the droplet manipulation on extreme wettability surfaces has achieved less progress, particularly for droplet manipulation on extreme wettability surfaces with a wide temperature range.

Current methods of manipulating droplets mainly use surface force gradient, which always require the responsiveness of substrates or droplets force sources. Droplet manipulation on wettability surfaces is a promising method for high-precision droplet manipulation [7]. The wettability difference surface with micro-nanoparticles can reduce surface adhesion and produce different tension gradients to achieve controllable droplet manipulation. The wettability surfaces are usually prepared by using femtosecond laser [8, 9], plasma method [10–12], masked ultraviolet (UV) methods [13, 14], mask electrochemical secondary etching method [15, 16] and mechanical processing method [17–19]. These wettability surfaces have been used to achieve underwater spontaneous transport of non-polar organic liquids [20], spontaneous droplet bouncing [6, 21], and droplet transport driven by temperature gradients and Laplace pressure differences [22, 23]. Despite a series of research on the preparation of extreme wettability surface and droplet manipulation was achieved, there are still some limitations in the existing research methods. For example, plasma modified extreme wettability surfaces cannot withstand high temperatures. The materials for UV radiation are limited. While electrowetting can be applied on structural surfaces, it can only be efficient unidirectionally. Droplet manipulation methods such as electrowetting and magnetic response are highly dependent on external energy input to generate surface tension gradients, which increase the complexity of manipulations platforms [24–26]. Other methods eliminate the need for electrode groups. Examples of these methods, surface charge printing or electrostatic repulsion methods, are susceptible to the extra steps to generate charges on substrates or droplets. Inspired by biologically functional surfaces, numerous strategies have been developed to allow for the spontaneous, directional and rapid transport of droplets without the need of any additional energy input by considering capillary force gradients, controlled asymmetric [27], surface charge gradients [28], structural gradient-induced-vapor layer gradients [29], and tip-induced flipping [30], wettability gradients [31], and the combination of them. For example, Ghosh et al [32] reported an open non-planar microfluidic platform consisting of a S-phobic substrate and a wedge-shaped S-philic track to achieve pump-free fluid transport drive at room temperature conditions. It is noteworthy that Li et al [33] reported the spontaneous, long-range and unidirectional flow of water liquid from the low-temperature region to the high-temperature region on a specially designed topological surface. These previous methods contribute to our understanding of the physicochemical mechanism of liquid directional transport and the design of novel microfluidic devices [34]. However, the stability and effectiveness of the above methods at high temperatures remain to be investigated. Moreover, existing droplet manipulation technology is difficult to precisely control droplets for high speed or long distance transportation, and high cost of manipulation devices. It is worth pointing out that, existing droplet manipulation focuses on uniformity wettability surfaces at room temperature [35, 36]. Droplet manipulation of non-uniformly wettability surfaces over a wide temperature range is widely used in microelectronic heat dissipation, inkjet printing and high-temperature microfluidic chips. The heat transfer characteristics, bounce phenomenon, and evaporation mechanism of droplets on non-uniformly wettability difference surfaces under high temperature conditions still need further study. Moreover, the preparation process of patterned wettability surfaces using industrial methods and the realization of controllable droplet manipulation on extremely wettability surfaces over a wide temperature range are also limited reported.

Here, we report a facile and industrially applicable method for preparing S-phobic surfaces, mask chemical etching was used to fabricate large scale and large area surfaces with wettability differences, micromilling was used to fabricate large, complex, internally smooth hydrophilic groove patterns directly on flat and curved S-phobic substrates, and enables controlled droplet bouncing, evaporation, and transport over a wide temperature range. Systematic mechanistic studies are also carried out. First, extreme wettability surfaces with wettability differences were prepared on Al surfaces by a composite industrial process of electrochemical mask etching and micro-milling. Then, by studying the thermal coupling characteristics, the evaporation process and mechanism of droplet on the extreme wettability surface at different temperatures, controlled evaporation and controlled bouncing of the droplet in a wide temperature range were investigated. Finally, based on the evaporation regulation and bouncing mechanism of droplets on an extreme wettability surface, by using Laplace pressure gradients and temperature gradients, we realized controlled transport of droplets over a wide temperature range with confluence, split-flow, and gravity-resistant transport. This research has potential applications in these fields such as microfluidic systems, biomedicine, and energy harvesting.

2. Preparation and characterization of extreme wettability surface

2.1. Preparation of extreme wettability surface

Extremely wettability surfaces are functional surfaces with S-phobic and S-philic patterns. The preparation method is shown in figure 1, and the preparation process consists of three steps. Step I: two Al plates (S1 and S2) were removed from the
oxide layer, and then the S1 and mask-covered S2 were electrochemically etched in 0.2 mol l\(^{-1}\) NaCl solution for 6 min, then washed with deionized water and dry with hot air. A S-phobic Al surface S1, and a S-phobic-hydrophilic Al surface S2 with wettability differences were obtained by removing the mask after immersion in 1 wt.% fluoroalkylsilane (FAS) ethanol solution for 40 min. Step II: the hydrophilic region is micro-milled in the fixed domain on the aluminum-based S-phobic surface S1 by using a mechanical machining method, and a high-precision patterned surfaces with stable wettability differences for experimental studies of controlled evaporation and controlled transport of liquid droplets was fabricated successfully. Step III: the S-phobic Al surface S1 prepared in step I was immersed in 0.2 mol l\(^{-1}\) NaCl solution for 4 min for mask electrochemical etching (MEE), and the mask was removed after boiling water immersion to obtain the extreme wettability surface. The S-phobic-hydrophilic and S-phobic-S-philic extreme wettability surfaces were used for the experimental study of controlled bouncing. Milling equipment is computer numerical control (CNC) engraving equipment (YD3040, Shenzhen yidiao Technology Co., Ltd, China), the surface morphology and chemical composition of hydrophilic, S-phobic, and S-philic Al surfaces were characterized by scanning electron microscopy (SEM, SUPRA 55 SAPHIRE, Germany), energy dispersive x-ray spectroscopy (EDS, SUPRA 55 SAPHIRE, Germany), and Fourier transform infrared spectroscopy (FTIR, JACSCO, Japan).

2.2. Extreme wettability surface characterization

The contact angle of water droplets on an ordinary hydrophilic Al substrate is 71 ± 2°, as shown in figure 2(a), with a smooth surface and a surface roughness Ra of 235 nm (figure 2(a4)). The energy spectrum consists of C and O (figure 2(a2)). After NaCl etching and FAS low surface energy modification [37], the Al surfaces were S-phobic with a water contact angle of 152 ± 2° and a sliding angle of only 1°, as shown in figure 2(b). The S-phobic properties were the result of the irregular micro/nano-rectangular structures obtained from etching (figure 2(b1)) and the low surface energy due to the FAS ethanol solution modification, with a rough surface and a surface roughness Ra of 3.943 µm (figure 2(b4)). After the FAS modification, F appeared in the EDS spectrum. The elements of C, N, O, F and the vibrational peaks of –CH\(_2\)–, Si–C and Si–O–Si groups in the FTIR were all from FAS, as shown in figure 2(b2) and (b3). After MEE in the 0.2 mol l\(^{-1}\) NaCl solution or fixed-domain milling on a S-phobic Al surfaces, the surface could be effectively transformed into a S-philic surface or S-philic pattern. The transition of the wettability after MEE and fixed-domain milling treatment was not due to a change in surface morphology but was the result of the removal of the low surface energy groups (–CH\(_2\)–, Si–C and Si–O–Si). Figure 2(c1) and (c4) show the SEM images, EDS, FTIR spectra and the surface roughness of the S-philic Al surfaces after MEE. The morphology of Al surfaces after MEE was found to be similar to the S-phobic surface and still consisting of irregular rectangular craters and raised micro/nano-structures, but the surface roughness Ra was 3.921 µm. Furthermore, the EDS results showed that no F element appeared after the MEE, which indicated that the substance left after the low surface energy modification of FAS is completely removed. In addition, the characteristic peaks of –CH\(_2\)–, Si–C and Si–O–Si groups in the FTIR spectrum at 2916.32 cm\(^{-1}\), 1262.66 cm\(^{-1}\) and 1048.23 cm\(^{-1}\) showed slightly increased intensity. This is the result of the active particles in the MEE and fixed-domain milling treatment potentially minimizing the low surface energy groups (–CH\(_2\)–, Si–C and Si–O–Si). It can be seen that the S-phobic-S-philic extreme wettability
Figure 2. Characterizations of the extreme wettability patterns. (a) Images of ordinary hydrophilic Al substrate. (a1) SEM image, (a2) EDS, (a3) FTIR spectra and (a4) surface roughness of ordinary Al surfaces. (b) Images of S-phobic Al surface. (b1) SEM image, (b2) EDS, (b3) FTIR spectra and (b4) surface roughness of S-phobic Al surface. (c) Images of S-philic Al surface. (c1) SEM image, (c2) EDS, (c3) FTIR spectra and (c4) surface roughness of S-philic Al surface.
surfaces or patterns preparation can be achieved by MEE method and fixed domain micro-milling of the mechanical processing method.

3. Results and discussion

3.1. Controlled evaporation of droplets on wettability differences surfaces

Droplet evaporation plays an important role in microelectronic heat dissipation, inkjet printing, and controlled heat transfer. Numerical simulations and evaporation experiments were performed to investigate the heat transfer characteristics and internal mobility of droplets. A three-dimensional geometric model of the droplet was developed to simulate the evaporation kinetics of the droplet on hydrophilic and S-phobic Al surfaces. The droplet was initially considered to be at a uniform temperature of 293.15 K. The initial velocity inside the droplet was assumed to be zero, the droplet-free surface (droplet—air interface) was at atmospheric pressure (101.32 kPa). The contact angle of the droplet on the S-phobic and hydrophilic Al surfaces was set as 150° and 90°, respectively. The radius of contact between the spherical crown droplet and the S-phobic Al surface was 0.5 mm, and that between the hemispherical droplet and the hydrophilic Al sheet was 2 mm. After meshing with the physical control grid sequence, the coupled fields of temperature, flowline and velocity fields of droplet on the hydrophilic Al surfaces were determined. The simulation results are shown in figure 3. It can be seen that the temperature at the bottom of the droplet on the S-phobic surface was higher (370 K) when the droplet was heated for 3 s, and the temperature in the middle and upper part was 320 K (figure 3(a)). Moreover, in figure 3(a) the flowline field and velocity field of the droplet are presented, and the color change of the flow line corresponds to the magnitude change of the velocity in the velocity field, it can be noticed that the flow velocity in the bottom region of the droplet was the highest (0.14 m s⁻¹). In order to describe the flowline field of the droplet more clearly, we take one-half of the droplet section for observation, as shown in figure 3(b), the flowline inside the droplet was formed by a circulation cells, and the evaporation process for the whole droplet on the S-phobic surface...
presented a constant contact angle (CCA) evaporation mode [38]. This is due to the fact that the contact angle between the droplet and the solid surface remained constant when the droplet evaporated on the solid surface because the heat was transferred from the bottom part of the droplet to the upper part during the evaporation process. The combined effect of Marangoni flow and internal natural convection due to surface tension gradients caused by temperature differences was observed at different locations on the droplet surface, resulting in the formation of a internal circulation cell. In contrast, on the hydrophilic surface, the temperature at the bottom part of the droplet was higher (370 K) after 3 s, and the temperature at the top of the droplet was 310 K, the flow velocity is higher in the central region ($4.0 \times 10^{-3}$ m s$^{-1}$) and lower in the edge and surface regions, as shown in figure 3(c). Figure 3(d) shows a one-half droplet section showing the flowline visualization of the velocity inside droplet; a circulation cell was formed inside the droplet, but the evaporation process on the hydrophilic surface presented a constant contact radius (CCR), that is, the contact radius between the droplet and the solid surface remained constant.

To visually demonstrate the controlled evaporation behavior of droplets on patterned high-wettability surfaces, four hydrophilic micropits of different diameters were milled on the S-phobic Al substrate with a depth of 300 $\mu$m. The samples were placed on a thermostatic heating table and heated to 100 $^\circ$C. Then, 5 $\mu$l of deionized water was dropped onto these four micro pits, and the average evaporation times were 33, 45, 55, and 60 s for the diameters of 1.2, 0.9, 0.6, and 0.3 mm, respectively, as shown in figure 4(a). The results demonstrated that the evaporation time of the same volume of droplets on the micropits decreased with an increase in the diameter of the hydrophilic micropits, that is, the larger the diameter of the micropits, the shorter the evaporation time.

Inspired by the abovementioned results, controlled evaporation of droplets on hydrophilic circular groove patterns and hydrophilic micropit dot patterns on S-phobic surfaces were investigated. Hydrophilic micropits were milled on the S-phobic Al substrate with a depth of 300 $\mu$m, with the largest external circle having a diameter of 1.2 mm, the second circle with a diameter of 0.9 mm, and the innermost micropit 0.6 mm. The sample was heated to 100 $^\circ$C. Deionized water (2.5 $\mu$l, colored with red or blue ink for easy observation) was dropped on the micropits. The droplets on the outermost circle of hydrophilic micropits evaporated first, followed by the droplets on the second circle of hydrophilic micropits, and finally, the droplets on the innermost hydrophilic micropits, as shown in figure 4(b). In the hydrophilic micropit dot pattern, the hydrophilic dot diameter of the abbreviation “HNU” of Hunan University was 0.5 mm and that of the others was 1 mm, and the depth was 300 $\mu$m. With a 1 $\mu$l droplet was put into the micropit, the temperature was 100 $^\circ$C. The droplet that did not evaporate at 18 s formed HNU, as shown in figure 4(c).

3.2. Controlled bouncing of droplets on extremely wettable surfaces over a wide temperature range

The principle of directional transfer of liquid droplets over a wide temperature range can be applied to bionic progenitors.
such as power generation, green nanofabrication, antifouling and actuators. To determine the inherent mechanism of droplets bumping against nonuniformly wettable surfaces at different temperatures, a study on the regularity of controlled droplets bouncing under room temperature and high temperature conditions was conducted. In the experiment, a Sony DSC-RX100M5 high-speed camera was used to record the bumping process at 1000 frames s\(^{-1}\). The droplets were added from a height of 50 mm. The droplet thruster could be adjusted to different speeds according to the conditions of the experiment. An adjustable thermostatic heating platform with a digital display was used to heat the experimental sample, and the temperature range was 0 °C–450 °C, as shown in figure 5(a).

### 3.2.1 Controlled bouncing of droplets on surfaces with different wettabilities at room temperature

To study the interaction of droplets with surfaces with different wettabilities, the trajectory and landing distance of the rebound droplets were varied by controlling the wettability at the junction. As shown in figure 5(b), a 3.36 µl spherical droplet deviated from the junction by 1 mm, and the release height was 50 mm (the Weber number \( We = 13.7 \) [39]). At this time, the radius of the spherical droplet was 0.929 mm, which is approximately equal to the deviation, but the spreading radius of the droplet was slightly greater than 1 mm when it hit the solid surface, and the ratio of contact hydrophilic area to the maximum spreading area of the droplet was 12%. The directional bouncing regularity of droplets on substrates with different wettability was observed under these conditions.

As shown in figure 6(a), the water droplets exhibited a tendency to bounce toward the more wetted surface after slight contact with the hydrophilic region. The contact line trajectories of the impacted droplets on S-phobic and hydrophilic regions with time were shown in figure 6(b), the blue dashed line is the deviation line (collision centerline), and the red dashed line is the boundary line between the S-phobic and hydrophilic regions. Obvious differences in the contact angles of the two edges of the bouncing droplets in the S-phobic and hydrophilic regions were observed. When the contact line of the droplet on the hydrophilic surface was fixed, the contact line on the S-phobic surface moved rapidly toward the hydrophilic surface with a high lateral force. The combined force exerted by the unbalanced lateral forces on both sides caused the droplets to bounce directionally toward the hydrophilic region, droplets basically all move to the hydrophilic region after 18 ms, and only a very tiny volume of droplets were present in the superhydrophobic region.

Substrate wettability differences can also have an effect on droplet directional bounce. Figure 7(a) shows the directional bouncing of 3.36 µl of droplets on a S-phobic-S-philic substrate with an extreme wettability difference (the black line is the boundary line between the S-phobic interface and the S-philic or hydrophilic interface, that is the deviation of 0 mm in figure 5(b), where the droplet completely bounced from the S-phobic region to the S-philic region after 60 ms, while, on the substrate with medium wettability difference of S-phobic-hydrophilic, the droplet completely bounced from the S-phobic region to the hydrophilic region after 51 ms (figure 7(b)). The landing distance of droplet released from a fixed height on the boundary increases with the increase of wettability difference, as in figure 7(c), that is, the directional bounce distance of droplet on the S-phobic-S-philic surface is larger than the directional bounce distance of droplet on the S-phobic-hydrophilic surface. The reason of this is that the larger the wettability difference, the larger the combined force acting on the rebound droplet at a certain angle, resulting in an increase of its landing distance.

The effect of different hydrophilic region contact percentages on droplet directional bounce on S-phobic-hydrophilic substrates with wettability differences was studied. The ratio of the contact area with the hydrophilic region after spreading when the droplet with a volume of 3.36 µl hits the S-phobic-hydrophilic substrate was set to 12%, 22% and 50%, respectively. Directional bouncing of droplets was observed. In figures 8(a)–(c), the black line is the proportional line that divides the contact area between droplets with hydrophilic region. The initial reference point for the landing distance is the droplet center point when the contact ratio with the hydrophilic region is 50% after diffusion on the S-phobic-hydrophilic wettability difference substrate at 2 ms, which was recorded as \( A_i \) (\( i = 1, 2, 3 \)), namely, the junction of S-phobic and hydrophilic. When the droplet stopped after multiple

![Figure 5](image1.png)  
**Figure 5.** (a) Droplet bounce test platform, (b) schematic diagram of droplets hitting Al substrates with different wettability.

![Figure 6](image2.png)  
**Figure 6.** (a) Controlled bouncing of water droplets toward a more wetted surface after slight contact with the hydrophilic region. (b) Contact line trajectory of impacted droplets on S-phobic and hydrophilic regions.
rebounds, the droplet center point at this time was recorded as $S_i (i = 1, 2, 3)$, and the distance of $S_i A_i$ is the bounce distance of the droplet in different contact regions of the hydrophilic region, where $S_i A_i = (A_i C_i + A_i B_i) / 2$. The bounce height $h_i$ of droplet was defined as the distance between the center point of the droplet in the vertical direction and the wettability difference Al surface in bouncing, where $h_i = (h_t + h_b) / 2$.

Figures 8(a)–(c) show that the farthest directional bounce distances of droplets in 50%, 22%, and 12% hydrophilic region contact areas were 2.1, 5.8, and 6.9 mm, respectively. Figure 8(d) shows the variation in the droplet contact line trajectory based on the positions of droplets at different moments in the bouncing process. The changes in the droplet contact line trajectory were fitted according to the position of the droplet at different moments during the bouncing process. As the droplet and hydrophilic contact area percentage increases, the droplet adhesion force increases, and the viscous dissipation energy increases. In addition, the pegging effect in the hydrophilic region decreases the kinetic energy of the droplet, and the impacted droplet has less energy left for a directional rebound. Thus, the directional bounce distance and landing distance also decrease, as shown in figure 8(d). When the hydrophilic region contact area was increased to 22% and 50%, the pegging effect of the hydrophilic region on the droplets became more noticeable. The increased percentage of hydrophilic surfaces led to severe energy dissipation, and the droplets no longer retain enough kinetic energy to rebound from the surface and only move horizontally toward the hydrophilic region. Therefore, directional bouncing of droplets can be achieved by controlling the percentage of the contact area between the droplets and the hydrophilic region.

3.2.2. Controlled bouncing of droplets at extreme wettability junctions under high temperature. At a specific temperature, droplets present directional bouncing on S-phobic surfaces, and dramatic boiling occurs on S-philic surfaces [40]. While the motion regulation and mechanism of droplets on S-phobic-S-philic extreme wettability surfaces under high temperature conditions still need to be further investigated. Therefore, we designed an experimental platform to carry out the bouncing process of droplets hitting extreme wettability surfaces at different temperatures, as shown in figure 5(b), where the deviation was set as zero. When the droplet rebounded, the height from the center point of the droplet’s landing position to the junction was set to $h = 0.5$ cm. When the substrate temperature $T_S$ was below 200 °C, the droplets tended to migrate to the S-philic region (figure 9(a)). When $T_S$ was around 200 °C, the droplets generally maintained their motion above the boundary, and the bouncing direction was vertically upward (figure 9(b)). When $T_S$ was above 200 °C, the droplets moved toward the S-phobic region after the first bounce, but their first movement displacement was relatively short. The droplets bounced on the substrate several times, and

![Figure 7](image7.png) (a) Directional bouncing process of droplet on S-phobic-S-philic extreme wettability surface. (b) Directional bouncing process of droplet on S-phobic-hydrophilic substrate. (c) Trajectory of contact line of droplet with time for directional bouncing on S-phobic-S-philic and S-phobic-hydrophilic substrate.

![Figure 8](image8.png) (a)–(c) Directional bounce of droplet for 50%, 22%, and 12% hydrophilic area contact area, respectively. (d) Variation in the droplet contact line trajectory when the contact area percentage of hydrophilic area is different.

![Figure 9](image9.png)
the movement displacement gradually increased, as shown in figure 9(c).

To investigate the tendency of droplet movement, the geometric displacement of droplet after bouncing is the distance from the center of the landing position to the junction, the center of droplet landing position can be defined as \( d = (y_1 + y_2)/2 \), where \( y_1, y_2 \) were the distance between droplet edge and boundary. Toward the S-phobic region was considered negative, and toward the S-philic region was considered positive, as shown in figure 9(a). The bounce displacement of the droplets after the first rebound under this condition with respect to the temperature is shown in figure 10(a). When the temperature was 150 °C and 250 °C, the droplets moved 4 mm and 3.4 mm to the S-philic and S-phobic regions, respectively. The bouncing displacement \( d \) versus time \( t \) is shown in figure 10(b). It is known that the rising of surface temperature will form a continuous vapor film on the wettable surface, resulting in a film-boiling or Leidenfrost regime [41]. So the droplets had different evaporation states when they impacted the junction of S-philic and S-phobic, which resulted in an imbalance of forces on different parts of the droplets, thus resulting in the movement of droplets to different areas.

When \( T_s \) was below the Leidenfrost boiling point, the droplets spread rapidly into the hydrophilic region, which caused the droplets to move toward the hydrophilic region. When \( T_s \) was above the Leidenfrost boiling point, the thrust generated by the vapor layer caused the droplets to bounce vertically at the junction or move toward the S-philic region. Thus, it was demonstrated directional bouncing of droplets can be achieved in the heated wetting mode.

Figures 10(c) and (d) explain the principle of droplet bouncing under high temperature conditions on an extremely wettable substrate of S-philic and S-phobic substrates, where the droplet is subjected to a downward gravity \( G \), a surface tension \( F_t \) along the tangential direction of the droplet, a vertical upward elastic force \( F_p \), and a vapor thrust \( F_v \) caused by the boiling of liquid. When \( T_s \) is lower than the Leidenfrost transition point, the S-philic region does not reach the Leidenfrost effect point, the droplet is in boiling state, and the surface tension \( F_t \) of droplet plays a key role in the motion of droplet. When the same droplet drops exactly at the junction of S-phobic and S-philic, we obtained the \( F_{t1} = F_{t2} \), due to the contact area between the droplet and the substrate in the S-philic region part being larger than the S-phobic region. At this time, the surface tension generated by the droplet in the S-philic region is \( F_{t2} \), and the surface tension in the S-phobic region is \( F_{t1} \sin \theta = F_{t2} \sin \theta < F_{t2} \), therefore, the droplet moves toward the S-philic region (figure 9(a)). When \( T_s \) is higher than the Leidenfrost transition point, the droplet is removed from the substrate by the vapor thrust \( F_v \), which reduces the contact area between the droplet and substrate, so the surface tension \( F_t \) becomes a secondary force, and the vertical upward elastic force and thrust become the key factors driving the directional motion of droplet. When \( F_{b1} + F_{p1} = F_{b2} + F_{p2} \), the droplet rebounds vertically at the boundary (figure 9(b)). With the rise of \( T_s \), the greater wettability in the S-philic region causes the droplet to generate more vapor thrust than the superhydrophobic region, that is \( F_{b1} + F_{p1} < F_{b2} + F_{p2} \), resulting in the droplet bouncing toward the S-philic region (figure 9(c)).

3.3. Controlled transport of droplets on extreme wettability surfaces

3.3.1. Controlled transport of droplets in patterned microfluidic channels driven by Laplace pressure difference

The controlled evaporation study demonstrated that micromilling is a suitable method for fabricating complex hydrophilic groove structures on S-phobic substrates and can be employed for fabricating large-area, complex, and smooth hydrophilic groove patterns on flat or curved S-phobic substrates. We used micromilling to fabricate patterned microfluidic paths on Al S-phobic surfaces and then developed experiments and mechanistic analyses of droplet directional transport driven by Laplace pressure difference. An open-surface microfluidic system (depth: 100 \( \mu \)m) comprising two circular groove storage layers with diameters of 2.0 and 3.0 mm and a twisted channel with a width of 0.5 mm was milled on the S-phobic surface, as illustrated in figure 11(a). To observe the droplet driven by the Laplace pressure difference transport process, a 12.2 \( \mu \)l of deionized water was dropped into the large and small circular grooves, as shown in figures 11(b) and (c). The experimental results revealed that the droplets moved from the small circular groove to the large circular groove after 14 s, and only a very little amount of the 12.2 \( \mu \)l of deionized water in the large circular groove was transported to the small circular groove.
The radius of curvature (C) of a droplet on a surface microfluidic can be mathematically calculated, from which the internal Laplace pressure $\Delta P$ can be expressed as

$$\Delta P = 2\gamma L C = \frac{16\gamma L H}{D^2 + 4H^2}$$  \hspace{1cm} (1)

$$V = \frac{\pi}{6} \left( H^3 + \frac{3}{4}H D^2 \right)$$  \hspace{1cm} (2)

where $D$ is the diameter of a S-phobic of circular groove boundary, $H$ indicates the droplet height, and $\gamma L$ represents the surface tension coefficient of droplets. Equation (2) illustrates the relationship among the size of wetting pattern, the droplet height and volume. In figure 11(a), two circular channels with diameters $D_1$ and $D_2$ are connected by a surface microfluidic channel (of length $l$, width $w$, and height $h$), and the droplets move spontaneously under pressure in the direction of the Laplace pressure gradient until they are in equilibrium. The Laplace pressure difference $\Delta P$ between the two circular channels drives droplet transport at a volumetric flow rate $Q$, which is inversely proportional to the droplet flow resistance $R_e$ in the connected channels of the circular channels ($Q = \Delta P / R_e$).

The flow resistance coefficient in the connecting channel of a closed system can be approximated as $R_e = 3 \mu l / wh^3$, where $\mu$ is the viscosity coefficient of the droplet [42]. The surface tension-driven flow rate can be approximated by the rate of volume change of each droplet, where system evaporation is neglected. Therefore, ordinary differential equations can be established to describe the transport of droplets over the surface microfluid as follows [43]:

$$\frac{16\gamma L H_1}{D_1^2 + 4H_1^2} - \frac{16\gamma L H_2}{D_2^2 + 4H_2^2} = \frac{\mu}{wh} \frac{\pi}{8} \left( \frac{4H_1^2 + D_1^2}{8} \right) \frac{dH_1}{dt}$$

$$\frac{16\gamma L H_2}{D_2^2 + 4H_2^2} = \frac{\mu}{wh} \frac{\pi}{8} \left( \frac{4H_2^2 + D_2^2}{8} \right) \frac{dH_2}{dt}$$  \hspace{1cm} (3)

where $H_1$ and $H_2$ are the height of the two circular grooves.

The Laplace pressure difference $\Delta P$ between the two circular grooves drives the droplet movement at a volumetric flow rate $Q$, which is the rate of change of the large circular groove volume ($Q = \Delta V / dt$). The large circular groove droplet volume can be calculated from the spherical crown volume equation, where $H$ is the droplet height and $D$ is the droplet bottom diameter, which can be calculated from the following equation.
be used for high-throughput, high-efficiency drug screening. This patterned surface with a multi-branch shunt process can and saturation was reached when four droplets were added. per droplet, and the droplets spread rapidly in all directions, the droplets added to the central small circular slot was 11.02 large circular grooves with a diameter of 3 mm. The volume of lar groove has a diameter of 2 mm and is surrounded by four transport is illustrated in figure 13(a). To facilitate distinction, deionized water droplets were added simultaneously at both ends, with the droplets at one end left untreated and those at the other end stained with red ink. The droplets at both ends confluenced at the droplet, applications such as droplet split-flow and confluence can be achieved. Droplet confluence transport in a small circular groove (diameter: 2 mm) in the center and large circular grooves (diameter: 3 mm) at both ends is illustrated in figure 13(a). To facilitate distinction, deionized water droplets were added simultaneously at both ends, with the droplets at one end left untreated and those at the other end stained with red ink. The droplets at both ends confluenced at the central large circular groove after 25 s, and the intersection line inside the central large droplet could be clearly observed. This type of patterned surface can be used to study the mixing phenomenon of some chemical solutions. Droplet split-flow transport is illustrated in figure 13(b); the central small circular groove has a diameter of 2 mm and is surrounded by four large circular grooves with a diameter of 3 mm. The volume of droplets added to the central small circular slot was 11.02 µl per droplet, and the droplets spread rapidly in all directions, and saturation was reached when four droplets were added. This patterned surface with a multi-branch shunt process can be used for high-throughput, high-efficiency drug screening.

\[
\begin{align*}
V &= \frac{1}{3} \pi H^2 (3R - H) \\
(H - R)^2 + \left( \frac{D}{2} \right)^2 &= R^2
\end{align*}
\]  

By eliminating \( R \), we obtain the following equation:

\[
V = \left( \pi H/24 \right) \times (4H^2 + 3D^2).
\]  

The changes in the volume of droplets impacting the large circular groove and the change in the flow rate during the transport of droplets from the small circular groove to the large circular groove were calculated according to the formula (5), as illustrated in figure 12. The volume of droplets in the circular groove gradually increased with time, and the flow rate changed during the transport of droplets from the small circular groove to the large circular groove, presenting a trend of initial increase and subsequent decrease.

Based on the observation that the Laplace pressure difference can drive the droplet, applications such as droplet split-flow and confluence can be achieved. Droplet confluence transport from a two-phase flow system (small and large circular grooves) can be used to study the mixing phenomenon of some chemical solutions. Droplet split-flow transport is illustrated in figure 13(b); the central small circular groove has a diameter of 2 mm and is surrounded by four large circular grooves with a diameter of 3 mm. The volume of droplets added to the central small circular slot was 11.02 µl per droplet, and the droplets spread rapidly in all directions, and saturation was reached when four droplets were added. This patterned surface with a multi-branch shunt process can be used for high-throughput, high-efficiency drug screening.

3.3.2. Directional and gravity-resistant transport of droplets driven by temperature gradients. A surface tension gradient is generated between droplet and contact surface due to temperature gradient, and the droplet migrates from the region with lower surface tension to the region with higher surface tension [33]. As droplets presented a CCA evaporation mode on the S-phobic surface, generally, it is not favorable for the thermal capillary drive of droplets, so the ordinary hydrophilic aluminum plate with the size of 50 mm × 40 mm × 2 mm is used as the transport platform. A high-speed camera is used to record the directional transport of droplets driven by the temperature gradient. The inclination angle of hydrophilic aluminum plate on the condensing table can be adjusted by a lifting device (experimental setup is shown in figure 14(a)). The temperatures of the heating and condensing sides were set to 300 °C and 5 °C, respectively, meaning the temperature gradient was 5.9 °C mm⁻¹. Deionized water and anhydrous ethanol, both with a volume of 11 µl, and kerosene with a volume of 22 µl, were added onto the transport platform. The viscosities of deionized water, anhydrous ethanol and kerosene at room temperature are 0.8904 × 10⁻³ Pa s, 1.103 × 10⁻³ Pa s and 2.21 × 10⁻³ Pa s, respectively.

The experimental results show that the temperature gradient can not only drive deionized water but also a low viscosity organic liquid such as anhydrous ethanol, and a higher viscosity organic liquid such as kerosene, as shown in figure 14(b). When a droplet contacted with a solid surface of higher temperature, it will form a vapor layer under the droplet, which reduces friction during droplet transport. At the same time the droplets are affected by the temperature gradient to create a surface tension gradient, which can drive droplets to migrate from regions with lower surface tension to regions with higher surface tension. We also observed that droplet transport distance increased gradually with time, and contact angle also showed a trend of gradually decreasing during the transport process. When the temperature gradient decreases from 5.9 °C mm⁻¹ to 4.9 °C mm⁻¹, the migration rate of deionized water, anhydrous ethanol and kerosene were all decreased, as shown in figure 14(c). We inclined the substrate at a certain angle during the experiment so that the height of the...
condensing side was greater than that of the high temperature side and analyzed the anti-gravity transport of droplets under the effect of temperature gradient. Droplets were added using a syringe at the high temperature side, and due to the existence of temperature gradient, the contact angles of droplets at the high temperature regions and the low temperature regions are different, and the surface tension generated at the low temperature part is larger, so the droplets not only will not roll off from the hydrophilic Al surface, but also can achieve gravity-resistant transport from the high temperature regions to the low temperature regions. But the droplet will roll off the hydrophilic Al surface if there is no temperature gradient, so all three droplets were able to achieve gravity-resistant transport over a short distance from the high-temperature side to condensing side at a temperature gradient of 5.9 °C mm\(^{-1}\), and the maximum transport inclination is 3° through a large number of experiments (figure 14(d)). This transport method can be applied to robust rectifiers and cooling equipment that allow for sustainable and continuous condensation even at high supersaturation condition, and it is also required in thermal...
capillary heat pipes where a rapid and continuous supply of liquid from the condenser to the evaporator.

4. Conclusion

In summary, we developed a facile and industrially applicable method for preparing Al S-phobic surfaces, which enables controlled droplet bouncing, evaporation, and transport over a wide temperature range. Extreme wettability surfaces were prepared on Al surfaces by a composite process of electrochemical mask etching and micro-milling, and the Al S-phobic surface had a water contact angle of 152 ± 2°. S-phobic-hydrophilic wettability difference patterned surfaces can be prepared on Al S-phobic surfaces by micro-milling. The thermal coupling characteristics, evaporation process and mechanism of droplet on extreme wettability surfaces at different temperatures was also studied by experiments and simulations. Results indicated that droplets presented a CCA evaporation mode on the S-phobic surface and a CCR evaporation mode on the hydrophilic surface. The evaporation rate of droplets on S-phobic surfaces was lower than that of droplets on hydrophilic surfaces. Controlled evaporation of droplets on hydrophilic micropit dot matrix and circular groove patterns can be achieved by controlling the geometry of hydrophilic patterns. Droplets bounce directionally towards hydrophilic or S-philic surfaces at room temperature, and controlled substrate wettability difference and contact area ratio between droplets and hydrophilic surfaces enabled controlled bouncing. Droplets migrate to the S-philic region when the substrate temperature is lower than 200 °C, and the droplets move to the S-philic region when the temperature is higher than 200 °C. Controlled transport of droplets over a wide temperature range with confluence and split-flow by using Laplace pressure gradients on extremely wettable surfaces was realized. Temperature gradient drive can be used to realize directional and gravity-resistant transport of deionized water, anhydrous ethanol and kerosene with different viscosities, and the droplet migration velocity increases with the temperature gradient. This research has potential applications in the fields of microfluidic systems, biomedicine, and energy harvesting.

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Conflict of interest

The authors declare there is no conflict of interest.

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