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Topography-Directed Hot-Water Super-Repellent Surfaces

Pingan Zhu, Rifei Chen, and Liqiu Wang*

Natural and artificial super-repellent surfaces are frequently textured with pillar-based discrete structures rather than hole-based continuous ones because the former exhibits lower adhesion from the reduced length of the three-phase contact line. Counterintuitively, here, the unusual topographic effects are discovered on hot-water super-repellency where the continuous microcavity surface outperforms the discrete microneedle/micropillar surface. This anomaly arises from the different dependencies of liquid-repellency stability on the surface structure and water temperature in the two topographies. The unexpected wetting dynamics are interpreted by determining timescales for droplet evaporation, vapor condensation, and droplet bouncing. The associated heat transfer process is unique to the wetting states and remarkably distinct from each other in the two topographies. It is envisioned that hot-water super-repellent microcavity surfaces will be advantageous for a variety of applications, especially when both self-cleaning and thermal insulation are imperative, such as clothing for scald protection and digital microfluidics for exothermic reactions.

Repelling hot liquids is relevant to many industrial processes, including heat exchangers,[1] fuel-spray impingent,[2] water desalination,[3] and additive manufacturing,[4] as well as to our daily life, such as for scalding protection clothes[5] and anti-fouling kitchenware. In these situations, the heat transfer between hot liquids and cold surfaces is affected by the solid–liquid interaction,[6] which in turn influences the system performance. For example, the heat transfer efficiency determines the vapor flux of distillation in water harvesting;[3] protective clothes require thermal insulation between hot liquids and human bodies to avoid scalding. Despite its importance, the effort to study the mechanisms of super-repellency to hot liquids appears very limited.

In contrast to room-temperature water, hot water complicates the dynamics of liquid wetting and heat transfer with phase change processes, including the evaporation of hot water droplets and condensation of vapor on cold surfaces. Previous studies have mainly been focused on the fabrication of hot-water super-repellent surfaces, such as by spray coating, deposition, and electrophoresis-assisted coating, and their applications for self-cleaning and oil/water separation.[7–15] whereas only a few studies have reported on wetting mechanisms by hot water.[16,17] More recently, it was unveiled that hot-water droplet bouncing is dramatically affected by the size of surface structure:[18] both nanometric (=100 nm) and microscale (=10 µm) features are favorable to hot-water repellency, while the structure with a dimension in between (=1 µm) fails at repelling hot water. A cold solid surface can lose the repellency to hot water[5,16] by three mechanisms: reduced surface tension of hot water,[19] destruction of surface structures by elevated temperatures (for example, plant leaves with wax coatings[5,17]), and condensation of water vapor that forms liquid bridges connecting the hot water and surface asperities.[16] To maintain hot-water super-repellency, the surface design must overcome all three failure mechanisms. Among them, structure destruction can be easily circumvented by using materials with high melting points. Nevertheless, avoiding failure from the reduced surface tension of hot water and vapor condensation requires a comprehensive understanding of solid–liquid interactions involving temperature differences. Therefore, investigating the role of surface topography on hot-water wetting is crucial to the design of robust surfaces that are super-repellent to hot water.

Designs of hot-water super-repellent surfaces can be borrowed from superhydrophobic surfaces. Generally, a solid surface is physically roughed with reduced solid–liquid contact areas and chemically modified with low surface energy, on which water droplets are suspended in the well-known Cassie state[20] with entrapped air cushions. Surface topography affects the dynamics of liquid wetting. Most superhydrophobic surfaces are composed of discrete architectures with solid extrusions, such as pillars, needles, particles,[21] and those occurring on lotus leaves,[22] rather than continuous topologies with interconnected top surface structures including holes,[23,24] cages,[25] and those decorating the cuticles of springtails.[26] The reason for this trend may be that compared to continuous topographic
surfaces, discrete surfaces are lower in adhesion due to the reduced length of the three-phase contact line[27] and easier to fabricate using well-developed techniques such as etching and lithography. Considering that continuous and discrete structures are topologically complementary to each other (for example, holes and pillars), systematically comparing their performance on liquid wetting would deepen our fundamental understanding of hot-water repellency. As such, the present work aims to identify the difference between continuous and discrete surface topographies in repelling hot water by combining experimental studies with theoretical modeling.

Contrary to the common case in superhydrophobic surfaces, here we demonstrate that the continuous topographic microcavities, characterized by the re-entrant structure and higher breakthrough pressure, outperform the discrete topographic microneedles in repelling hot water for higher static contact angles, lower contact angle hysteresis, and easier droplet rebounding. We interpret their differences in wetting dynamics by the relative magnitudes of the timescales for hot-water droplet evaporation, vapor condensation, and contact between bouncing droplets and cold surfaces. It is found that heat transfer is related to the wetting states for the two surface topographies, where the entrapped air provides a more effective thermal insulating layer for nonwetted microcavities than wetted microneedles. The hot-water super-repellent microcavity surfaces would be useful in a range of applications, including scald-protection clothing requiring thermal insulation and high break-through pressure for microcavities in Figure 1A and microneedles in Figure 1C), as shown in Figure 1G. Unlike $P_n$, Equation (1) suggests that $P_c$ is invariant with $\theta_k$ provided that $\theta_k > 90^\circ$, less sensitive to variations in the solid fraction $f_s$ and converges to a nonzero positive value when $f_s \to 0$ (Figure 1G). At a given value of $\theta_k$, $P_c > P_n$ when $f_s$ is smaller than a certain threshold $f_{sc}$ (Figure 1G), arising from the re-entrant and interconnected microstructures of the microcavity surfaces, which leads to larger $\gamma_{cap}$ and $L_{unit}$. By equating $P_c$ and $P_n$, we find the critical $f_{sc}$

$$f_{sc} = \frac{\sqrt{3}}{\sqrt{3} + \pi \min^2 \left(\cos \theta_k, 0\right)}$$

depending solely on $\theta_k$ (Figure 1H). For $f_s < f_{sc}$, $P_c = \sqrt{\pi/3} \approx 0.355$. $P_c$ is always larger than $P_n$ at any $\theta_k$. This result is of practical interest because $f_s$ values are normally smaller than 0.1 for the purpose of high contact angles and low hysteresis. Therefore, the continuous microcavity topography would endow surfaces with more robust repellency than the discrete microneedle (pillar-based) topography.

The temperature of water droplets ($T_d$) affects the breakthrough pressure via influencing $\theta_k$ and $\gamma$. Here, we measure $\theta_k$ as the contact angle of droplets on nanoparticle coatings, which is larger than 90° for $T_d \leq T_d < 90$ °C (room temperature $T_d = 23$ °C, see Figure 1I). To compare $P_c$ with $P_n$, we derive the ratio of $P_c$ to $P_n$ when $\theta_k > 90^\circ$ (the ratio goes into infinity when $\theta_k \leq 90^\circ$ because of $P_n = 0$)

$$\frac{P_c}{P_n} = \frac{1}{\cos \theta_k \sqrt{\pi \left(1 - f_s\right)}}$$

As $\theta_k$ decreases with an increase in $T_d$, the ratio $P_c/P_n$ becomes larger at the higher water temperature $T_d$. Therefore, the hotter the water droplet is, the more robust the repellency becomes on microcavity surfaces than on microneedle surfaces.

$$P = \frac{4\sqrt{3}}{3} \frac{\gamma}{L f_s} \max(\sin \theta_k, 1)$$

in which $\theta_k$ is the equilibrium contact angle and $L$ is the side length of the hexagonal unit cell (Figure 1A,C).
As Equation (3) diverges when $\theta_E \rightarrow 90^\circ$ and $f_s \rightarrow 0$, we expect orders of magnitude enhancement in the stability of the Cassie state by microcavities (Figure S3, Supporting Information); for example, at $f_s = 0.05$ and $T_d = 90^\circ$C ($\theta_E = 99.7^\circ$), $P_c/P_n = 19.2$. Therefore, we expect that the continuous microcavity surface would surpass the discrete microneedle surface in super-repellency to hot water.

To compare the repellency of the microcavity and microneedle structures, we first investigated the static contact angles of hot-water droplets on two groups of microcavity and microneedle surfaces with $L = 80 \mu$m and $L = 25 \mu$m, respectively (Figure 2A–D). To isolate the effect of surface topography, we fabricated a micropillar surface with the same dimension ($L = 80 \mu$m and height $H = 80 \mu$m, see Figure 2E and Figure S4, Supporting Information) as that of the microcavity surface in Figure 2B and compared their repellency to hot-water droplets.

The contact angles $\theta^c$ and $\theta_s$ are measured after hot-water droplets cool down to ensure complete condensation. At room temperature ($T_0 = 23^\circ$C), all surfaces are superhydrophobic with [[$\theta^c = 164.5^\circ$, $\theta_s = 2.3^\circ$], [[$\theta^c = 153.0^\circ$, $\theta_s = 2.5^\circ$], [[$\theta^c = 167.4^\circ$, $\theta_s = 1.9^\circ$], [[$\theta^c = 161.6^\circ$, $\theta_s = 2.3^\circ$], and [[$\theta^c = 155.4^\circ$, $\theta_s = 5^\circ$] for structures shown in Figure 2A–E, respectively. Compared to the microcavity surfaces, the higher $\theta^c$ and lower $\theta_s$ values of the microneedle surfaces are attributed to their lower solid fraction $f_s$ and shorter three-phase contact line. As the droplet temperature $T_d$ increases, $\theta^c$ decreases dramatically on the microneedles and micropillars and is eventually smaller than that on the microcavities for both $L$ values (Figure 2F). Moreover, the microcavity surfaces display lower $\theta_s$ values than the microneedles and micropillars with the same $L$ (Figure 2G) for hot droplets. These observations suggest that microcavities outperform the microneedles and micropillars in repelling hot water.
The dimension of the microstructure influences hot-water repellency. Providing larger voids for vapor condensation, larger \( (L = 80 \, \mu m) \) and higher \( (H = 80 \, \mu m) \) structures display higher \( \theta^* \) and lower \( \theta_s \) values than smaller ones \( (L = 25 \, \mu m) \) for hot water (Figure 2F,G). Among all tested surfaces, only the microcavity and micropillar surfaces with \( L = 80 \, \mu m \) and \( H = 80 \, \mu m \) are slippery at all temperatures (up to 90 °C), while the other surfaces become too sticky to allow droplets to roll down when the water temperature is above a certain threshold (Figure 2G, 40 °C for the two microneedles and 70 °C for microcavities with \( L = 25 \, \mu m \)). For structures with the same dimension \( (L = 80 \, \mu m \) and \( H = 80 \, \mu m) \), the microcavity surface outperforms the micropillar surface by displaying a nearly constant \( \theta^* \) (≈150°) and a smaller \( \theta_s \), as the Cassie state of hot-water droplets are more stable with a higher breakthrough pressure on the microcavity surface than on the micropillar surface, as shown in Equation (3).

The microscopic condensation explains the observed difference in hot-water repellency on different surfaces. A hot water droplet sitting atop the cold surface evaporates, which provides vapor for the condensation of microdroplets at the lower voids between microstructures. Microdroplets grow...
in their sizes (with a characteristic timescale $t_c$ for growing into a size comparable to that of microstructures) until the upper hot-water droplet cools down to room temperature by evaporation (with a characteristic timescale $t_e$). The growing microdroplets may have a chance to form liquid bridges that connect the top hot-water droplet when $t_e > t_c$ in the wetting state (Figure 3A) or evaporate to disappear before contacting the top water droplet when $t_e < t_c$ in the nonwetting state (Figure 3B).

The evaporation time scales as $t_e \sim (T_0 - T_d)/(dT/dt)$, where $dT/dt$ is the rate of temperature change in the evaporating hot droplet. If heat transfer between the droplet and the air by convection and conduction is neglected, then the energy balance equation takes the following form

$$\rho_d V_d C_p \frac{dT}{dt} = -\dot{m} \Delta H_{vap}$$

where $T$, $\rho_d$, $V_d$, and $C_p$ are the temperature, density, volume, and constant pressure heat capacity of the droplet, respectively, $\dot{m}$ is the evaporation rate, and $\Delta H_{vap}$ is the enthalpy of vaporization. The evaporation rate can be derived from vapor diffusion

$$\dot{m} = 4\pi R_d D_v \rho_a \frac{P_a - P_{sat}}{P_0} \frac{M_v}{M_a}$$

indicating $R_d$ as the droplet radius, $D_v$ as the diffusion coefficient of water vapor in air, $\rho_a$ as the density of air, $P_0$ as the atmospheric pressure, $P_{sat}$ and $P_a$ as the saturation vapor pressure at the temperature of the droplet surface ($T_d$) and of the air ($T_0$), respectively, and $M_v$ and $M_a$ as the molecular weight of water vapor and of air, respectively. With the assumption of $V_d = 4\pi R_d^3/3$, the timescale $t_e$ is then expressed as

$$t_e = \frac{1}{3} \frac{R_d^3}{D_v} \frac{\rho_a C_p (T_d - T_0)}{\rho_d \Delta H_{vap}} \frac{P_0}{P_{sat} - P_0} \frac{M_v}{M_a}$$

Using Equation (6), we calculate $t_e \sim O(10) s$ for the evaporative cooling of millimeter-sized water droplets (Figure 3C) when $T_d$ ranges from $T_0$ to 100 °C and all values of material
properties are chosen at \( T_d \) (Section S2 and Figure S5 in the Supporting Information).

The condensation timescale \( t_c \) can be defined as \( t_c \sim H/(dr/dt) \), where \( H \) is the height of microstructures (or equivalently the height of voids between microstructures) and \( dr/dt \) is the growth rate of microdroplets with radius \( r \). Because the saturation timescale, \( t_s \sim L^2/D_v \sim O(10^{-4}) \) s, is much shorter than \( t_c \sim O(10) \) s, we can assume saturated vapor in microvoids during droplet cooling. The heat transfer rate through a microdroplet \( (q_d) \) compensates for the enthalpy change rate of newly condensed vapor, leading to the following formula

\[
q_d = \rho_d \Delta H_{\text{vap}} \frac{dV}{dt} \tag{7}
\]

where \( dV/dt = 2\pi r^2(1 - \cos \theta_d)dr/dt \) is the volume growth rate of microdroplets. To estimate \( q_d \) we adopt a heat transfer model that accounts for the total thermal resistance arising from the liquid–vapor interface, droplet conduction, and curvature of the microdroplet \( ^{33–35} \)

\[
q_d = \frac{\pi r^2(T_{\text{sat}} - T_c)(1 - r_{\text{min}}/r)}{2h_c(1 - \cos \theta_d) + 4k_i \sin \theta_i} \tag{8}
\]

where \( r_{\text{min}} = 2d^2 \rho_d \Delta H_{\text{vap}}(T_{\text{sat}} - T_c) \), \( T_{\text{sat}} = (T_d + T_0)/2 \) is the vapor saturation temperature, \( T_c \) is the temperature of solid structures with the assumption of \( T_c = T_0 \) for simplicity, \( k_i \) is the thermal conductivity of the microdroplet, and \( h_i \) is the interfacial heat transfer coefficient. Combining Equations (7) and (8) and choosing \( r = H \), we have

\[
t_c \sim \frac{H^2 \rho_d \Delta H_{\text{vap}}}{(T_{\text{sat}} - T_0)(H - r_{\text{min}})} \left( \frac{1}{h_i} + \frac{H \theta_d (1 - \cos \theta_d)}{2k_i \sin \theta_i} \right) \tag{9}
\]

which ranges from \( O(10^1) \) s to \( O(10^3) \) s when \( T_d \) increases from \( T_0 \) to 100 °C for \( H = 100 \mu m \), as shown in Figure 3D (see Section S2 in the Supporting Information for materials properties). Since \( t_c \) increases with \( H \) (Figure 3D), a smaller structure will have a shorter characteristic condensation time, on which wetting is easier to achieve by satisfying the condition of \( t_c < t_e \).

Therefore, surfaces with smaller structures are more susceptible to wetting by hot-water droplets than those with larger structures, consistent with our observations in Figure 2.

Figure 3E contrasts \( t_w \) with \( t_c \) for \( H = 100 \mu m \) and millimeter-sized water droplets, similar to the case (Figure 2A,B, \( L = 80 \mu m \)) we investigate in the present study (see Figure S6 in the Supporting Information for the comparison with other \( H \) values). The value of \( t_w \) is comparable with \( t_c \) in the transitional temperature range of 30 °C < \( T_d \) < 40 °C (depending on the droplet size), below which \( t_c < t_w \) indicates nonwetting and above which \( t_c > t_w \) suggests wetting. This prediction agrees well with our observations for the microneedle surfaces, on which hot droplets firmly stick due to full wetting when \( T_d \geq 40 °C \) (Figure 2G). For microwater surfaces, the presence of the top continuous structures may provide physical barriers for preventing the coalescence between the hot droplets and microdroplets, thereby retaining the nonwetting state even when \( T_d \geq 40 °C \). We observed partial wetting (Figure 3F, some of the voids between the microneedles are wetted) and total wetting (Figure 3G, all voids underneath the hot-water droplet are wetted) of microneedle surfaces by 40 °C and 90 °C droplets, respectively. In contrast, dewetting due to the evaporation of microdroplets takes place on microcavities (fully dewetting at 40 °C in Figure 3H and partially dewetting at 90 °C in Figure 3I). After the removal of water droplets, large water residuals are left on the microneedles, while no (40 °C) or only a few (90 °C) residuals are left on microwater, highlighting the significant difference in the wetting state between the two surface topographies.

When a hot-water droplet impinges a superhydrophobic surface, there is a chance that the droplet bounces off the surface without wetting if the condensation microdroplets are not large enough to form liquid bridges during the contact period of the hot droplet with the solid surface. We observed the bouncing of hot-water droplets on both microneedles (Figure 4A) and microcavities (Figure 4B). On the microneedle surface, only droplets with \( T_d \leq 50 °C \) rebound fully from the surface, but those with higher temperature \( (T_d \geq 60 °C) \) rebound partially, leaving behind some water residuals sticking on the surface due to wetting (the size of the sticking residual increases as \( T_d \) increases). In comparison, all droplets with \( T_0 \leq T_d \leq 90 °C \) can bounce off the microcavity surface fully without wetting (Figure 4A,B and Figure S7, Supporting Information).

The contact time \( t_d \) of a bouncing droplet scales as the inertia-capillary timescale, \( t_d = (\rho_d R_d^3)/\gamma^2 \)

\[
t_d = C \left( \frac{\rho_d R_d^3}{\gamma} \right)^{1/2} \tag{10}
\]

where \( C \) is the prefactor.\(^{36}\) Fitting of experimental data gives \( C = 3.1 \) for room-temperature droplets bouncing off the microneedle and microcavity surfaces when the Weber number \( We \simeq 19 \) where \( We = 2\rho_d U^2 R_d/\gamma \) with \( U \) being the velocity of the droplet at impact (Figure 4C). For a millimeter-sized water droplet with \( T_0 \leq T_d \leq 90 °C \), \( t_b \) is on the order of \( O(10^{-3}) \) s (Figure 4A,B and Figure S8). We find that the prefactor \( C \) is constant \( (C = 2.77) \) for hot-water droplets impinging on the microcavity surface but increases when \( T_d \geq 60 °C \) on the microneedle surface (Figure 4D), consistent with the bouncing dynamics documented in Figure 4A,B. The restitution coefficient, defined as \( e = H_e/H_0 \) (\( H_e \) and \( H_0 \) represent the maximum height of the rebounding droplets and the initial release height of droplets, respectively), is used to quantify the loss of droplet momentum after bouncing. The value of \( e \) basically remains constant for the microcavity surface but undergoes a sharp decrease at \( T_d = 60 °C \) on the microneedle surface (Figure 4E) as a result of surface wetting.

For hot impinging droplets, the competition between \( t_d \) and \( t_c \) determines the wetting state, i.e., \( t_d > t_c \) for wetting, whereas \( t_d < t_c \) for nonwetting. Experiments indicate that \( t_d \sim O(10^{-3}) \) s (see Figure 4A,B), much smaller than \( t_c \sim O(10^3) \) s (Figure 3E, \( H = 100 \mu m \)) for microneedles and microcavities, which predicts the non-wetting of both surfaces during droplet impingement. Nevertheless, the prediction is violated by the impingement of droplets with \( T_d \geq 60 °C \) on the microneedle surface. Microscopic observation reveals quite fast wetting (within 4 ms) on the microneedle surface for 70 °C droplets (Figure 5A); in contrast, no wetting was observed on the
microcavity surface under the same conditions (Figure 5B).
As such, a train of hot-water droplets sticks on an inclined microcavity surface (Figure 5C), whereas each droplet can shed away the inclined microcavity surface (Figure 5D).

The ultrafast wetting of the microneedle surface is attributed to its low breakthrough pressure. When a droplet impinges on a solid surface, an effective water hammer pressure ($P_{\text{ewh}} \sim \rho d U_c$, with $c$ being the velocity of sound in water) and a dynamic pressure ($P_d = \rho d U^2/2$) compete with the breakthrough pressure for the wetting transition during the initial contact and latter spreading stages, respectively. The lower breakthrough pressure of microneedles makes them more prone to wetting than microcavities. In this case, the condensation time is estimated to be $t_c \sim \frac{H_{\text{eff}}}{d \frac{d}{dt}}$ for the microneedle surface, with the effective height $H_{\text{eff}}$ ranging between 100 µm and 50 nm (the roughness of nanoparticle coatings, see Figure 1F). Using $H_{\text{eff}}$, $t_c$ is reduced by several orders of magnitude (exemplified by $H = 50$ nm, Figure 3D), $t_c < O(10^{-8})$ s $< t_d \sim O(10^{-3})$ s, which predicts the wetting on the microneedle surface.

The difference in the repellency to hot-water droplets on microneedle and microcavity surfaces renders the heat transfer process distinct from each other. Compared to the microneedle surface, the heat flux from the hot-water droplet to the glass substrate ($q_{ls}$) is expected to be lower on the microcavity surface because of the entrapped air that performs as a thermal insulation layer with a larger thermal resistance (Figure 6A). Therefore, the microcavity-coated substrate would have a smaller temperature ($T_{\text{bott}}$), as observed in Figure 6B. Upon the deposit of hot-water droplets, $T_{\text{bott}}$ undergoes a sharp rise and peaks within several seconds, followed by a gradual decrease to a level lower than the room temperature $T_0$ (inset in Figure 6B), which is attributed to droplet evaporation.

We adopted a lumped capacitance model[39] to describe the transient heat transfer of substrate cooling

$$\frac{T_{\text{bott}}(t) - T_{\text{min}}}{T_{\text{max}} - T_{\text{min}}} = \exp \left\{ - \frac{h_{\text{eff}}}{\rho_s z_s C_s} \right\}$$  \hspace{1cm} (11)

where $T_{\text{min}}$ and $T_{\text{max}}$ are the minima and maxima of the substrate temperature, respectively, $h_{\text{eff}}$ is the effective heat transfer coefficient, and $\rho_s$, $z_s$, and $C_s$ are the density, height, and heat capacity of the substrate, respectively. We obtained
the exponent of \((-h_{\text{eff}}/\rho_s z_s C_s)\) by fitting the experimental data (Figure S9, Supporting Information) and calculated \(h_{\text{eff}}\) with known values of \(\rho_s\), \(z_s\), and \(C_s\), as shown in Figure 6C. Using \(h_{\text{eff}}\), we determined the Biot number \(\text{Bi} = h_{\text{eff}} z_s / k_s \approx 0.1\) (Figure 6C) with \(k_s\) being the thermal conductivity of glass, indicating that it is reasonable to assume a uniform temperature distribution within the glass substrate in the lumped capacitance model.

The \(h_{\text{eff}}\) reflects the cooling rate of the substrate; a larger \(h_{\text{eff}}\) represents a faster cooling down rate. The cooling rate is determined by and increases with the heat flux difference \((q_{sa}'' - q_{ls}''\)) where \(q_{sa}''\) is the heat flux from the substrate to the air. As \(q_{sa}''\) is lower through microcavities than through microneedles due to air-layer insulation, we conjecture that \(h_{\text{eff}}\) would be larger for the substrate coated with the microcavity surface than with the microneedle surface, which agrees well with experiments (Figure 6C). When the droplet temperature is higher, more vapor condensation takes place in microcavities such that the insulation of the air layer becomes weaker, reducing the difference in \(h_{\text{eff}}\) between the substrates coated by the two surfaces. From linear fitting, the \(h_{\text{eff}}\) of the two surfaces intersects at \(T_d \approx 98.1\) °C, where the air layer vanishes and the microcavity surface is fully wetted by condensation, behaving exactly the same as the microneedle surface. The intersection method may be useful in predicting the critical droplet temperature at which a surface entirely loses the liquid repellency.

We further investigated the temperature at the top of the two surfaces, \(T_{\text{top}}\) (Figure 6A). Compared to discrete microneedles, continuous microcavities are more favorable to heat diffusing radially outward away from the center of the hot droplets along the top surface due to the interconnectivity of the solid structures. The enhanced lateral thermal diffusion explains the observed higher maxima of \(T_{\text{top}}\) on the microcavity surface than on the microneedle surface (Figure 6D).

As one potential application, we performed exothermic reactions using neutralization between HCl and NaOH as a model system on the two surface topographies. Litmus was added into the HCl aqueous droplet to visualize the reaction (Figure 7A,B). The contact angle of the HCl droplet decreases slightly by 5.7° (from 137.8° to 132.1°, Figure 7B) after the addition of NaOH for the reaction on the microcavity surface, in stark contrast to the large decrease of 23.1° (from 133.1° to 111.8°, Figure 7A) on the microneedle surface. Once neutralization begins, numerous bubbles appear at the bottom of microneedles and then slowly disappear (Figure 7C). In contrast, bubbles only occur at the top layer of microcavities with much smaller sizes (too small to be visible by naked eyes without magnification, Figure 7D). The microbubbles arise from the expansion of nanoscale voids (Figure 1F) heated by the exothermic reaction. The collapse of bubbles may induce surface wetting that accounts for the decreased contact angles after the reaction. Compared to the microneedle surface, wetting is less detrimental to the microcavity surface because it is limited to the top layer. We observed the sliding down of droplets along the tilted microcavity surface after the reaction between 4 mM HCl and 4 mM NaOH, indicating the slippery state.
Thermography allowed us to reveal the difference in the evolution of the temperature field after the reaction on the two surfaces (Figure 7E). The droplet is a heat source with a higher temperature than the surroundings (Figure 7E,F). Compared with the droplet on the microneedle surface, the droplet on the microcavity surface is always higher in temperature and cools down at a lower rate (Figure 7G). Moreover, the surrounding temperature gradually increases for the microcavity surface, while it quickly decreases after an initial increase for the microneedle surface (Figure 7H). Such differences are highly related to the wetting state of the surface. The observations are consistent with the heat transfer analysis in Figure 6. The non-wetting of the microcavity surface provides a thermal insulating layer of air between the droplet and the substrate, by which the droplet cools down more slowly and the microcavity surface is gradually heated due to the lateral thermal diffusion. However, the wetting of the microcavity surface transfers most of the heat from the droplet to the substrate, which induces a more rapid cooling down of the droplet and the surroundings.

Indeed, the distinct heat transfer characteristics of the super-repellent microcavity surface would be very useful in the application of self-cleaning and protective coatings to prevent the coated objects from simultaneous fouling and thermal damage. For example, the surface can be used in digital microfluidics for performing exothermic reactions and manipulating droplets with varied temperatures in chemical and biological assays; it can also be used in the fabrication of protective clothing for thermal isolation when hot water contacts clothes.

In summary, we identify that the continuous microcavity surface displays more robust super-repellency to hot water than the discrete microneedle surface. The former distinguishes from the latter by the way in which the breakthrough pressure depends on the solid fraction and water temperature. Our theoretical model shows that a smaller solid fraction and higher water temperature leads to more robustness in the stability of liquid repellency on microcavity surfaces. Topographically, the interconnected solid structures provide physical barriers that segregate the microcavity surface into top and bottom layers, on which the dynamics of wetting and heat transfer are almost independent of each other. Therefore, most wetting events are confined to the top layer that is in direct contact with the hot water, while the bottom layer is nonwetted to maintain super-repellency for the microcavity surface. In contrast, the microneedle structures are less robust in shielding the bottom surface from hot water due to the lack of physical barriers and are thereby more susceptible to wetting.
We utilized droplet microfluidics to fabricate microcavities and microneedles with the same dimension, both of which are coated with silanized silica nanoparticles for superhydrophobicity at room temperature. The microcavity surface displays super-repellency to water droplets at elevated temperatures, exhibiting higher apparent contact angles and lower adhesion than the microneedle surface; dynamically, hot-water droplets totally bounce off the microcavity surface at all tested temperatures (up to 90 °C), whereas sticking droplets only partially rebound from the microneedle surface when the temperature of the water droplets is higher than 50 °C. We developed theoretical models to estimate the characteristic timescales for droplet evaporation, vapor condensation, and droplet bouncing, which elucidate the observed differences in wetting dynamics between the two surface topographies. The hot-water super-repellency endows the microcavity surface with a distinct heat transfer process where the entrapped air cushion imposes a thermal insulating layer between the hot droplet and substrate. The microcavity surface retains the nonwetting state after performing the neutralization reaction. We expect that the microcavity topography will open new avenues for applications of super-repellency coupled with heat transfer. For example,
microwavable surfaces can be used as coatings for self-cleaning and thermal insulation.

**Experimental Section**

**Fabrication of Microwavable, Microneedle, and Micropillar Surfaces:**

The fabrication of microwavable surfaces was described in detail in the previous studies\cite{21,22,28} and involves four stages: emulsion generation, emulsion dispersion, solvent evaporation, and template removal. First, monodisperse emulsions are produced in a capillary microfluidic device, where silicone oil (20 cSt; Aldrich) droplets (with 2 wt% Dow Corning 749 Fluid as the surfactant) were dispersed in a poly(vinyl alcohol) (PVA, Mw 13 000–23 000, 87–89% hydrolyzed; Aldrich) aqueous solution. Then the emulsion was deposited onto a glass substrate, after which the silicone oil droplets self-assembled into ordered hexagonal arrays while the PVA solution evaporates at room temperature.\cite{28} The evaporation of water solidifies the PVA membrane, which wraps the silicone oil droplet arrays. Finally, the PVA membrane was immersed in toluene (99.8%; Sigma-Aldrich) for 1 h to wash out the silicone oil droplets, followed by drying the membrane in a vented hood. Eliminating the silicone oil droplets produces microwavable surfaces of the same size. To prevent the PVA surface from dissolving into water, PVA was crosslinked with glutaraldehyde (50 wt% in water; Sigma-Aldrich). A detailed description of the type and dimension of microstructures is included in the previous study.\cite{28}

The microwavable surface was fabricated by peeling off the top layer of the microwavable surface using adhesive tape. This ensures the fabrication of microwavable and microneedle surfaces with the same dimension for comparison.

The height $H$ of the microfluidically fabricated microcavity structure is related to its unit length $L$ in the form of $H = \pi L/3 \approx L$, as reported in the previous work.\cite{22} Silicon micropillar arrays were fabricated with $L = 80 \, \mu m$ and $H = 80 \, \mu m$ by etching. First, a layer of aluminum was deposited on the silicon wafer by e-beam evaporation (TF500, HHV), on top of which a layer of photoresist (AZ MIR 701, MicroChemicals) was coated and then exposed with direct laser writing (DWL 66+, Heidelberg Instruments). After developing, the exposed aluminum was removed by an inductively coupled plasma (ICP, GSE200, NAURA) with Cl$_2$ and BCl$_3$. Finally, silicon was etched by the ICP with O$_2$ and SF$_6$ for the production of micropillars with predefined heights.

To obtain superhydrophobicity at room temperature, all surfaces were coated with silanized silica nanoparticles (diameter $\approx 30$ nm) using commercialized Glaco (Soft99). After coating, the surfaces were baked at $80 \, ^{\circ}$C for 30 min.

**Visualizing the Wetting Dynamics:**

The macroscopic wetting dynamics of water droplets were visualized by a high-speed camera (Phantom M110) equipped with a camera lens (Sigma, 30 mm, f/1.4). The microscopic visualization of droplet wetting was performed using an inverted optical microscope (Nikon Eclipse TS100) equipped with a high-speed camera (Phantom M110). Recorded images and videos were analyzed using ImageJ software for the measurement of contact angles and sliding angles. In characterizing the wetting by static hot-water droplets, the images/videos were taken $\approx 1$ min after the deposition of droplets to allow them to cool down. 10 $\mu$L water droplets were used for the measurement of contact angles.

**Neutralization Reaction:**

To perform neutralization, an aqueous HCl droplet was first deposited on the test surface, followed by dripping an aqueous NaOH droplet. The coalescence of the two droplets initiated the neutralization reaction. The concentration of the acid and alkali solutions ranged from 2 to 6 M. To visualize the reaction, litmus was added to the HCl solution, which displays a red color; an increase in the pH value with the addition of NaOH for the reaction can change the color from red to blue. To enhance the visual contrast, the reaction between 4.2 $\mu$L 6 M HCl droplet and 5.8 $\mu$L 6 M NaOH droplet was used in Figure 7A-B. For other experiments, 5 $\mu$L HCl and 5 $\mu$L NaOH droplets were used, as those in Figure 7C–H. Neutralization was also performed using 2 and 4 M solutions, where the droplet rolls off both the microwavable and microneedle surfaces after the reaction between 2 M HCl and 2 M NaOH solutions and rolls off only the microwavable surface after the reaction between 4 M HCl and 4 M NaOH solutions.

**Characterization:**

The surface morphology was characterized by scanning electron microscopy (SEM, Hitachi S4800 and S3400N and Zeiss EVO MA10) and atomic force microscopy (Bruker MultiMode 8). The temperature of the glass substrate ($T_{\text{glass}}$) and test surfaces ($T_{\text{surf}}$) was automatically measured by thermocouples (K-type) using a data acquisition system (Keysight 34970A Data Acquisition/Switch Unit). The temperature field of the surfaces was measured by an infrared thermal imager (Fluke, TiS40) for the neutralization experiment.

**Supporting Information**

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

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

heat transfer, liquid repellency, structure–property relationship, wetting dynamics
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