Electronic Supplementary Material (ESI) for Nanoscale.

Tuning and predicting the wetting of nanoengineered material surfaces

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# Equal contribution

Supporting Information

Care was taken so that the variation of *n* was the same for the three different particle sizes (Figure SI 1). The particle density at a fixed position *x* was varied by changing the deposition flux. The amount of material deposited per unit area, *m* ($m \cong \rho n d^3$, ρ – density of the particles) was kept approximately proportional to the particle size, i.e. $m \cong$ const *d*, and we expected $n \cong d^{-2}$. A log-log plot (see inset in Figure 3) shows that the power *k* in $n \cong d^{-k}$, varied from $k = 2.4$ at $x = 1$ mm to $k = 2.1$ at $x = 9$ mm.

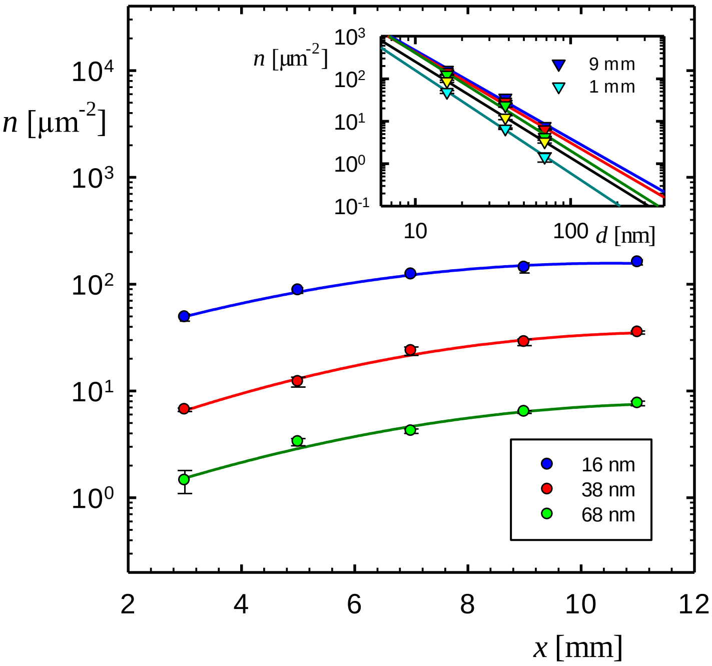

Figure SI-1. Number density, *n*, of nanoparticles on different locations, *x*, along the surface gradient. Inset: particle density, *n*, versus particle size, *d*.

The average interparticle distance, λ, is directly related to the particle density ($\lambda = n^{-½}$) and decreases along the gradient (increasing *x*) – Figure SI-2.a. It is always significantly larger than the particle size –

typically 5 times or more. This confirms that the thickness of a monolayer of particles is never exceeded. The average distance λ can also be regarded as the average size of the surface pores formed in between the nanoparticles. This average pore size varies between about 100 and 800 nm (Figure SI-2.a). Finally, the projected area of the deposited nanoparticles per unit surface area, *C*, is obtained as $C = \pi d^2 n/4$. This projected relative area fraction occupied by particles (or surface coverage) is very similar for the three particle sizes; it is relatively small (always less than 5%) and it increases approximately linearly along the surface gradient (Figure SI-2.b).

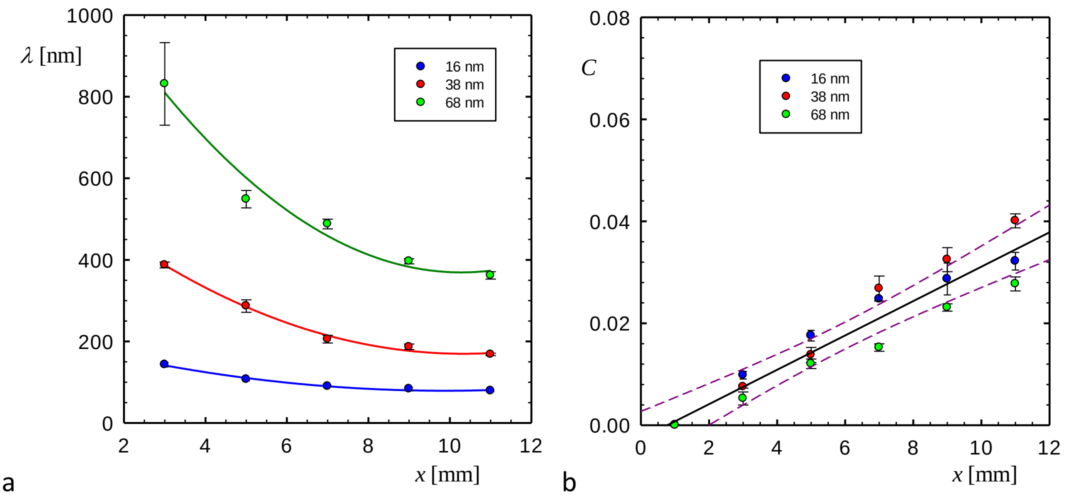

Figure SI-2. (a) RMS roughness, R_{RMS}, on samples decorated with nanoparticles (size 16, 38 and 68 nm) along the particle density gradient, *x*. (b) Average interparticle distance, λ, as function of location *x*. (c) Surface coverage, *C*, as a function of location, *x*, along the surface gradient.

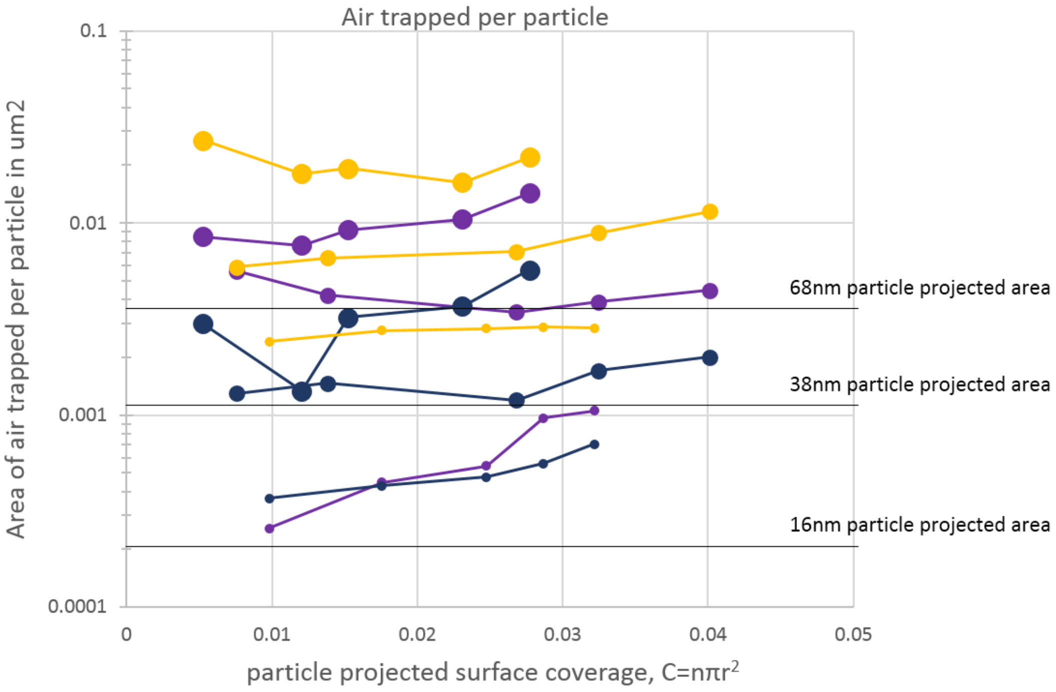

Figure SI-3: Air trapped per particles for the 3 coatings (ppOD in yellow, ppAA in purple and ppAc in blue) and for the 3 particles size (increasing dot size for 16, 38 and 68 nm) as a function of the particle projected surface coverage. The black line represent the projected area for a single particle, as a guide to the eyes.

At similar coverage:

1) More air is trapped by the more hydrophobic coating (yellow-purple-blue decreasing)
2) The larger the particle the more air trapped per particle.

For all particle size and coatings, the area air trapped per particle in only slightly larger than the particle projected area itself.

Detailed model derivation:

Based on the geometry illustrated in figure 5.b, the Wenzel factor of the solid-liquid interface, r_{ϕ_s}, is:

$$r_{\phi_s} = \frac{real\ \phi_s\ surface\ area}{projected\ \phi_s\ surface\ area}$$

$$r_{\phi_s} = \frac{1 - truncated\ cone\ projection + half\ spherical\ cap\ area}{1 - \phi_v}$$

$$r_{\phi_s} = \frac{1 - n\pi(2R)^2 + \frac{1}{2}n\pi(2R)^2}{1 - 3\sqrt{2}n\pi R^2}$$

$$r_{\phi_s} = \frac{1 - 2n\pi R^2}{1 - 3\sqrt{2}n\pi R^2}$$

And so the extended Cassie equation becomes:

$$cos\theta = -1 + (1 - n\sqrt{2}\pi 3R^2)\left(\frac{1 - 2n\pi R^2}{1 - 3\sqrt{2}n\pi R^2}\cos\theta_Y + 1\right)$$

Or, after simplifications,

$$cos\theta = \cos\theta_Y - n\pi R^2(3\sqrt{2} + 2\cos\theta_Y)$$

The contact angle obtained from this model is compared to the experimental data in Figure 8.