Supporting Information for

Reentrant Cavities Enhance Resilience to the Cassie-to-Wenzel State Transition on Superhydrophobic Surfaces during Electrowetting

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1 DROPLET BASE AREA CALCULATIONS

The droplet base areas of the Cassie and the composite states are calculated using the droplet volume, contact angle, and microstructure dimensions: stem diameter (*d*), cap diameter (*D*), cap height (*h*), stem height (*H*) and microstructure pitch (*P*). The volume of a droplet, *V*, on a surface having a contact angle of θ and a footprint radius R_b is given by

$$V = \frac{\pi}{3} R_b^3 F \tag{1}$$

where $F = \frac{(2+\cos\theta)(1-\cos\theta)^2}{(1-\cos^2\theta)^{3/2}}$. The base radius of a droplet in the Cassie state, $R_{b,C}$, on a surface with cylindrical microposts, hence, can be expressed as $R_{b,C} = \sqrt[3]{\frac{3V}{\pi F}}$.

It is assumed that the contact angle of the droplet in the composite state is the same as that of a droplet in the Cassie state. We also assume that for a droplet in the composite state, the liquid-vapor (*l*-*v*) interface infiltrating a unit cell is a spherical interface which makes a contact angle with the micropost walls equal to Young's contact angle. This configuration is illustrated in Figure S1. The footprint of this three-dimensional interface shape in the unit cell is not circular, and hence, an equivalent base radius, R_e, is defined for the footprint of the liquid-vapor interface in a unit cell such that the base area of the actual interface is equal to the area of a circle of radius R_e:

$$\pi R_e^2 = P^2\left(1-f\right) \tag{2}$$

R_e is used to further calculate other values.

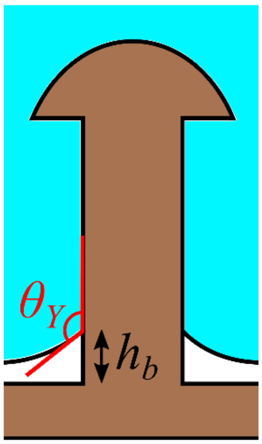

Figure S1 Illustration of the contact angle between the *l*-*v* interstitial interface and the micropost side walls and the height at which the interface touches the sidewalls.

The base area of a droplet in the composite state on cylindrical microposts is found by solving the following equation

$$V = A_{b,comp}{}^{3/2}\zeta(\theta) + A_{b,comp}\left((1-f)(H-h_b) + P(1-f)^{3/2}\zeta(\theta_Y)\right) \qquad (3)$$

where $\zeta(\theta) = \dfrac{V_{spherical,cap}}{A_{b,comp}{}^{3/2}} = \dfrac{(2+\xi(\theta))(\xi(\theta)-1)^{1/2}}{6\pi^{1/2}}$, $A_{b,comp}$ is the base area of the droplet in the composite state, and $\xi(\theta)$ is the ratio of the area of the spherical cap to the base area, $\xi(\theta) = \dfrac{2}{1+\cos\theta}$. $f = \dfrac{\pi d^2}{4P^2}$ is the solid fraction, and h_b is the height from the bottom surface at which the *l-v* interface touches the micropost wall (see Figure S1) which is calculated as $h_b = \dfrac{-R_e(1-\sin\theta_Y)}{\cos\theta_Y}$. θ_Y is Young's contact angle. The first term on the right-hand side of equation (3) is the volume of the spherical cap of the droplet and the second term is the volume of the liquid inside the interstices.

An analogous approach is employed for the mushroom structures with slight modifications owing to the different microstructure geometry. The base area of a droplet in the Cassie state on the mushroom structured surface is computed from

$$V = A_{b,C}{}^{3/2}\zeta(\theta) - A_{b,C}\frac{\pi h D^2}{24P^2}\left(3 + \frac{4h^2}{D^2}\right) \qquad (4)$$

$A_{b,C}$ is the base area of the droplet in the Cassie state. The first term on the right-hand side of equation (4) is the volume of the spherical cap of the droplet and the second term is the total volume of the caps of the mushroom structures underneath the droplet, which must be subtracted from the spherical cap volume. The base area of a droplet in the composite state on a mushroom structure is found by solving the following equation

$$V = A_{b,comp}{}^{3/2}\zeta(\theta) + A_{b,comp}\left(\beta(H-h_b) + P\beta^{3/2}\zeta(\theta_Y)\right) - A_{b,comp}\frac{\pi h D^2}{24P^2}\left(3 + \frac{4h^2}{D^2}\right) \qquad (5)$$

in which $A_{b,comp}$ is the base area of the droplet in the composite state and $\beta = \frac{P^2 - 0.25\pi d^2}{P^2}$. The first term on the right hand side of equation (5) is the volume of the spherical cap of the droplet above the microstructures, the second term is the volume of the liquid inside the interstices, and the third term is the total volume of the caps of the mushroom structures underneath the droplet.

2 INTERFACIAL AREAS OF A DROPLET IN THE COMPOSITE STATE ON A MUSHROOM STRUCTURE

Figure S2 is a schematic representation of the different components of the interfacial areas (A_{lv}, A_{sv} and A_{sl}) which are used to calculate the energy of a droplet sitting atop a mushroom structure in the composite state (equation (4) in the main article). The area labelled 1a, $A_{b,comp}\xi(\theta)$, is the *l-v* upper surface area of the droplet and 1b, $A_{b,comp}\beta\xi(\theta_Y)$, is the *l-v* interstitial area. The area 2a, $A_{b,comp}\frac{\pi d h_b}{P^2}$, is the *s-v* interfacial area on the stems and 2b, $A_{b,comp}\beta$, is that on the bottom solid surface. The areas 3a, $A_{b,comp} f$, and 3b, $A_{b,comp}\left(\alpha - \frac{\pi d h_b}{P^2}\right)$, are the *s-l* interfacial areas on the mushroom caps and on the stems underneath the mushroom caps.

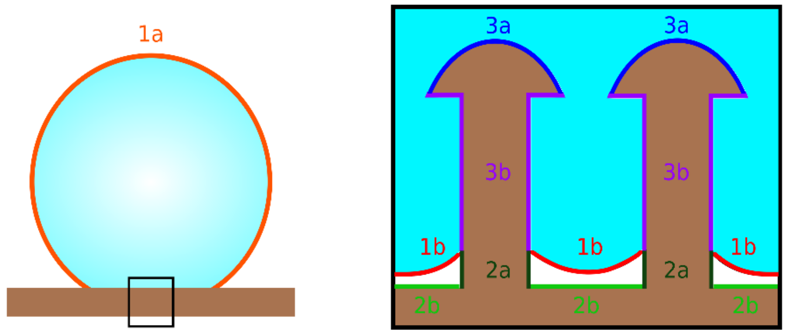

Figure S2 Components of the interfacial areas for a droplet in a composite state on a mushroom structure: 1a and 1b are the components of the *l*-*v* interface, 2a and 2b are those of the *s*-*v* interface, 3a and 3b are those of the *s*-*l* interface.

3 DETERMINATION OF WETTING STATES AND TRANSITION VOLTAGE

The measured contact angle as a function of the increasing voltage applied during electrowetting is shown for one example experimental case in Figure S3. The wetting state of the droplet (Cassie or Wenzel) during this electrowetting experiment can be judged by visual inspection and the contact angle measurement. When the droplet sits in the Cassie state, backlight is observed to pass between the microstructures under the droplet (illustrated in Figure S3 b). The transition from the Cassie to Wenzel states is marked by a sudden decrease in the contact angle with a small increment in the applied voltage (occurs at 99 V in Figure S3). Once the droplet is in the Wenzel state, light is no longer observed to pass beneath the droplet (illustrated in Figure S3 c).

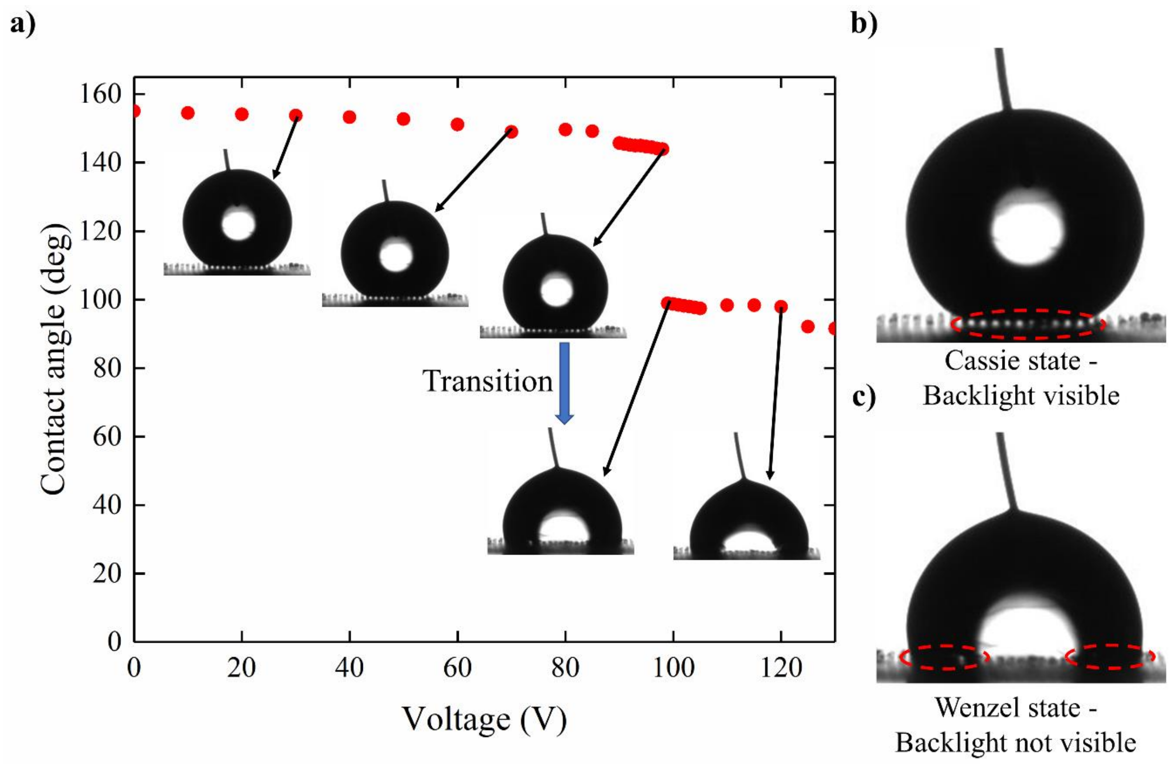

Figure S3 (a) Measured contact angle as electrowetting voltage is increased for a mushroom structured surface (d = 34.5 µm; D/d = 1.56), with inset side-view images of the droplet sitting on the microstructure. Magnified images of the droplet in the (b) Cassie state and (c) Wenzel state.

4 CONTACT ANGLE HYSTERESIS EXPERIMENTS

A 2 µl droplet of DI water is deposited on the surface using the automated dispensing system of the goniometer. With the needle of the dispensing system inserted into the droplet, DI water is injected in steps of 0.25 µl and the contact angle is measured at each step till the droplet contact line starts moving (at which point the contact angle measured is recorded to be the advancing contact angle). Water is then drawn out of the droplet in steps of 0.25 µl and the contact angle is measured till the droplet front starts receding (at which point the contact angle measured is recorded to be the receding contact angle). The difference between the advancing and the receding contact angles is the contact angle hysteresis (CAH). Contact angle measurements with increasing (advancing mode) and decreasing (receding mode) droplet volume are depicted in Figure S4. The CAH measurement plot shown is for cylindrical microposts with d = 45.5 μm, H = 30 μm and P = 30 μm. Three repeated CAH measurements are made for each fabricated surface. The advancing and receding contact angles and the contact angle hysteresis values are reported in the main article.

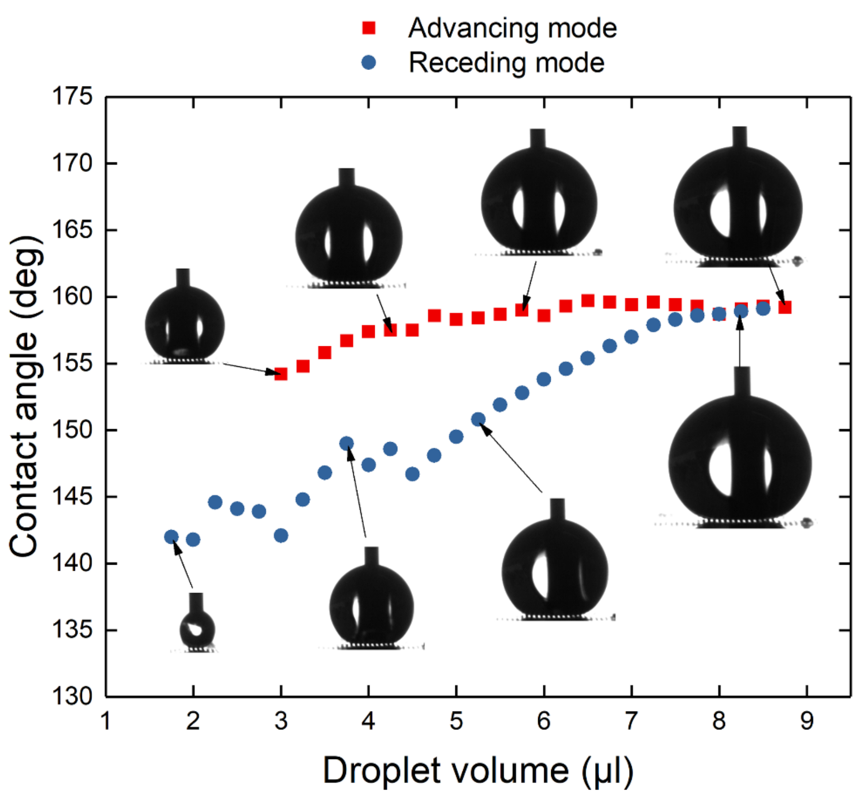

Figure S4 Contact angle changes during the contact angle hysteresis measurement. The advancing and the receding contact angles for this measurement are 159.7 deg and 141.8 deg, respectively and thus the contact angle hysteresis is 17.9 deg. The side-view images of the droplet are shown at selected volumes.