*Electronic Supplementary Information*

# Hierarchical Patterning of Hydrogels by Replica Molding of Impregnated Breath Figures Leads to Superoleophobicity

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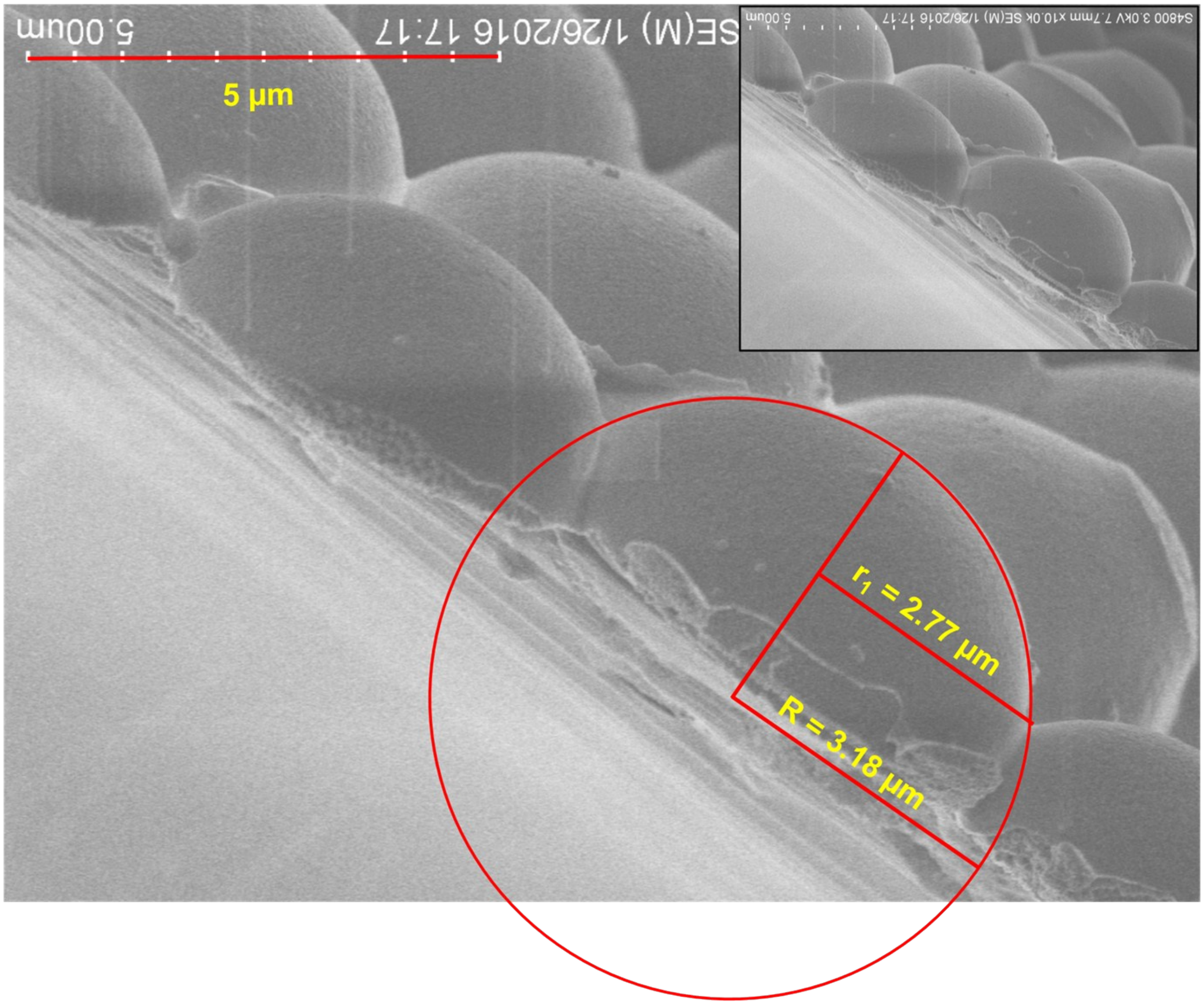


Fig. S1: Estimation of the dimensions of the swollen hydrogel protrusions.

***Estimation of the surface roughness***

The cryo-SEM image of the cross section of the swollen patterned hydrogel in Fig. S1 was utilized to estimate the dimensions of the pattern in the form of spherical caps with a hexagonal base. A circle was drawn to fit the curvature of the spherical cap and the radius of the sphere, $R$ was measured to be 3.18 μm. The scale bar of the micrograph was used as the reference. The radius of the base of the spherical cap, $r_1$ was then measured to be 2.77 μm. The oil contact angle, θ, of of oil (DCE) on the flat submerged poly(2-hydroxyethylmethacrylate) (pHEMA) hydrogel was

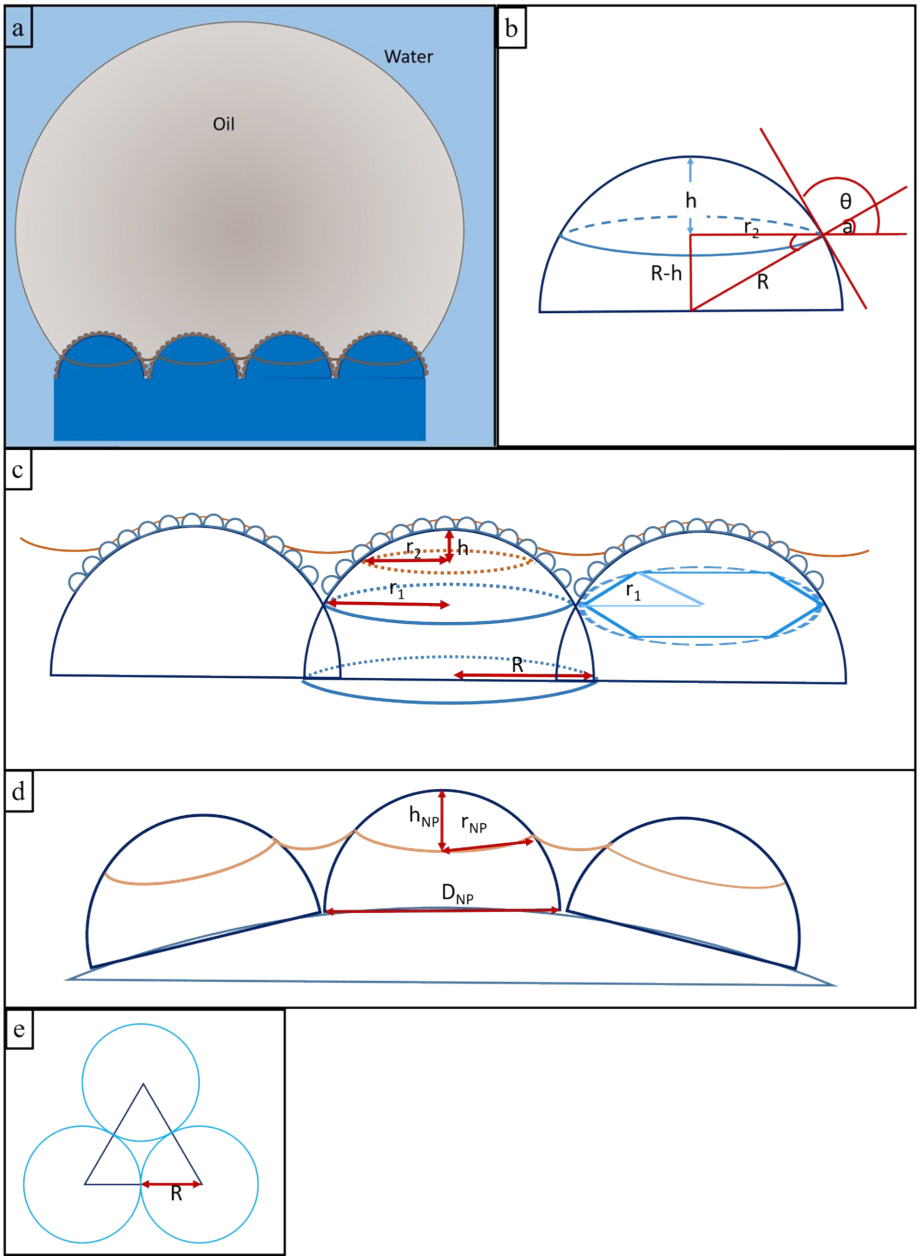


Fig. S2: Profile of the oil droplet partially wetting the rough hydrogel surface. b) Schematic showing the relation of the flat contact angle with the height of the spherical cap upon partial wetting. c) Since the oil drop does not wet all the nanoparticles on a protrusion, it covers each protrusion partially in the form of another spherical cap. d) The oil drop partially wets the nanoparticles and the contact area is in the form of a spherical cap. e) Top view of hexagonally packed spheres on a flat surface. The fraction of the projected area occupied by the spheres is $\pi/(2\sqrt{3})$.

experimentally measured as 134.8° ± 2.5°. Since hydrogels swell in water and are hydrophilic, a hydration layer may exist between the submerged hydrogel and the oil drop. For the purpose of simplicity, we assume that the hydrogel has a thin hydration layer leading to an effective surface energy calculated from the oil contact angle, $\theta$, of the submerged flat hydrogel. As illustrated in Fig. S2, the value of the surface energy will be the same irrespective of whether the surface is flat or patterned and is then used to estimate the contact angle of the rough surface in the partially wetted "fakir" state. When the oil drop partially wets a rough surface lined with hemispherical protrusions, an interface in the form of a spherical cap is formed. Fig. S2c illustrates the oil drop partially wetting the protrusions and also partially wetting the nanoparticles. The area of contact of the oil drop and the nanoparticles is a spherical cap as shown in Fig. S2d. From the geometrical relationship $\sin(\theta - \pi/2) = (D/2 - h_{NP})/(\frac{D}{2})$, the height $h_{NP}$, of this spherical cap is determined as 14.77 nm with D being the diameter of the nanoparticle (100 nm). We assume that the oil drop does not contact all the nanoparticles on individual protrusions, forming another spherical cap on each protrusion. Because of the much smaller size of the nanoparticles as compared to the micron-sized protrusions, we assume that the geometrical relationship $\sin(\theta - \pi/2) = (R - h)/R$ also holds for calculating the height of the spherical cap on each protrusion where $h$ is the height of the spherical cap and $R$ is the radius of the spherical protrusion. The value of $h$ is estimated as 0.94 µm from the value of $R$ (3.18 µm) and $\theta$ (134.8°).

With the specific geometry shown in Fig. S2, the roughness factor ($r^*$) can be determined by:

$$r^* = \frac{area\ of\ solid - oil\ contact}{projected\ area\ of\ the\ solid - oil\ contact} = \frac{\pi D h_{NP}}{\pi r_{NP}^2}$$

(1)

When the hydrogel is swollen, the base of each protrusion is hexagonal with area $A = 3\left(\frac{\sqrt{3}}{2}r_1^2\right)$ although the surface area will be that of a spherical cap of radius $r_1$ ($< R$). Since the oil drop partially wets the surface of the nanoparticles and the surface of the protrusions, the fractional area of contact with oil, $f$, has two components, $f_1$ and $f_2$ where

$$f_1 = \frac{projected\ area\ of\ protrusion - oil\ contact}{projected\ area\ of\ one\ protrusion}$$

, and

$$f_2 = \frac{projected\ area\ of\ nanoparticle - oil\ contact}{projected\ area\ of\ a\ nanoparticle}$$

$f$ is then determined by the following relation,

$$f = \frac{projected\ area\ of\ solid - oil\ contact}{projected\ area\ of\ the\ composite\ surface} = f_1 \times f_2 = \left(\frac{2\pi r_2^2}{3\sqrt{3}r_1^2}\right) \times \left(\frac{\pi r_{NP}^2}{\frac{\pi D^2}{4}}\ \frac{\pi}{2\sqrt{3}}\right) \quad (2)$$

where $r_2$ is the radius of the spherical cap formed when the oil drop partially wets a protrusion, $r_{NP}$ is the radius of the spherical cap formed when the oil drop partially wets a nanoparticle and $\pi/(2\sqrt{3})$ is the fraction of the area occupied by the spherical nanoparticles on the surface of the protrusion as shown in Fig. S2e. Here the surface curvature of the protrusions is ignored and a hexagonal packing of the nanoparticles is assumed in calculating $f_2$. The area of the base in estimating $f_1$ is a hexagon with an area, $A$ ($3\left(\frac{\sqrt{3}}{2}r_1^2\right)$). The radius, $r_2$, is related to the height, $h$, of the spherical cap on the protrusion by the relation $r_2^2 = 2Rh - h^2$ and is calculated as 2.26 μm. Similarly, the radius, $r_{NP}$, is related to the height, $h_{NP}$, of the spherical cap on the nanoparticle by the relation $r_{NP}^2 = Dh_{NP} - h_{NP}^2$ and is calculated as 35.48 nm. The values of $r^*$ and $f$ are then estimated as 1.173 and 0.368 respectively from the relations 1 and 2 above. These values were then used to estimate the contact angle ($\theta^*$) in the partially wetting Cassie-Baxter state using the equation [$\cos\theta^* = r^* f \cos\theta - (1 - f)$] and was evaluated to be 159.42°.