Supporting Information for:

Nanoparticle Dispersion and Separation in Superhydrophilic Nanostructures

Andrew Tunell,[1] Kun-Chieh Chien, [1] Samuel Lee, [1] Nirmalay Barua, [1] Alexandra Paul, [2] Sapun H. Parekh, [2] Tanya Hutter, [1] and Chih-Hao Chang[1,]*

[1]Walker Department of Mechanical Engineering, The University of Texas at Austin

[2]Department of Biomedical Engineering, The University of Texas at Austin

*Corresponding author: chichang@utexas.edu

Supplementary Information A: Modeling of Structure Roughness

The theoretical estimation of the diffusion constant, which establishes the rate at which a fluid will move through the nanostructures is highly dependent on the structure's surface energy as well as geometry. In determining the geometric factors, two SEMs of the surface were analyzed as shown in Figure S1(a,b)

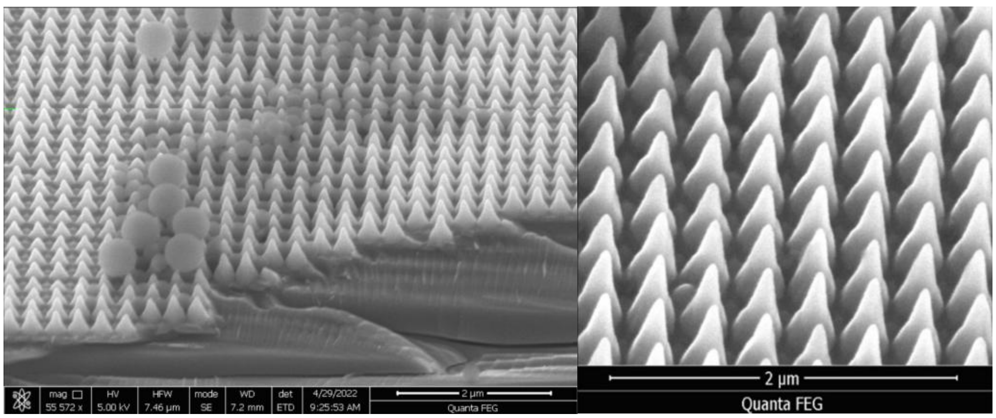

FIGURE S1. SEM images of the fabricated structures at a 45° angle used for extracting geometric properties of the nanostructures.

The tilt of the images was taken into account when extracting heigh data of the structures from the figure. Furthermore, it was found that there is a small variation in the structure's height across the sample due to non-uniform etching or exposure. From this analysis the structures were measured to have a height of 599 ± 26 nm, a period of 314 ± 11 nm, and a tip radius of 34 ± 5 nm. The uncertainty is found by taking the standard deviation of the 40 measurements taken from each of these geometric factors.

Using these measurements the roughness factor of the sample was determined by taking the ratio of actual surface area to the projected surface area. Considering a single nanocone as one unit cell, the actual surface area to project surface area is defined in Equation S.1 shown below.

$$R = \frac{\sqrt{h^2+r^2}}{r} \tag{S.1}$$

Where R is the roughness factor, h is the height of the nanocone, and r is the radius at the base of the nano cones. Using the measured values this gave a value of $R = 3.94$.

Supplementary Information B: Modeling of Diffusion Constant

The theoretical modeling of wicking seen in the nanostructures is described in this section. The model is based on a balance of capillary and viscous forces, which drive and obstruct fluid flow, respectively. From Bico et al. the condition for wicking on a nanostructured surface is $\theta < \theta_c$. The critical angle, θ_c can be found using the following equation S.2.[1]

$$\cos\theta_c = \frac{1-\phi_s}{R-\phi_s} \tag{S.2}$$

Where θ is the liquid contact angle on an unstructured reference sample, ϕ_s is the ratio of area that remains dry to the projected area, and R is the surface roughness. In our work, we were not able to directly measure ϕ_s, however, this can be obtained by measuring the contact angle of the unstructured(θ) and structured(θ*) surfaces using a goniometer, these values were found to be 25° and 5° respectively. The critical angle can therefore be found using equation S.3.

$$\phi_s = \frac{1-\cos\theta^*}{1-\cos\theta} \tag{S.3}$$

This gives ϕ_s to be 0.04, showing that very little of the structure is expected to remain dry. From this θ_c is found to be 75°. In balancing the capillary and viscous forces, the Washburn law is used to determine the capillary pressure in the structure.[2]

$$\Delta P_c = \frac{\gamma(\cos\theta - \cos\theta_c)}{h\ \cos\theta_c} \tag{S.4}$$

Where ΔP_c is the capillary pressure, γ is the surface tension of the fluid, and h is the height of the channel. The simplified Navier-Stokes' equation for steady-state incompressible flow in the z-direction through an open channel, $-\frac{\Delta P}{\mu z} = (\frac{\partial^2 U}{\partial x^2} + \frac{\partial^2 U}{\partial y^2})$ can then be used, where ΔP is the capillary pressure, and $U(x,y)$ is the velocity profile. The following boundary conditions are used, $U(0,y)=0$, $U(x,l)=0$, $U(w',y) = 0$, and, $U(x,2h) = 0$. Solving and averaging over a cross section gives the mean velocity, U_{mean}, shown below.

$$U_{mean} = C\frac{64\Delta P}{\pi^6 \mu z\left(\frac{1}{(w\prime)^2}+\frac{1}{4h^2}\right)} \tag{S.5}$$

Where C is found as $\pi^6/768$ and w' is the effective channel width.[3] The U_{mean} of flow through a rough surface is derived by Bico et al. as $U_{mean} = \frac{\Delta P h^2}{3\mu z\, \beta}$ where $\beta = 1 + \frac{4h^2}{(w')^2}$.[1] Balancing Equation 4 for capillary pressure and Equation 5 for viscous forces and integrating allows for the diffusion constant, defined by $z = \sqrt{Dt}$, to be found.

$$D = \frac{2\gamma h}{3\mu\beta}\,\frac{(\cos\theta - \cos\theta_c)}{\cos\theta_c} \tag{S.6}$$

Using the known values of the fabricated nanostructured surface, Equation S.6 can be used to estimate the diffusion constant. In the case of DI water, 7.28×10^{-2} N/m is used for the surface tension, γ, and 8.9×10^{-4} Pa·s is used for the viscosity, μ. The height, h, was found to be 599 nm, and due to the conical shape of the structures, 75% of the length of the period, 314 nm, was used for the effective channel width, w'. This gave a value for β of 26.8. Including the previously mentioned contact angles, the diffusion constant is calculated to be D = 3.28 mm/s^2. Using standard error propagation with the uncertainties of the geometric measurements, the uncertainty of the diffusion constant was found to be ± 0.26 mm^2/s.

Supplementary Information C: Experimental Diffusion Constant

To experimentally determine the diffusion constant an overhead video was taken of the structured surface and a droplet was applied. The distance of the wicking front from the initial site of the droplet application was then measured over a period of one minute, this data is plotted below in Figure S2.

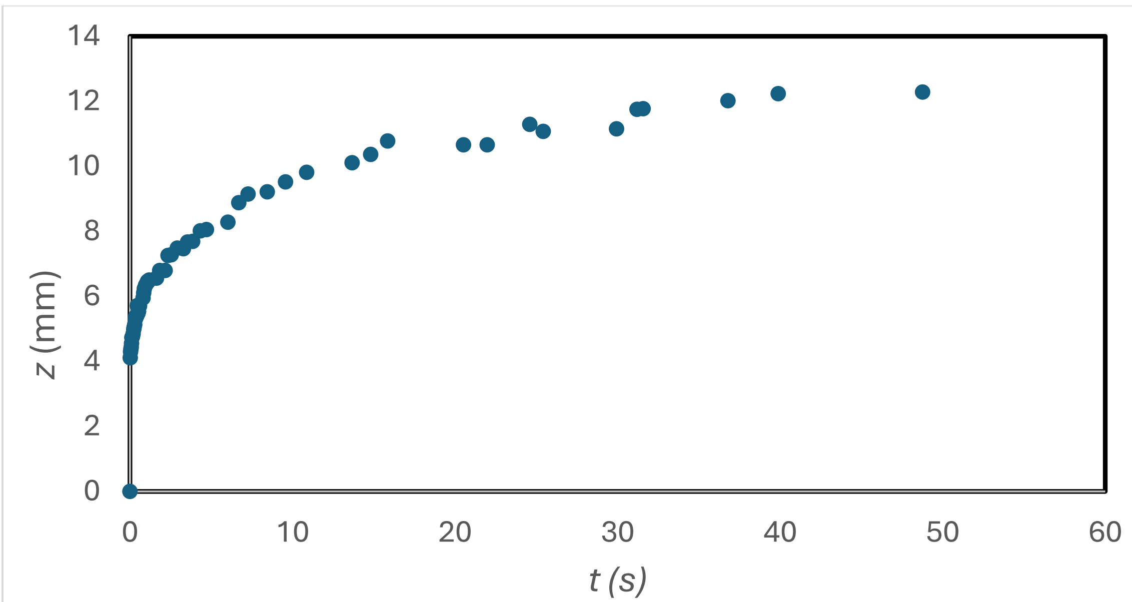

FIGURE S2. Plot of the measured distance of the wicking front on a superhydrophilic nanostructured surface with respect to time from the application of a droplet.

The square root of the time values was taken and the data shown in Figure S2 was plotted again. This time z and t had a linear relationship with a slope of 1.89 mm/s$^{1/2}$. Squaring the slope returns the diffusion constant, D = 3.57 mm/s^2.[4]

Supplementary Information D: Details of Structure Fabrication

Figure S3 shows a simple diagram for the fabrication steps to create the high aspect ratio wicking nanostructures. Additional processes are performed after the pattern was transferred into the silicon wafer. This includes an RCA clean to remove the remaining polymer mask leaving only the silicon substrate. Oxygen plasma etching was also performed immediately before each particle wicking experiment was conducted. Additional fabrication details are provided in the Methods section of the main text.

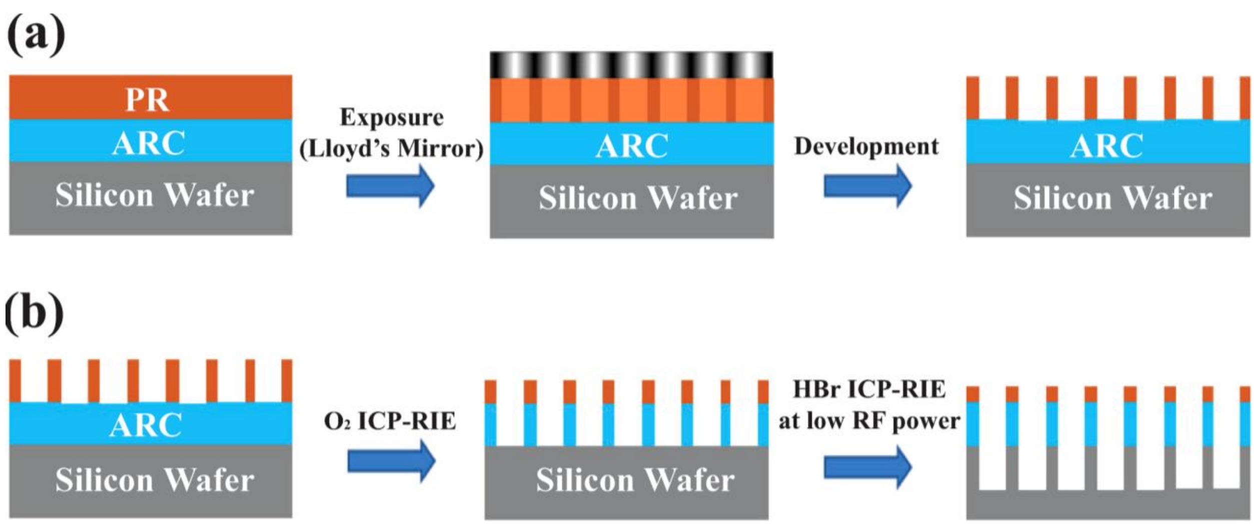

FIGURE S3. Diagram of the fabrication steps to create the high aspect ratio periodic nanostructures using low power RF etching.