Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information for Universal wetting transition of an evaporating water droplet on hydrophobic micro- and nano-structures

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S1 Supplementary Images of Superhydrophobic Nanostructures

Figure S1 shows scanning electron microscope (SEM) images of the nano-patterned surfaces used: with the pillar diameter of (a) 200 nm and (b) 400 nm.

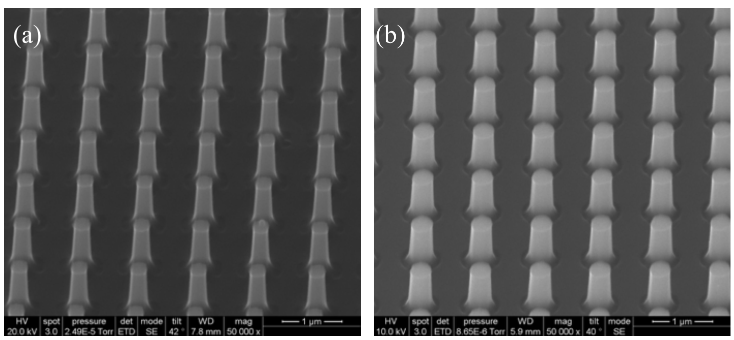

Figure S1 SEM Images of Superhydrophobic Nanostructures used: the nano-cylinders of diameter of 200 nm and 400 nm in (a) and (b), respectively.

S2 Non-spherical drop shape and gravitational effect

Figure S2 shows a representative image of an initial droplet shape and the fitting result of contact angle (165°) by the ADSA method (dashed red line), which solves the Laplace equation with the gravitational effect [44] (by O. Rio and A. Neumann). The fitting result is compared to a spherical cap approximation, which is based on (1) the same droplet volume and contact angle (in yellow) or (2) the same volume and contact radius (in blue). As revealed in Fig. S2, the drop is deformed by gravity since the drop height is similar to the capillary length. As a result, the ADSA method is used to increase the accuracy of the measurement of the droplet volume, contact angle and radius. During evaporation, as time increases the drop becomes smaller and converges to a spherical cap (as gravity becomes negligible). From the figure, one can see that a deviation from the spherical cap can induce a significant error on the contact angle (by 15°) or radius measurements. This may result in a discrepancy observed on the experimental dimensionless evaporation rate in Figure 3, where spherical shape is assumed in the both evaporation models.

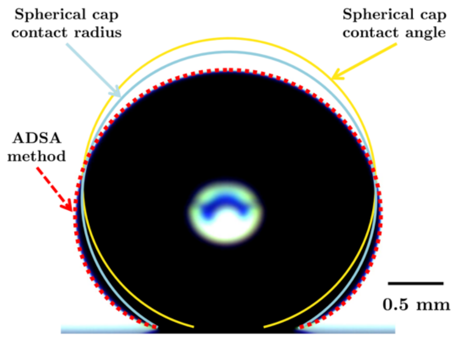

Figure S2 Non-spherical drop shape. A representative image of an initial droplet having a volume of 10 μL and a contact angle around 165° by the ADSA method (shown by dashed red line). Whereas, different fitting results are found by spherical cap approximations using (1) the same droplet volume and contact angle (in yellow line) or (2) the same volume and contact radius (in blue line). By using the spherical cap approximation one can found the height of the droplet to be 2.63 mm, similar to the capillary length (of 2.71 mm). Thus, at such high contact angle the droplet is deformed by gravity.

S3 Supplementary Note on Evaporation Flux

Sessile drop evaporation is assumed to be quasi-steady (so that diffusion time scale is much smaller than total evaporation time), and the surface is included by imposing a null vapor flux through the substrate normal. Under these conditions, the mass outflux is given by:

$$\dot{M} = \frac{dM}{dt} = -\pi R_b D(c_S - c_\infty) f(\theta), \tag{1}$$

$$f(\theta) = \frac{\sin\theta}{1+\cos\theta} + 4\int_0^\infty \frac{1+\cosh 2\theta\tau}{\sinh 2\pi\tau} \tanh\left((\pi-\theta)\tau\right) d\tau, \tag{2}$$

where M is the droplet mass, D is the vapor diffusion coefficient, c_S is the saturated vapor concentration at the drop surface, c_∞ is the vapor concentration at infinity, R_b is the base radius, and θ is the contact angle. The drop shape is modeled as a spherical cap. The non-uniform vapor concentration field induced by the substrate is expressed by the function f, which depends solely on the contact angle.

Experiments were conducted at $25°C$ with 16% relative humidity (H_a). Under these conditions water density is $\rho = 997.04$ kg/m^3, vapor diffusion coefficient is $D = 28.2\ 10^{-6}$ m^2/s, the saturated vapor concentration is $c_S = 2.3\ 10^{-3}$ kg/m^3, and the vapor concentration at infinity is $c_\infty = H_a c_S$.

S4 Error Analysis of Contact Angle

The contact angle in previous studies is usually extracted based on the drop base radius (R_b) and height (H) using the spherical cap approximation ($\theta = \cos^{-1}\left(\frac{R_b{}^2 - H^2}{R_b{}^2 + H^2}\right)$). The measurement error or uncertainty of R_b and H can contribute to the uncertainty of the contact angle, estimated using the following analysis of error propagation.

$$\Delta\theta = \sqrt{\left(\frac{\partial\theta}{\partial R_b}\Delta R_b\right)^2 + \left(\frac{\partial\theta}{\partial H}\Delta H\right)^2} = \frac{R_b{}^2 + H^2}{2HR_b}\sqrt{\left(\frac{4R_b H^2 \Delta R_b}{(R_b{}^2+H^2)^2}\right)^2 + \left(\frac{-4R_b{}^2 H\Delta H}{(R_b{}^2+H^2)^2}\right)^2}.$$

The equation can be simplifies:

$$\Delta\theta = \frac{2}{R_b{}^2 + H^2}\sqrt{H^2 \Delta R_b{}^2 + R_b{}^2 \Delta H^2}.$$

By assuming typical value as $R_b \approx H \approx 200\mu$m and $\Delta R_b \approx \Delta H \approx 20\mu$m, the resulting error on the contact angle is:

$$\Delta\theta \approx \frac{\sqrt{2}\Delta R_b}{R_b} \approx 8.1^\circ$$

This error or uncertainty can contribute to the partial deviation observed between the theoretical prediction and the experimental data in Fig. 5.

S5 Supplementary Video

The video shows the wetting transition during drop evaporation on a low roughness surface (D = 200 nm, H = 1 μm, P=2 μm and r = 1.16) corresponding to the data in Fig 4. During the first stage, the droplet evaporates in a Cassie-Baxter state, with a moving contact line. Once the contact angle reach the critical contact angle (149.5°), after 945 s, the drop transits toward a completely wetting (Wenzel) state.