Supporting Information

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SI Materials and Methods

Fabrication of PDMS Pillars. The microstructures consisted of poly (dimethylsiloxane) (PDMS) pillars arranged in a square lattice on glass. The PDMS pillars were prepared by soft-molding of PDMS (Sylgard 184; Dow Corning) on SU-8 patterned templates that were hydrophobized with (1*H*,1*H*,2*H*,2*H*)-perfluorooctyl-trichlorosilane. PDMS was fluorescently labeled with *N*-(2,6-diisopropylphenyl)-3,4-perylenedicarboxylic acid monoimide (PMI) dye that was mixed with PDMS and the cross-linker (0.05 mg/mL). The blend was poured onto the template and covered with a coverslip (170 μm thick). The sample was heated up and kept at 90 °C for 4 h. Finally, the coverslip with the attached PDMS pillars was slowly removed from the template.

Fabrication of SU-8 Pillars. The pillar structures were made by photolithography using a SU-8 photoresist (Microchem). Glass slides with a thickness of 170 μm were cleaned with acetone in an ultrasound bath and dried in a vacuum oven (Heraeus) at 170 °C. The SU-8 2025 (or SU-8 2005) photoresist was first mixed with the hydrophobic PMI dye at a concentration of 0.05 mg/mL. Then the mixture was spin-coated on the glass slides. The substrates were then soft baked at 95 °C for 4 min and allowed to cool down slowly for 1 h. Then they were exposed to UV light (mercury lamp at 350 W) for 35 s (or 30 s) using a Karl-Suss mask aligner and baked at 95 °C for 4 min. The substrates were cooled down slowly for 12 h and finally developed with a SU-8 developer (Microchem) and rinsed with 2-propanol. To hydrolyze the surface of SU-8 and create OH groups, the surfaces were treated with 1 M HCl and 0.1 M NaOH overnight at room temperature. Finally, the surfaces were hydrophobized with (1*H*,1*H*,2*H*,2*H*)-perfluorooctyl-trichlorosilane by chemical vapor deposition. The thickness of the films was 23 μm, or 5 μm as verified by scanning electron microscopy and confocal microscopy.

Contact Angle Measurements. Contact angle measurements were performed with a contact angle meter (DataPhysics; OCA35). Static contact angles were measured depositing a liquid droplet of 6 μL on the surface. Dynamic contact angles (advancing and receding contact angles) were measured using a sessile droplet of 5 μL, with the needle in it, and then subsequently increasing and decreasing the liquid volume at a rate of 1 μL/s.

Interfacial Tension. Interfacial tension was measured following the Wilhelmy plate method, using a platinum plate, with a DCAT11 tensiometer (DataPhysics Instruments).

Scanning Electron Microscopy. The morphology of the substrates was characterized by scanning electron microscopy (SEM) with a LEO 1530 Gemini (Zeiss) at low operating voltages (0.5–1.4 kV). The samples were not modified before measurement.

Confocal Microscopy. A Leica TCS SP5 II–STED CW inverted confocal microscope with five detectors was used. The spectral ranges could be freely varied, allowing the measurement of the emission from different dyes and the reflected light from the interfaces simultaneously. Hydrophobic PMI dye was added to PDMS or SU-8. For water, various hydrophilic dyes were tested. Most dyes tend to adsorb at the water–PDMS or water–air interface, changing the interfacial tensions. Water-soluble *N*,*N*′-(2,6-diisopropylphenyl)-1,6,7,12-tetra(1-methylpyridinium-3-yloxy)-perylene-3,4,9,10-tetracarboxylic acid diimide tetramethane-sulfonate (WS-PDI) was the most hydrophilic dye. The high efficiency of WS-PDI in water arises from the diisopropylphenyl groups that hinder stacking and the high hydrophilicity of pyridinium salt. A concentration of 0.1 mg/mL is sufficient to image the dyed water drop by laser scanning confocal microscopy. At these concentrations, the dye hardly changes the surface tension γ of water. At a concentration of 0.1 mg/mL (0.06 mM) in water, the surface tension of the solution was 71 mN/m, only slightly lower than that of pure water, γ_{LV} = 72 mN/m (γ = 72 mN/m at 0.05 mg/mL and γ = 70 mN/m at 0.2 mg/mL). The emission maximum of PMI in PDMS is at λ_{PMI} = 525 nm and for WS-PDI in water at $\lambda_{WS\text{-}PDI}$ = 590 nm, i.e., well above that of PMI, so the overlap in fluorescence from dyed PDMS and water was minimal. To excite the dyes, two wavelengths were used: PMI was excited using the argon line at 488 nm; WS-PDI was excited using the 561-nm wavelength of a DPSS laser.

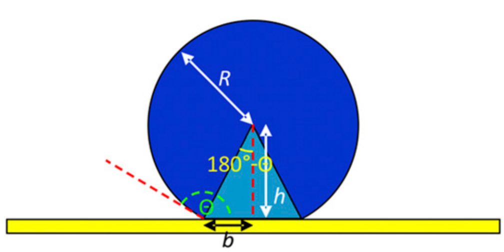

Fig. S1. Drop volume and radius. We assume that a drop on a superhydrophobic surface has the shape of a spherical cap. The volume of the drop is the sum of a spherical sector with the same water–air surface, and a cone having the water–substrate surface as base. The outer surface of the spherical sector is equal to its projection to a cylinder with radius *R* (Archimedes). Thus,

$$V_{sector} = \frac{R}{3}2\pi R(R+h), \quad V_{cone} = \frac{1}{3}\pi b^2 h \quad \Rightarrow$$

$$V_{sector} = \frac{R}{3}2\pi R^2(1-\cos\Theta), \quad V_{cone} = -\frac{1}{3}\pi R^3 \sin^2\Theta\cos\Theta \quad \Rightarrow$$

$$V = \frac{\pi R^3}{3}\left(2(1-\cos\Theta) - \sin^2\Theta\cos\Theta\right) = \frac{\pi R^3}{3}\left(2 - 3\cos\Theta + \cos^3\Theta\right).$$

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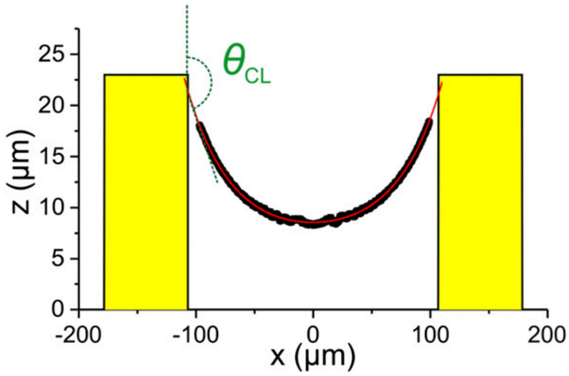


Fig. S2. Measurement of the contact angle θ_{CL}. The profile of the air cushion can be determined up to 0.05*d* from the side wall of a pillar. The high refractive index of the pillars (n = 1.6) prevents to measure the profile of the water–air interface closer to the walls. The profile along a diagonal of the quadratically arranged pillar arrays is fitted with the empirical equation $h_{air} = a\cosh\frac{x}{b}$ and is extrapolated to the edge of the pillars (red line). The tangent at the edge with respect to the vertical yields the contact angle.

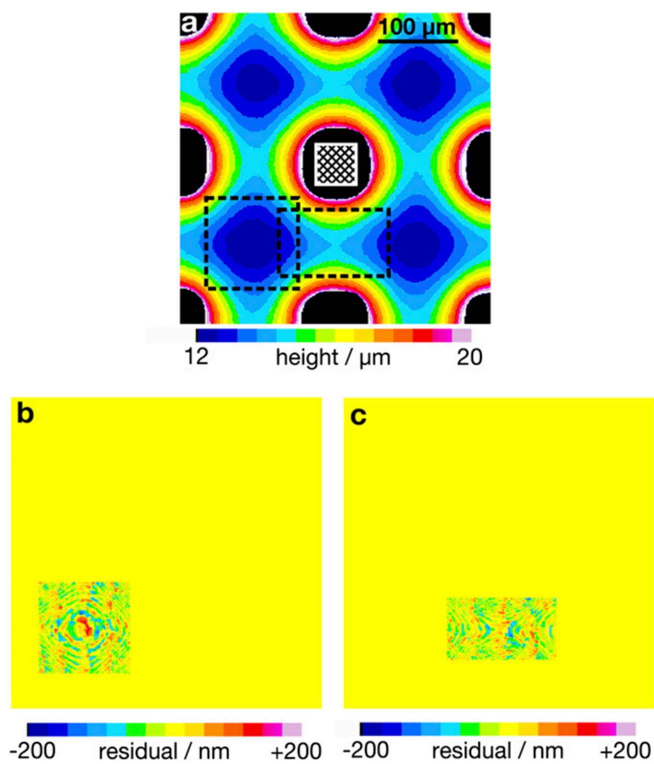


Fig. S3. Calculation of the Laplace pressure of a drop deposited on an array of pillars. (*A*) Contour plot of the height h_{air} of the air cushion. The mean curvature H (= 1/R for spherical drops) is equal at every position of the water–air interface, because a deformation of the drop due to gravity can be neglected. The areas enclosed in dashed rectangles are fitted with a function $h(x,y)$ that is the sum containing terms x^n, y^n, $x^n y^m$ up to the sixth order. The mean curvature is calculated at the center of each rectangle: $H = \frac{h_{xx}(1+h_y^2) + h_{yy}(1+h_x^2) - 2h_{xy}h_x h_y}{2(1+h_x^2+h_y^2)^{3/2}}$, where $h_{i,j}$ denotes the partial derivative of h with respect to i, j. Evaluation of the curvature at the points of highest symmetry minimizes the error in the calculation. The curvatures calculated around the minimum and the saddle point are 0.87 ± 0.05 and $0.79 \pm 0.10\ mm^{-1}$, respectively. They are equal within the accuracy of the measurements. The fit around the minimum is used in all cases in the manuscript. (*B*) Residual of the fit around the minimum and (*C*) the saddle point.

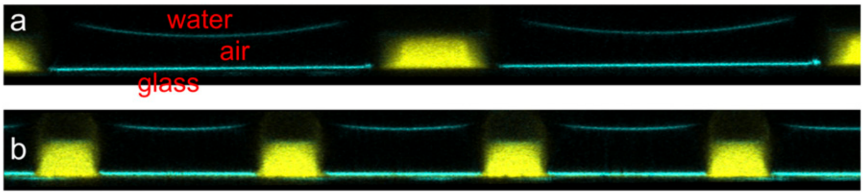
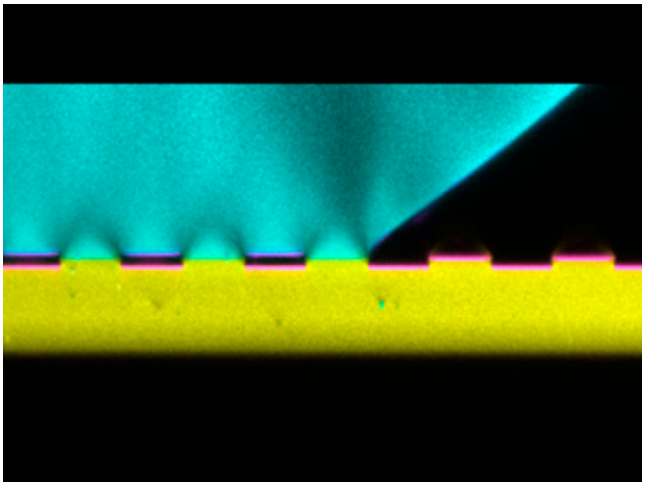
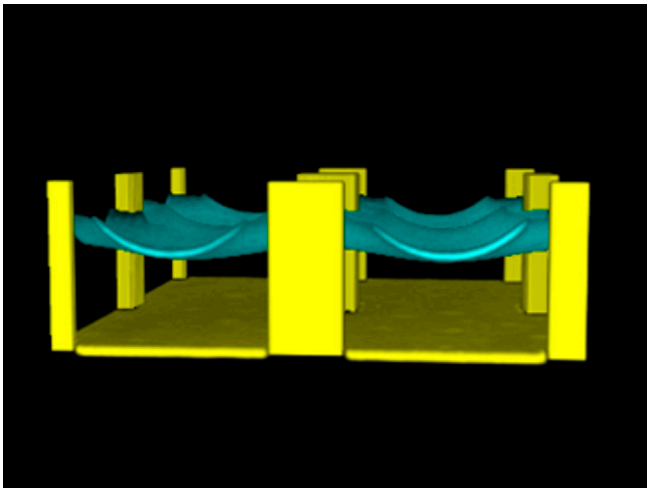


Fig. S4. Index of refraction. Vertical images taken by laser scanning confocal microscopy of drops deposited on arrays of pillars. The reflection (cyan) and fluorescence of the PDMS pillars (yellow) are measured along the main axis: (*A*) a = 50 μm, d = 200 μm, h = 23 μm, (*B*) a = 25 μm, d = 100 μm, h = 23 μm. To accurately depict the height of the air cushions (n = 1.0) a dry objective was used. However, therefore the refractive index of objective did not match those of SU-8 (n = 1.6; data from MicroChem). The pillars appear shorter by a factor of 1.6, i.e., they appear to have a height of about 15 μm. Refraction from the pillars defocus the laser beam and the reflection of light near the edge of the pillars, so the shape of the water-air cushion cannot be determined closer than 0.05 d from the pillars. Because the height of the pillars is known from SEM, we inserted artificial pillars to avoid confusion.



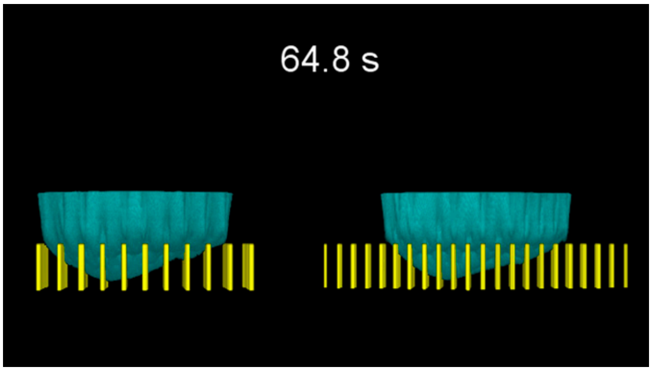
Movie S1. The movie is compiled of two-dimensional images taken by laser scanning confocal microscopy. It shows vertical sections through an evaporating water drop deposited on PDMS pillars. The dimensions of the pillars are as follows: diameter a = 20 μm, height h = 5 μm, and pillar–pillar distance d = 40 μm. The images are recorded at a frame rate of 1 frame per min. Fluorescent emission from water and PDMS is shown in cyan and yellow, respectively, and reflection in magenta. The sensitivity of the fluorescence detector was adjusted during the measurement to correct for the increasing dye concentration in water.

Movie S1



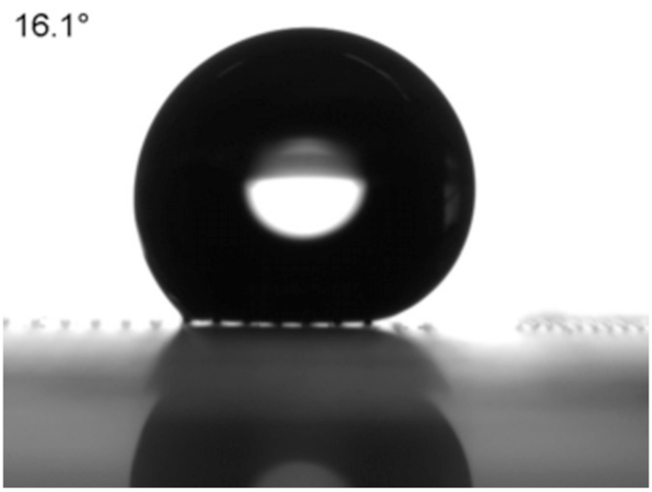
Movie S2. Three-dimensional movie showing the Cassie-to-Wenzel transition via the sagging mechanism. The reflection of light from the SU-8–air (yellow) and air–water (cyan) interface, and one pillar are shown. One 3D stack was recorded every 83 s. The distance between pillars is d = 200 μm and their height h = 23 μm. The z axis is 5× magnified for clarity.

Movie S2



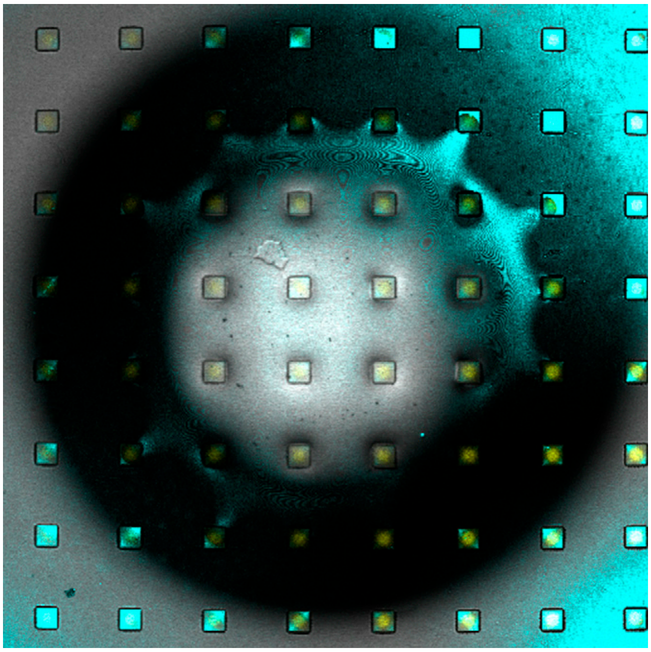
Movie S3. Time-resolved 3D movie of the depinning impalement transition. A drop was deposited on a pillar array and evaporated slowly. After the diameter reached about 200 μm, the water started sliding the sides of the pillars. The same drop is viewed along the main axis (*Left*) and the diagonal (*Right*). Wetting of the substrate does not cause a jump of the rim. One 3D image was recorded every 0.9 s. The dimensions of the SU-8 pillars are as follows: a = 5 μm, d = 20 μm, h = 5 μm. The z axis is 10× magnified.

Movie S3



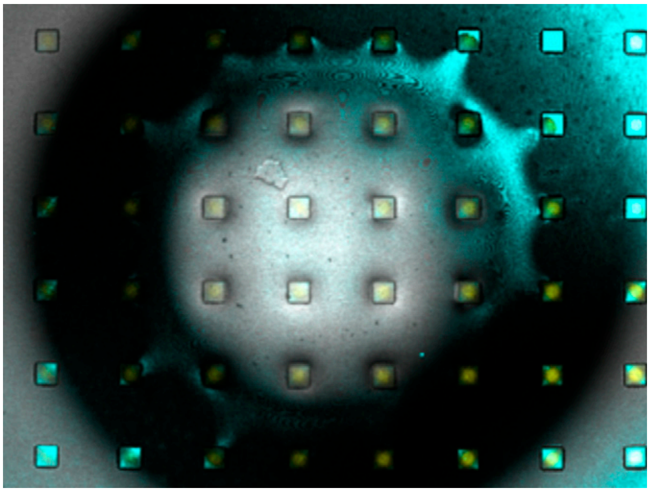
Movie S4. Roll-off of a 6-μL-sized drop deposited on an array of SU-8 pillars. The dimensions of the SU-8 pillars are as follows: = a = 50 μm, d = 200 μm, h = 23 μm. The stage was tilted at a rate of 0.6 °/s.

Movie S4



Movie S5. Evolution of the rim of a drop and the impalement transition. The reflection of the water–air cushion interface (cyan), fluorescence from the pillars (yellow), and transmission (gray) are shown. After wetting of the substrate, micrometer-sized air bubbles are left at the backside of the pillars with respect to the flow direction. In course of time, the size of the bubbles continuously decreased. After about 10 min, the bubbles disappeared. Wetting of the substrate is accompanied by a jump of the rim. The dimensions of the SU-8 pillars are as follows: $a = 50$ μm, $d = 200$ μm, $h = 23$ μm. Frame rate: 13 frames/s (100× faster than actual rate).

Movie S5



Movie S6. Droplets remain on top of pillars after depinning (*Upper Right*). The dimensions of the SU-8 pillars are as follows: $a = 50$ μm, $d = 200$ μm, $h = 23$ μm. Frame rate: 8 frames/s (each frame repeated six times to avoid low frame rate that causes problems with some programs).

Movie S6