

Supporting Information

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Transparent, Flexible, Superomniphobic Surfaces with Ultra-Low Contact Angle Hysteresis**

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Supporting Information

Section 1: Experimental Details

Photolithography: A 3 μm thick layer of photoresist (SPR 220-3.0, Shipley) was spin-coated on a silicon wafer and baked for 90 sec at 115 $^{\circ}\text{C}$. The lateral layouts of the micropattern were defined by 365 nm UV exposure (Karl Suss MA6 mask aligner) and developing in AZ300 MIF. Inductively coupled plasma reactive-ion etching (ICP-RIE, STS Pegasus) formed ~ 20 μm and 40 μm deep micropore arrays in the exposed regions, and the photoresist was stripped (Baker PRS 2000).

Master Molding: Polydimethylsiloxane (PDMS, Sylgard 184 Kit, Dow-Corning) was mixed in a 10:1 (w/w) ratio as received and poured over Si masks at room temperature. The mixture was degassed and subsequently cured for 3h at 80 $^{\circ}\text{C}$. The PDMS was removed from the mask, leaving a square array of pillars. 20 mg mL⁻¹ solutions of 25 wt% 1H,1H,2H,2H-heptadecafluorodecyl polyhedral oligomeric silsesquioxane (F-POSS) + PDMS were prepared in Asahiklin 225 (AK225, Asahi Glass Co.). The pillars were sprayed using an airbrush (Paasche Airbrush Co., product code 02661400031-1) at a distance of 10 cm with an N₂ pressure of 58 psi. Sprayed pillars were subsequently cured again at 80 $^{\circ}\text{C}$ for 3h.

Contact Angle Measurements: Contact angles were measured using a Ramé-Hart 200-F1 goniometer. Measurements were made by advancing and receding a single droplet of liquid (≈ 2 μL) from a 2 mL micrometer syringe (Gilmont). Averages from at least five independent measurements are reported. The surface tension of probe liquids was evaluated using the pendant drop method and all values fell within $\pm 5\%$ of literature values.

Microscopy: Surfaces were imaged using a Phillips XL30 scanning electron microscope (SEM) at 15 kV. A thin layer (≈ 50 nm) of gold was sputtered onto the surfaces to reduce charging.

Spraying movies were obtained using a VistaVision VWR optical microscope with a 5X objective. At 15 second intervals the substrates were transferred from the spraying apparatus to the microscope stage.

Transparency and Flexibility: A Varian Cary 50 Bio UV-Vis Spectrometer was used to obtain transmittance data in the 200-800 nm range at a scanning speed of 600 nm s^{-1} . Averages of three independent measurements are reported. Figure 3c was obtained by placing the sprayed pillar substrate atop an iPhone 3GS backlit by a repeated image of 'M's. For Figure 4b-c a single droplet ($\approx 2 \text{ }\mu\text{L}$) of liquid is placed on the sprayed pillar surface which has been bent inside a scintillation vial (diameter = 2 cm). The video is obtained with a Casio EX-F1 camera, analyzed using Windows Movie Maker and the photos (along with Figure 1a) are constructed using Adobe Photoshop CS5.1.

Section 2: The fabricated PDMS micro-pillars.

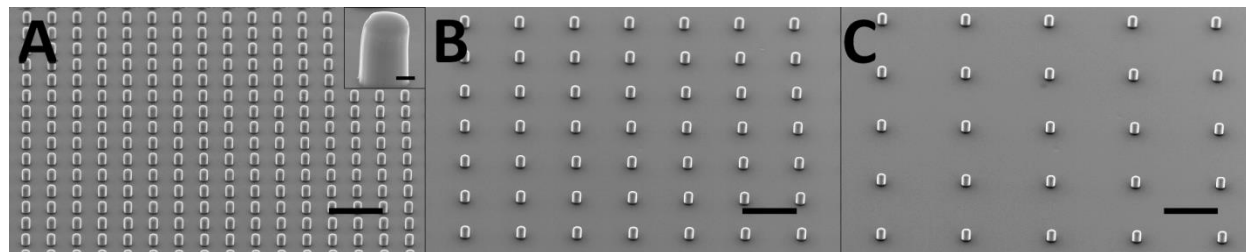


Figure S1. A-C) SEM micrographs of 20 μm high PDMS pillars with $D^* = 10, 42$ and 100 respectively, without any spray coating. Images are taken at 45° from the horizontal. Scale bars are 100 μm . The inset in A shows a single pillar; scale bar is 5 μm .

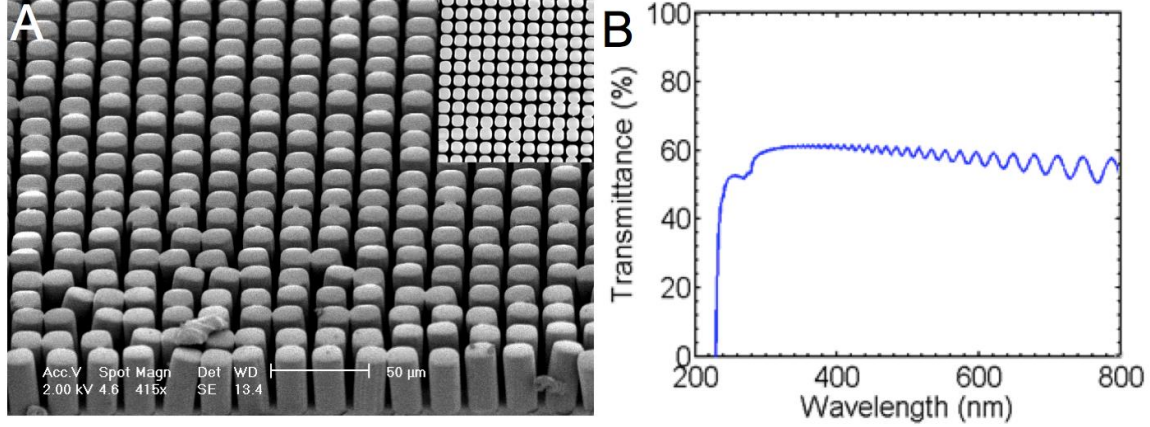


Figure S2. Although a smooth PDMS film is roughly 96% transparent in the visible range, PDMS micropillars can cause significant light scattering. A) SEM micrograph of 30 μm high pillars with a $D^* \approx 1$ seen from a 65° angle from the horizontal. The inset is a top view of the pillars. B) Transmittance as a function of wavelength for the structure seen in (A).

Section 3: Design Parameters

A hierarchical structure's apparent contact angle can be found recursively, by examining the texture on each length scale.¹⁻⁴ For our microscale geometry of cylindrical pillars,

$D_{pillar}^* = \left(\frac{R_{pillar} + D_{pillar}}{R_{pillar}} \right)^2$. The Cassie-Baxter equation can be rewritten using this formalism as

$$\cos \theta_{pillar}^* = -1 + \frac{1}{\sqrt{D_{pillar}^*}} [\sin \theta + (\pi - \theta) \cos \theta] \quad (1)$$

where θ is the Young's contact angle. However, with a hierarchical structure, the correct contact angle to be used in Eq. 1 is not the Young's contact angle, but the apparent contact angle on the smaller (nano) length scale, $\theta_{particle}^*$ ^{2,5}. Thus, under the assumption that all pillars are completely covered with particles (a good assumption for spray times > 30 seconds), the apparent contact angle of our hierarchical surface is given by

$$\cos \theta_{hierarchical}^* = -1 + \frac{1}{\sqrt{D_{pillar}^*}} \left[\sin \theta_{particle}^* + (\pi - \theta_{particle}^*) \cos \theta_{particle}^* \right]. \quad (2)$$

To predict if a given spray time, on a surface of known D^* , will support a composite interface, a modified expression for the robustness factor A^* is necessary. As particles begin to form an overhang on the PDMS micro-pillars, a ‘hoodoo’-like^{6,7} structure is formed, which requires the use of a previously developed A^* expression⁶. In this case, the robustness factor is given by the harmonic mean between a droplet’s dimensionless sagging height (characterized by H^*) and its dimensionless sagging angle (characterized by T^*). For the hoodoo-like substrates discussed here:

$$H^* = \frac{2R\ell_{cap} \left[(1 - \cos \theta) + \frac{H}{R} \right]}{D^2(1 + \sqrt{D^*})} \quad \text{and} \quad T^* = \frac{\ell_{cap} \sin(\theta - \psi_{min})}{D(1 + \sqrt{D^*})} \quad (3,4)$$

where ψ_{min} is the minimum texture angle^{6,7} ($\psi_{min} = 0^\circ$ in this case). All other symbols have been defined previously. Under the assumption that $\theta < 90^\circ$, the robustness factor becomes

$$\frac{1}{A^*} = \frac{1}{H^*} + \frac{1}{T^*}. \quad (5)$$

The values of the robustness factors for water, hexadecane and ethanol, for the various surfaces developed here are shown in Table S1.

Table S1. Robustness factor A^* for three different probe liquids for spray times of 30, 60 and 120 seconds on surfaces with D^* values of 10, 42 and 100. Values in red denote surfaces that cannot support the given probe liquid in the Cassie state.

D^*	A^*_{Water}			$A^*_{Hexadecane}$		$A^*_{Ethanol}$		
	30 sec	60 sec	120 sec	30 sec	60 sec	30 sec	60 sec	120 sec
10	27.8	31.1	33.9	2.91	14.9	0.39	5.27	5.72
42	4.89	5.69	6.3	2.35	2.74	0.95	1.1	1.66
100	1.94	3.31	3.78	0.94	1.85	0.42	0.92	1.04

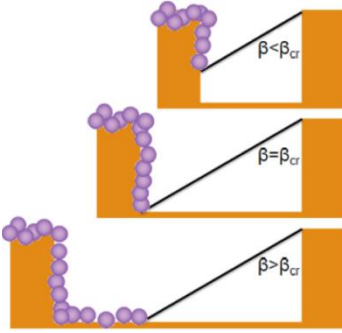


Figure S3: A schematic illustrating the various possible cases when β is either less than, equal to, or greater than β_{cr} . The effects of varying β on controllable particle deposition can also be seen.

Section 4: Boundary Layer Thickness Derivation

Starting from Equation 3 from the main manuscript, the boundary layer thickness is,

$$\delta = 2.4 \sqrt{\frac{\nu}{a}} \quad (6)$$

Where ν is the kinematic viscosity and 'a' is a constant arising from the nondimensional velocity

V_y . For a hydrodynamically smooth surface, the correct velocity scale (for V_y) is \sqrt{va} , thus

$$a = V_y^2 / \nu \quad (7)$$

Using (7), the boundary layer thickness can be rearranged to

$$\delta = 2.4\nu / V_y \quad (8)$$

where V_y is the mainstream velocity of the flow. By measuring the mass flow rate Q (22 mg/s at an N_2 pressure of 58 PSI) and nozzle diameter d (790 μm), the boundary layer thickness can be found using,

$$\delta = 2.4 \frac{\pi d^2 \mu}{4Q} \quad (9)$$

where μ is the viscosity of the sprayed mixture (N_2 and polymer solution). Therefore, measuring simple known quantities like the diameter of the spray gun, and mass flow rate of the spray feed, the boundary layer thickness can be readily evaluated using (9).

References:

- [1] W. Choi, A. Tuteja, S. Chhatre, J. M. Mabry, R. E. Cohen, G. H. McKinley, *Adv. Mater.*, **2009**, 21, 2190.
- [2] A. K. Kota, Y. Li, J. M. Mabry, A. Tuteja, *Adv. Mater.*, **2012**, 24, 5838.
- [3] S. Pan, A. K. Kota, J. M. Mabry, A. Tuteja, *J. Am. Chem. Soc.*, **2013**, 135, 578.
- [4] S. Herminghaus, *Europhys. Lett.*, **2000**, 52, 165.
- [5] S. S. Chhatre, W. Choi, A. Tuteja, K.-C. Park, J. M. Mabry, G. H. McKinley, R. E. Cohen, *Langmuir*, **2009**, 26, 4027.
- [6] A. Tuteja, W. Choi, J. M. Mabry, G. H. McKinley, R. E. Cohen, *Proc. Natl. Acad. Sci. U S A*, **2008**, 105, 18200.
- [7] A. Tuteja, W. Choi, M. Ma, J. M. Mabry, S. A. Mazzella, G. C. Rutledge, G. H. McKinley, R. E. Cohen, *Science*, **2007**, 318, 1618.

Movie M1. This video shows the PDMS+F-POSS mixture being spray-coated onto a flat piece of PDMS. The video is taken using a microscope with a 5x objective. The substrate is sprayed every 15 seconds and then moved under the microscope for imaging.

Movie M2. This video shows 20 μm high PDMS pillars with $D^*=100$ being spray-coated by PDMS+F-POSS. The video illustrates how most of the particles agglomerate on the pillar tops and sides, and little aggregates in between the pillars. The video is taken at the same time and in the same way as Movie S1.

Movie M3. This video shows 40 μm high PDMS pillars with $D^*=100$ being spray-coated by PDMS+F-POSS. The video illustrates how an increase in pillar height drastically changes how particles aggregate on the substrate. This phenomena supports the model suggested in the main manuscript. Again, the video is taken at the same time and in the same way as Movie S1.

Movie M4. This video illustrates both the flexibility and low contact angle hysteresis of the surfaces fabricated in this work. 20 μm high PDMS pillars with $D^*=100$ are spray coated for 120 seconds. The surface is then bend into a scintillation vial that has been cut in half, producing an arc. 2 μL droplets of water, coffee, vegetable oil and ethanol are then placed onto the surface. The droplets roll back and forth several times before pinning at the edge of the surface.