Tuning Surface Wettability Using Single Layered and Hierarchically Ordered Arrays of

Spherical Colloidal Particles

Ila Badge, Sarang P. Bhawalkar, Li Jia, and Ali Dhinojwala*

Supporting Information:



Figure S1 : SEM image of single layer HNCP array of 250 nm silica particles



Figure S2 : SEM image of single layer HNCP array of 500 nm silica particle

1. Single Layer Roughness

Hexagonal Unit cell calculations:

Area of the Hexagon =
$$A_H = 6\left(\frac{1}{2} \times \frac{L_1}{\sqrt{3}} \times \frac{L_1}{2}\right)$$
 (1.1)

The total solid surface area is the area of the hexagon in addition to the surface area of the particle (Assuming single point contact between the particle and the flat surface).

Surface Area of the Sphere =
$$A_{Sp} = \pi D_1^2$$
 (1.2)

where D_1 is the particle diameter.

(1) <u>Wenzel state calculations:</u>

Roughness factor (R_1) defined as the ratio of total surface area to the projected area is calculated using following equation.

$$R_{1} = \frac{A_{H} + A_{Sp}}{A_{H}} = \frac{\frac{\sqrt{3}L_{1}^{2}}{2} + \pi D_{1}^{2}}{\frac{\sqrt{3}L_{1}^{2}}{2}} = 1 + \frac{2\pi}{\sqrt{3}r_{1}^{2}}$$
(1.3)

The roughness of the PECVD layer deposited on the surface (R_2) also adds to the overall surface roughness. The effective roughness of the surface (R) is thus, defined using following equation:

$$R = R_1 R_2 \tag{1.4}$$

Wenzel state contact angle (θ_W) thus, can be calculated using following equation:

$$\cos\theta_W = R\,\cos\theta_Y\tag{1.5}$$

180 170 160 Contact Angle (°) 150 Wenzel Model 140 250 nm \mathbb{X} 🔺 500 nm 130 Ж \times 2.7 microns 120 <u>× 100 nm</u> Ж 110 100 2 1 1.5 2.5 3 r_1

Here, θ_Y is the equilibrium contact angle defined for a homogenous surface.

Figure S3. Plot of contact angle vs r_1 for different sized silica particles and the calculated Wenzel model

The derivation of equations assumes that the particles are perfectly spherical. However, the particles are in fact spheres with the base flattened at a certain point defined by the angle α (see figure S4). This assumption renders the following relationship.

$$\frac{Height}{Diameter} = \frac{1}{2} (1 + \cos \alpha) \tag{1.6}$$

The shape of the particle does not affect the Cassie-Baxter equation, however the roughness factor calculation for the Wenzel state requires taking into account the changed shape of the particles.



Figure S4. The angle α defined for particles coated using PECVD

The surface area of the part of the sphere and the roughness factor are subsequently different from before.

Surface Area of part of the sphere
$$=\frac{\pi D_1^2(1+\cos\alpha)}{2}$$
 (1.7)

$$\therefore R_1 = \frac{A_H + Area of the part sphere - Area of the circle under the sphere}{A_H}$$
(1.8)

$$\therefore R_1 = \frac{\frac{\sqrt{3}L_1^2}{2} + \frac{\pi D_1^2 (1 + \cos \alpha)}{2} - \frac{\pi D_1^2 \sin^2 \alpha}{4}}{\frac{\sqrt{3}L_1^2}{2}} = 1 + \frac{\pi (1 + \cos \alpha)}{\sqrt{3}r_1^2} - \frac{\pi \sin^2 \alpha}{2\sqrt{3}r_1^2}$$
(1.9)

In order to calculate α , we measured diameter of the particles (D) from SEM images and using ImageJ software. We used AFM height images to measure height of the particles (H). The particle height profiles calculated for number of different particles gives the average H of the particles coated with a PECVD layer.

In the schematics of different wetting state cases of dual roughness, this angle is denoted as α_1 . It should be noted here that α_1 is actually α measured for 2700 nm particles ($\alpha_1 = 42.3^\circ$).

Particle	Diameter (nm)	Height (nm)	Height/Diameter	α
100 nm	222 ± 11	131 ± 5	0.59	79.6
250 nm	319 ± 21	241 ±14	0.76	58.7
500 nm	495 ± 28	414 ± 23	0.83	48.7
2700 nm	2850 ± 73	2500 ± 65	0.87	42.3

Table 1. Diameter, height and calculated α for the spheres coated using PECVD



Figure S5. Model Wenzel curves for different sized silica particles. The contact angles are calculated for spherical cap shape of the particle using the values of α measured experimentally (table 1).



Figure S6. Plot of contact angle vs r_1 for 100 nm particles using the new roughness factor and comparison to the experimental data points is also shown.



Figure S7. Plot of contact angle vs r_1 for 250 nm particles using the new roughness factor. A comparison to the experimental data points is also shown.



Figure S8. Plot of contact angle vs r_1 for 500 nm particles using the new roughness factor. A comparison to the experimental data points is also shown.



Figure S9. Plot of contact angle vs r_1 for 2700 nm particles using the new roughness factor. A comparison to the experimental data points is also shown.

AFM measurements to measure R₂:

As mentioned before, the roughness of the PECVD coating layer (R_2) needs to be accounted for in order to estimate overall roughness (R). We used Atomic Force Microscopy (AFM) for measurement of R_2 . The height images were acquired on a silicon wafer with a layer of PECVD of 1H,1H,2H-perfluoro-1-dodecene, deposited under same conditions as that of the HNCP pattern of particles. We used Nanaoscope IIIa, DI multimode SPM (Digital Instruments) for acquiring the AFM images. AFM tip with a resonant frequency between 300-400 kHz was used. The images were taken in a Tapping mode of the tip. For larger scan sizes (5 μ m - 20 μ m), scan frequency of 0.5 Hz was used, whereas for smaller scans (500 nm - 2 μ m) scan frequency of 0.25 Hz was used.



Figure S10 : AFM 2D height image of 1H,1H,2H-perfluoro-1-dodecene deposited by PECVD on

the surface of clean Silicon wafer, scan size : $1\mu m$.



Figure S11 : *AFM 3D height image of 1H,1H,2H-perfluoro-1-dodecene deposited by PECVD on the surface of clean Silicon wafer, scan size : 1µm.*

The image analysis gives the value of surface roughness (R') for each scan size. A plot of R' versus scan size was obtained. The data was fitted to an exponential function and the curve extrapolated to scan size = 0 gives the value of R_2 as 1.19 ± 0.05 .



Figure S12. *R'* calculated using AFM image analysis for a PECVD coating of 1H,1H,2Hperfluoro-1-dodecene as a function of scan size. The extrapolation to zero scan size gives the value of R_2 .

(2) <u>Cassie-Baxter state calculations:</u>

In case of the Cassie-Baxter state, the liquid prefers to rest on top of the rough features leading to presence of air pockets in the gaps between the rough features. The equation for calculating contact angle for this state can be derived using free energy arguments as follows.

Let us assume a droplet of water with volume V which when placed on the rough surface takes up a spherical cap shape with a contact angle of θ_{CB} . Let r_b be the radius of the spherical cap. Let the wetting state of the droplet be Cassie-Baxter i.e. there exist air pockets between the liquid and solid. The change in free energy of the system (ΔG) is given by the following equation.

$$\Delta G = \gamma_{LV} (A_C + A_L) + (\gamma_{SL} - \gamma_{SV}) A_S - \gamma_{LV} S \tag{1.10}$$

Here, A_c is the curved surface area of a spherical cap, A_L is the area of contact at the liquid-vapor interface at the base of the cap, A_S is the area of contact at the solid-liquid interface and S is the surface area of the water droplet before it contacts the solid surface, which is constant for a constant volume of the droplet. γ_{LV} , γ_{SL} and γ_{SV} are the surface tensions at the liquid-vapor, solid-liquid and solid-vapor interfaces respectively. Let A_f be the projected area of spherical cap and let $f_1 = A_S/A_f$ and $f_2 = A_L/A_f$. Also, from Young's equation we know that $\gamma_{SV} - \gamma_{SL} =$ $\gamma_{LV} \cos \theta_Y$. Appropriate substitutions in equation 1.10 reduce it to the following equation:

$$\Delta G = \gamma_{LV} [A_C + A_f (f_2 - f_1 \cos \theta_Y) - S]$$
(1.11)

Taking derivative on both sides and substituting $d(\Delta G) = 0$ and $\frac{dA_C}{dA_f} = \cos\theta_{CB}$, we get the

following equation for Cassie-Baxter state:

$$\cos\theta_{CB} = f_1 \cos\theta_Y - f_2 \tag{1.12}$$

For our model calculations we used a single hexagonal unit cell containing one spherical particle (as discussed in the paper). Let $\overline{A_S}$, $\overline{A_L}$ and $\overline{A_f}$ be the area of solid-liquid interface, liquid-vapor interface and projected surface areas of a unit cell respectively and let 'n' be the total number of unit cells constituting the surface.

$$\therefore f_1 = \frac{n.\bar{A_S}}{n.\bar{A_f}} = \frac{\bar{A_S}}{\bar{A_f}}$$
(1.13)

$$f_2 = \frac{n.\bar{A_L}}{n.\bar{A_f}} = \frac{\bar{A_L}}{\bar{A_f}}$$
(1.14)

Unit Cell Calculations: Cassie-Baxter state

For unit cell with single layer roughness, as shown in figure 1c, the area fractions and thus, the contact angles are calculated as follows:

$$\bar{A}_{S} = \frac{\pi D_{1}^{2}}{2} (1 - \cos \alpha_{CB}) \tag{1.15}$$

$$\bar{A}_{L} = \frac{\sqrt{3}L_{1}^{2}}{2} - \frac{\pi D_{1}^{2} \sin^{2} \alpha_{CB}}{4}$$
(1.16)

$$A_{f} = \frac{\sqrt{3}L_{1}^{2}}{2} \tag{1.17}$$

Substituting equations 1.15, 1.16 and 1.17 in equations 1.13 and 1.14, we get:

$$f_1 = \frac{\pi (1 - \cos \alpha_{CB})}{\sqrt{3}r_1^2}$$
 and $f_2 = (1 - \frac{\pi \sin^2 \alpha_{CB}}{2\sqrt{3}r_1^2})$ (1.18)

Substituting f_1 and f_2 in equation 1.12 gives the equation for Cassie-Baxter angle as follows:

$$\cos\theta_{CB} = \frac{\pi(1 - \cos\alpha_{CB})}{\sqrt{3}r_1^2} \cos\theta_Y - \left(1 - \frac{\pi \sin^2\alpha_{CB}}{2\sqrt{3}r_1^2}\right)$$
(1.19)

2. Dual Roughness - Unit Cell calculations:

In the case of dual roughness, the parameters L_1 , D_1 , r_1 correspond to the layer of bigger particles; L_2 , D_2 and r_2 correspond to that of small particles. α_1 is the parameter that defines the flattened base of the spherical particles.

(1) <u>Wenzel State:</u>

Total number of small particles in Unit cell (x)

 $=\frac{Total \ available \ surface \ area \ in \ unit \ cell \ (not \ including \ the \ small \ particles)}{Total \ surface \ area \ of \ unit \ cell \ containing \ one \ small \ particle}$

$$\therefore x = \frac{\frac{\sqrt{3}L_1^2}{2} + \frac{\pi D_1^2}{2}(1 + \cos\alpha_1) - \frac{\pi D_1^2}{4}\sin^2\alpha_1}{\frac{\sqrt{3}L_2^2}{2}}$$
(2.1)

Total surface area of one unit cell = Total projected area of the unit cell + Total surface area of the big particle +

Total surface area of the small particles in the unit cell -

surface area of the projection underneath the big particle

Total surface area of one unit cell = $\frac{\sqrt{3}}{2}L_1^2 + x\pi D_2^2 + \frac{\pi D_1^2(1+\cos\alpha_1)}{2} - \frac{\pi D_1^2}{4}\sin^2\alpha_1$

Roughness Factor =
$$\frac{\frac{\sqrt{3}}{2}L_{1}^{2} + x\pi D_{2}^{2} + \frac{\pi D_{1}^{2}(1 + \cos\alpha_{1})}{2} - \frac{\pi D_{1}^{2}}{4}\sin^{2}\alpha_{1}}{\frac{\sqrt{3}L_{1}^{2}}{2}}$$

: Roughness Factor =
$$\left(1 + \frac{2\pi}{\sqrt{3}r_2^2}\right) \left(1 + \frac{\pi(1 + \cos\alpha_1)}{\sqrt{3}r_1^2} - \frac{\pi \sin^2 \alpha_1}{2\sqrt{3}r_1^2}\right)$$
 (2.2)

$$\operatorname{Let} R_2 = \left(1 + \frac{2\pi}{\sqrt{3}r_2^2}\right) \tag{2.3}$$

and
$$R_1 = \left(1 + \frac{\pi(1 + \cos\alpha_1)}{\sqrt{3}r_1^2} - \frac{\pi\sin^2\alpha_1}{2\sqrt{3}r_1^2}\right)$$
 (2.4)

From equations 2.3 and 2.4, we know that R_1 and R_2 exclusively correspond to big particle layer and small particle layer respectively. Let R_3 be the roughness of the PECVD coating layer in this case. Thus, the effective roughness (R) for the Wenzel state of dual roughness can be defined as follows:

$$R = R_1 \cdot R_2 \cdot R_3 \tag{2.5}$$



Figure S13. Plot of contact angle vs r_1 for a Wenzel wetting state for a surface with hierarchical roughness. Intrinsic water contact angle on a smooth surface is 110° and $r_2 = 2$. The real values of θ_W exist only in the range of $r_1 = 2.3-3$ in this case.

Dual roughness: HMDSO Coating:

Similar to single layer roughness, R₃ in this case was also estimated using AFM analysis.



Figure S14. *R'* calculated using AFM image analysis for a PECVD coating of 1H,1H,2Hperfluoro-1-dodecene as a function of scan size.

The extrapolation to scan size zero gives the value of R_3 as 1.21.

(2) Cassie-Baxter state:

A schematic of Cassie-Baxter state for dual roughness is shown schematically in figure 4b. The fractions for dual roughness can be calculated in a way similar to that of Cassie-Baxter state of single roughness.

 $\overline{A}_{S} = #$ of small particles $(x') \times Wet$ area of one particle

$$\therefore \bar{A}_{S} = \frac{\pi (D_{1}^{2}/2)(1 - \cos\alpha_{1CB})}{\sqrt{3}L_{2}^{2}/2} \times \frac{\pi D_{2}^{2}(1 - \cos\alpha_{2CB})}{2}$$
(2.6)

 $\overline{A}_L = (x'. interfacial area of L - V contact interface of small particle unit cell) + (interfacial area of L - V contact interface of big particle unit cell)$

L-V interface here implies liquid-vapor interface.

$$\therefore \bar{A}_{L} = \frac{\pi (D_{1}^{2}/2)(1 - \cos\alpha_{1CB})}{\sqrt{3}L_{2}^{2}/2} \times \left(\frac{\sqrt{3}L_{2}^{2}}{2} - \frac{\pi D_{2}^{2} \sin^{2}\alpha_{CB}}{4}\right) + \frac{\sqrt{3}L_{1}^{2}}{2} - \frac{\pi (D_{1} + 2D_{2})^{2} \sin^{2}\alpha_{1CB}}{4}$$

$$(2.7)$$

$$A_{f} = \frac{\sqrt{3}L_{1}^{2}}{2}$$

$$(2.8)$$

It can be assumed that $(D_1 + 2D_2)^2 \approx D_1^2$ (2.9)

Substituting equations 2.6, 2.7, 2.8 and 2.9 in equation 1.12, we get the following equations for calculating f_1 , f_2 and thus, the contact angle for Cassie-Baxter state.

$$f_1 = \frac{\pi^2 (1 - \cos \alpha_{1CB}) (1 - \cos \alpha_{2CB})}{3r_1^2 r_2^2}$$
(2.10)

$$f_2 = 1 - \frac{\pi \sin^2 \alpha_{1CB}}{2\sqrt{3}r_1^2} + \frac{\pi (1 - \cos \alpha_{1CB})}{\sqrt{3}r_1^2} \times \left(1 - \frac{\pi \sin^2 \alpha_{2CB}}{2\sqrt{3}r_2^2}\right)$$
(2.11)

$$\cos\theta_{CB} = \frac{\pi^{2}(1-\cos\alpha_{1CB})(1-\cos\alpha_{2CB})}{3r_{1}^{2}r_{2}^{2}}\cos\theta_{Y} - \left[1 - \frac{\pi\sin^{2}\alpha_{1CB}}{2\sqrt{3}r_{1}^{2}} + \frac{\pi(1-\cos\alpha_{1CB})}{\sqrt{3}r_{1}^{2}} \times \left(1 - \frac{\pi\sin^{2}\alpha_{2CB}}{2\sqrt{3}r_{2}^{2}}\right)\right]$$
(2.12)

(3) Penetrating Cassie-Baxter state:

A schematic of Penetrating Cassie-Baxter state is shown in figure 4c. Since, this state exhibits partial Cassie-Baxter character equation 1.12 can be used to calculate the respective contact angles. The fractions for this type of wetting state can be calculated using following equations.

$$\bar{A}_{S} = \left[\frac{\frac{\sqrt{3}L_{1}^{2}}{2} - \frac{\pi D_{1}^{2} \sin^{2} \alpha_{1}}{4} + \frac{\pi D_{1}^{2} (1 + \cos \alpha_{1})}{2}}{\frac{\sqrt{3}L_{2}^{2}}{2}}\right] \times \frac{\pi D_{2}^{2} (1 - \cos \alpha_{PC})}{2}$$
(2.13)

$$\bar{A}_{L} = \left[\frac{\frac{\sqrt{3}L_{1}^{2}}{2} - \frac{\pi D_{1}^{2} \sin^{2} \alpha_{1}}{4} + \frac{\pi D_{1}^{2} (1 + \cos \alpha_{1})}{2}}{\frac{\sqrt{3}L_{2}^{2}}{2}}\right] \left[\frac{\sqrt{3}L_{2}^{2}}{2} - \frac{\pi D_{2}^{2} \sin^{2} \alpha_{PC}}{4}\right]$$
(2.14)

$$A_{f} = \frac{\sqrt{3}L_{1}^{2}}{2}$$
(2.15)

16

Equations 2.13 and 2.14 can be simplified by defining a common factor K.

$$K = 1 - \frac{\pi \sin^2 \alpha_1}{2\sqrt{3}r_1^2} + \frac{\pi (1 + \cos \alpha_1)}{\sqrt{3}r_1^2}$$
(2.16)

Substituting equations 2.13, 2.14, 2.15 and 2.16 in equation 1.12 gives the equation to calculate f_1 , f_2 and thus, contact angle for penetrating Cassie-Baxter state (θ_{PCB}).

$$f_1 = K(\frac{\pi(1 - \cos \alpha_{PC})}{\sqrt{3}r_2^2}) \text{ and } f_2 = K\left(1 - \frac{\pi \sin^2 \alpha_{PC}}{2\sqrt{3}r_2^2}\right)$$
 (2.17)

$$\therefore \cos \theta_{PCB} = K \left[\frac{\pi (1 - \cos \alpha_{PC})}{\sqrt{3}r_2^2} \cos \theta_Y - \left(1 - \frac{\pi \sin^2 \alpha_{PC}}{2\sqrt{3}r_2^2} \right) \right]$$
(2.18)

For the r_2 values that we used in our experiments (1.5 and 2), no real values of θ_{PC} could be calculated using any value of fitting parameter α_{PC} . However, for lower values of r_2 (0.9 for 1H,1H,of 2H-perfluoro-1-dodecene and 1 for HMDSO) real values of θ_{PC} could be calculated and compared with θ_W and θ_{CB} .



Figure S15 : Contact angles predicted for dual roughness unit cell model using Penetrating-Cassie-Baxter wetting state equations and compared to corresponding Cassie-Baxter state, $\theta_Y = 110^{\circ}$, $r_2 = 0.9$ and $\alpha_{PC} = 70^{\circ}$



Figure S16 : Contact angles predicted for dual roughness unit cell model using Penetrating-Cassie-Baxter wetting state equations and compared to corresponding Wenzel and Cassie-Baxter states, $\theta_{Y} = 95^{\circ}$, $r_{2} = 1$ and $\alpha_{PC} = 80$

3. Free energy calculations for different wetting states:

In order to be able to predict the most stable wetting state and to calculate the energy barrier between different possible wetting states, we calculated free energy for each wetting state. The free energy equations are derived as follows.

Similar to the derivation of Cassie-Baxter equation, let a droplet of water with volume V be deposited on a rough surface. The droplet takes up a spherical cap shape with radius r_b and forms a contact angle of θ . The change in free energy for this case is calculated using equation 1.11.

S in equation 1.11 has a constant value for a given volume of a droplet and thus, it results in a constant relative change in all the respective free energies of wetting states. The constant value contributed to the overall free energy change is thus, not accounted for in the calculations here.

Now, for a spherical cap with contact angle θ ,

$$A_c = 2\pi r_b^2 (1 - \cos\theta) \tag{3.1}$$

Let A_f be the projected area of the spherical cap (as defined before in the case of Cassie-Baxter equation derivation).

$$\therefore A_f = \pi r_b^2 \sin^2 \theta \tag{3.2}$$

Substituting equations 3.1 and 3.2 in equation 1.11 we get,

$$\Delta G = \gamma_{LV} \pi r_b^2 [2 - 2\cos\theta + \sin^2\theta (f_2 - f_1 \cos\theta_Y)]$$
(3.3)

$$Now, V = \frac{\pi r_b^3}{3} (2 - 3\cos\theta + \cos^3\theta)$$
(3.4)

20

$$\therefore r_b^2 = (\frac{3V}{\pi})^{2/3} \left(2 - 3\cos\theta + \cos^3\theta\right)^{-2/3}$$
(3.5)

Substituting for r_b^2 (equation 3.5) in equation 3.3, we get an equation of free energy in terms of apparent contact angle as follows:

$$G^* = \frac{\Delta G}{\gamma_{LV} \pi^{\frac{1}{3}} (3V)^{\frac{2}{3}}} = (2 - 3\cos\theta + \cos^3\theta)^{-2/3} [2 - 2\cos\theta + \sin^2\theta (f_2 - f_1 \cos\theta_Y)]$$
(3.6)

In the case of Wenzel state, $f_2 = 0$, $f_1 = R$ and $\theta = \theta_W$

Equation 3.6 thus reduces to:

$$G^*_W = (2 - 3\cos\theta_W + \cos^3\theta_W)^{-2/3} [2 - 2\cos\theta_W - R\sin^2\theta_W \cos\theta_Y]$$
(3.7)

In the case of Cassie-Baxter and Penetrating Cassie-Baxter states, equation 3.6 could be used to calculate G^* , with appropriate substitutions made for apparent contact angle (either predicted using model or measured experimentally), f_1 and f_2 .



Figure S17. Plot of free energy G^* values vs r_1 for Wenzel and Cassie-Baxter states for single layer HNCP array of 250 nm particles



Figure S18. Comparison of G^* values vs r_1 for Wenzel(W) and Cassie-Baxter (CB) states for HMDSO coated dual roughness surface, CB-1.5 and W-1.5correspond to $r_2=1.5$; CB-2 and W-2 correspond to $r_2=2$.



Figure S19. Comparison of G* profiles as a function of r_1 for Cassie-Baxter (CB) and Penetrating-Cassie-Baxter (PCB) states for 1H.1H,2H-perfluoro-1-dodecene PECVD coated dual roughness surface, $\theta_Y = 110^\circ$, $r_2 = 0.9$, $\alpha_{PC} = 70^\circ$, $\alpha_{1CB} = 30^\circ$ and $\alpha_{2CB} = 70^\circ$.



Figure S20. Comparison of G* profiles as a function of r_1 for Wenzel (W), Cassie-Baxter (CB) and Penetrating-Cassie-Baxter (PCB) states for HMDSO PECVD coated dual roughness surface, $\theta_Y = 95^\circ, \alpha_1 = 42.3, r_2 = 1, \alpha_{PC} = 80^\circ, \alpha_{1CB} = 45^\circ$ and $\alpha_{2CB} = 85^\circ$.

Chemical composition of the PECVD coating:

We used XPS to determine the chemical composition of the coating formed using PECVD on the surface of HNCP patterns. We acquired XPS spectra using PHI Quantum 2000 XPS microprobe that uses Al K α radiation. The data for survey spectra were obtained over 0eV-1100eV range of binding energy. We used 117.5 eV pass energy and 0.5 eV step size for survey spectra. These spectra were used to determine the atomic composition of elements on the surface. For further quantification, the high resolution spectra over narrower range of binding energies were acquired and analyzed.



Figure S21. A survey spectrum of PECVD coating of 1H,1H,2H-perfluoro-1-docence on the surface of HNCP pattern.

The survey scans were used to estimate the atomic compositions of the PECVD coating on flat Si wafer and patterned surfaces. On comparing the results, we see that both the spectra show identical elemental peaks. The presence of identical peaks in survey spectra of the two also implies that the coating thickness is more than the typical analysis depth of 10 nm of XPS scans,

which is consistent with the PECVD coated particle thickness measurements we carried out using AFM. (Table 1)



Figure S22. *C1s spectra of PECVD coating of 1H,1H,2H-perfluoro-1-dodecene on the surface of cleaned Silicon wafer (a) and HNCP pattern (b).*

The spectra (a) and (b) in figure S23 look very similar implying that the surface functionality on flat Si wafer and the patterned HNCP array are the same. The peak assignments confirm that all the peak positions correspond to different C atoms in the precursor molecule structure. The results are tabulated below.

Table 2. Peak position and assignments for high resolution XPS C1s spectra of PECVD layer of 1H,1H,2H-perfluoro-1-dodecene on the surface of flat Si wafer and HNCP array of spherical particles

Peak Positions and Assignments						
Peak ID	Binding					
	Flat Si	Structured HNCP pattern	Peak Assignments			
1	286.21	286.47	<u>C</u> -CF _n			
2	288.47	288.66	<u>C</u> F-CF _n			
3	291	290.98	$\underline{C}F_2$			
4	292.94	293	<u>C</u> F ₃			

The similar characteristics are seen in the case of PECVD HMDSO coated HNCP arrays when compared to the HMDSO coating on the surface of flat Si.



Figure S23. A survey spectrum of PECVD coating of HMDSO on the surface of HNCP pattern.



Figure S24. *C1s spectra of PECVD coating of HMDSO on the surface of cleaned Silicon wafer* (*a*) and HNCP pattern (*b*).

Table 3. Peak position and assignments for high resolution XPS C1s spectra of PECVD layer of HMDSO on the surface of flat Si wafer and HNCP array of spherical particles

	Peak Positions		Peak Assignments	
	Flat Si	HNCP pattern		
1	283.36	283.34	$Si-CH_3$ or $Si-CH_2-CH_2$ -	
2	284.3	284.27	Si- $\underline{C}H_3$ or Si- $\underline{C}H_2$ -CH ₂ -	
3	286.5	286.14	- <u>C</u> -O-	