

## Supporting Information

# Aqueous dispersions of lipid nanoparticles wet Hydrophobic and Superhydrophobic Surfaces

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### **Cubosome Preparation:**

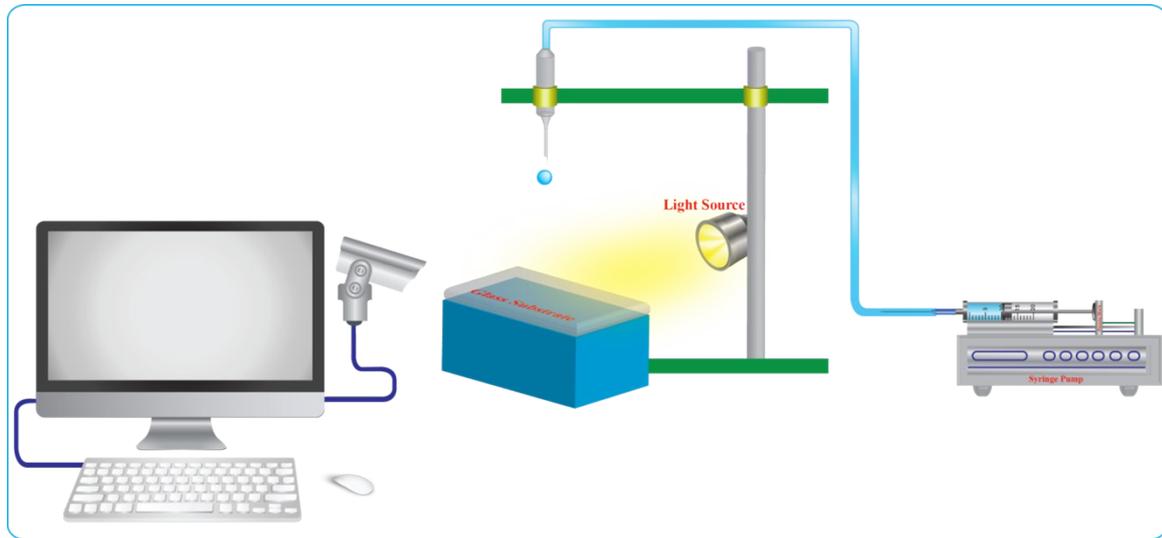
Cubosomes were prepared using previously reported literature protocols.<sup>1</sup> Glycerol monooleate (GMO) is a white solid at room temperature, and was stored at -80 °C to prevent chemical degradation. Before sample preparation, we melt the GMO by heating it at 80 °C. The GMO/F127 blend was prepared by mixing GMO and Pluronic (F127) in 100:5 ratio. The blend was mixed by stirring and heating it at 80 °C for 30 minutes. Finally we add the blend to water. For example, to prepare 10 g sample solution, 0.315 g of GMO/F127 blend (in 100:5 ratio) were mixed with 9.695 g of DI water. The GMO/F127/water blend was mixed using an Ultra Turrax T25 from IKA operated at 10000 rpm for 10-15 minutes. The white milky solution indicates the formation of lipid nanoparticles, known as *cubosomes*. We have previously reported cryo-TEM, SAXS and DLS characterization of cubosomes prepared using this protocol.<sup>1</sup>

**Preparation of hydrophobic surface:** Firstly, we cleaned the glass slide using an acidic piranha etch. The etched slides were stored in water. Before hydrophobic modification, we dried the etched glass slides using inert N<sub>2</sub>. We took toluene in a petri dish and dipped the dry glass slide into it and placed it on a hot plate with a magnetic stirrer. Then, we added 10-15 μl of octyl trimethoxy silane drops to the toluene while stirring. Silanization of the glass surface was carried out at 60 °C. Finally we rinsed the modified glass slide with copious amounts of toluene to remove excess/unreacted silane. Hydrophobization was confirmed by measuring the contact angle of water on the modified glass surface ( $\theta = 104 \pm 2^\circ$ ).

**High Speed imaging set up:** For drop impact experiments, we record videos using a high speed video camera that grabs 3000 frames/s with an exposure of 40 μs. The camera was inclined at 15° to improve the drop visualisation (Figure S1).

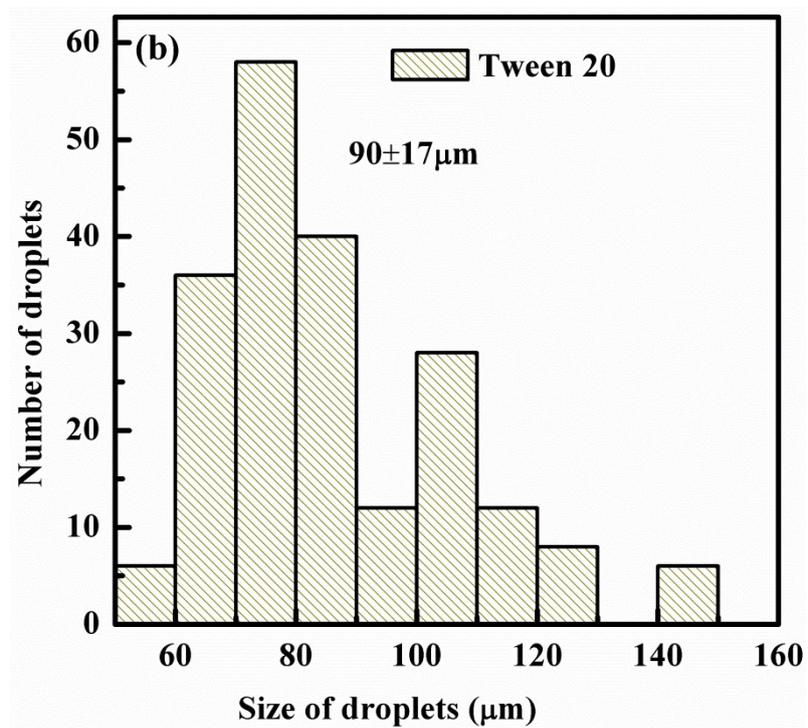
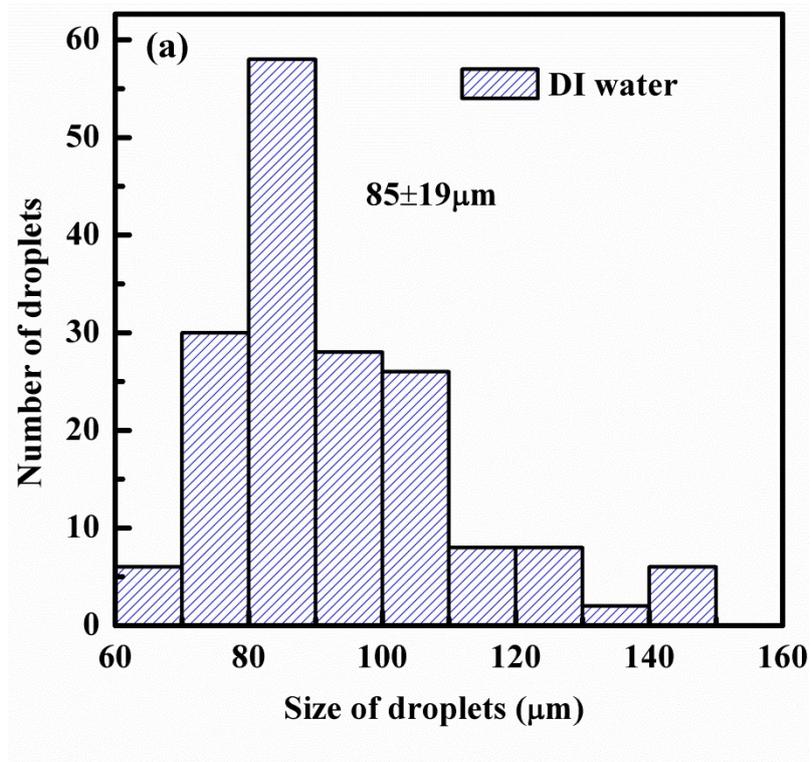
We generate a liquid drop with the help of a Harvard syringe pump connected to a needle through silicon tube of inner diameter 2 mm. The inner diameter of needle nozzle is 0.35(±0.01) mm, the nozzle of same inner diameter was used for all the experiments (yields a droplet volume ~ 10 μl). We heat the needle tip slightly before injecting the liquid through it, which allows us to generate a symmetrical liquid droplet. Initially, the drop of diameter 2.25 ±0.1 mm (averaged over many drops before it impacts). The drop is impacted on the target

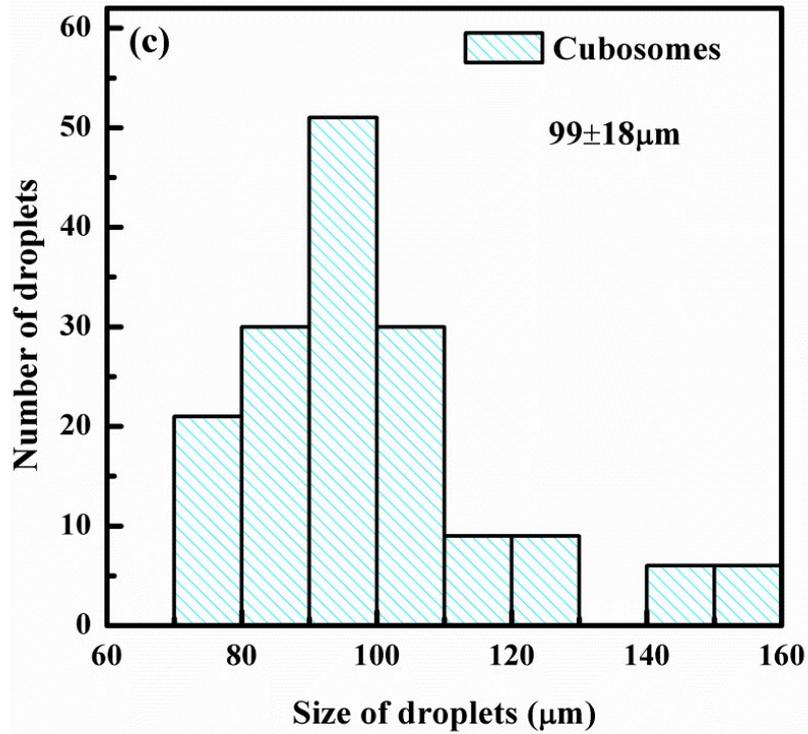
surface from 30cm height with an impact velocity of 2.42 m/s. After recording the videos of drop impingement on the substrate, we analyse the drop dynamics using Image J software.



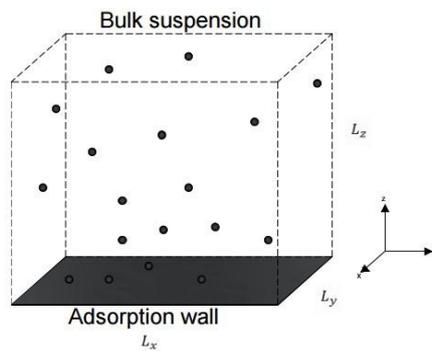
**Figure S1:** Experimental set up for high speed imaging of drop impact.

Spray:

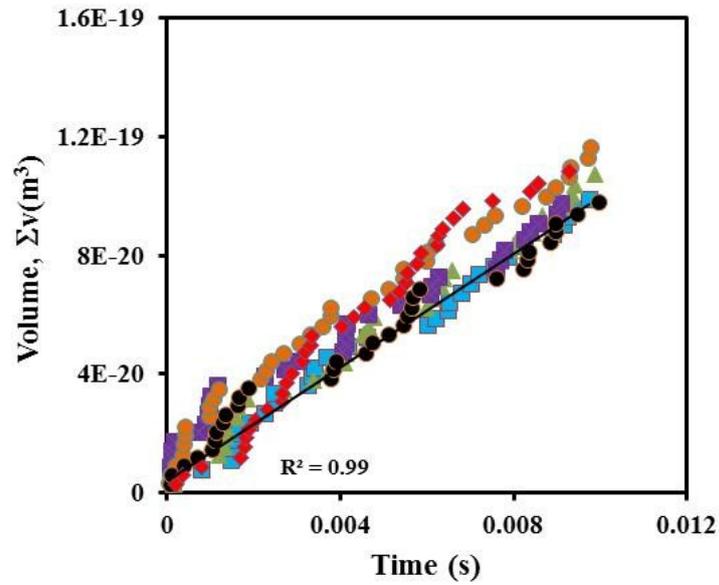




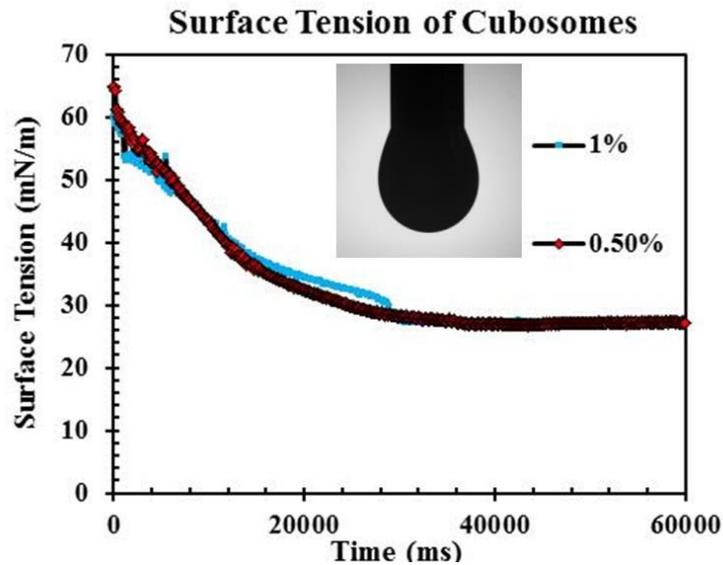
**Figure S2:** Droplet size distribution for liquids sprayed using the commercial sprayer used in our experiments. Liquid was sprayed and droplets issuing from the nozzle were imaged in air, before they impacted a substrate. We present data for droplet size distributions for (a) water, (b) 1% Tween 20, (c) 1% Cubosomes.



**Figure S3:** Simulation box demonstrates the particles diffusion on the adsorbing surface from the bulk.<sup>2</sup>



**Figure S4:** The cumulative adsorbed volume of cubosomes obtained from multiple simulation runs (as indicated by symbols in different colours) for cubosome concentration,  $\Phi=0.9\%$ . The adsorbed volume of cubosomes varies linearly with time. The adsorption rate,  $r_{BD}$ , is obtained as the slope of this data. Similar data was obtained for simulations at different cubosome concentrations.



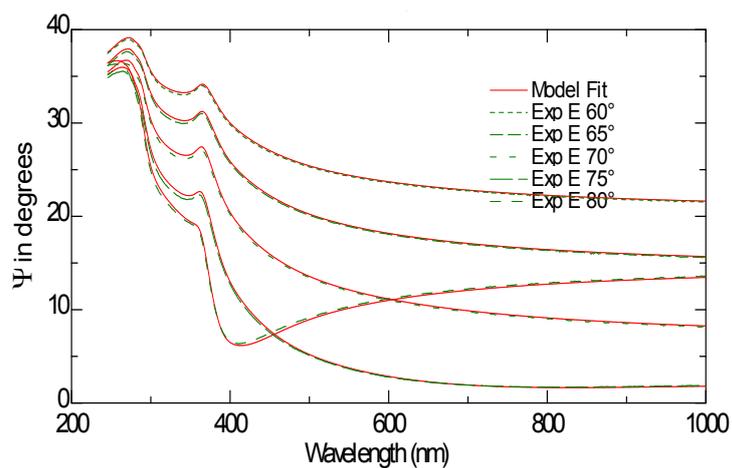
**Figure S5.** The dynamic surface tension of an aqueous drop of lipid nanoparticles is measured using pendant drop method. We used drops of lipid nano particle dispersions at different concentrations viz.  $\Phi=0.5\%$  and  $1\%$  and measured the dynamic surface tension for

60 seconds. We observe that the drop attains an equilibrium surface tension  $\sim 29\text{mN/m}$  in about 10 s.

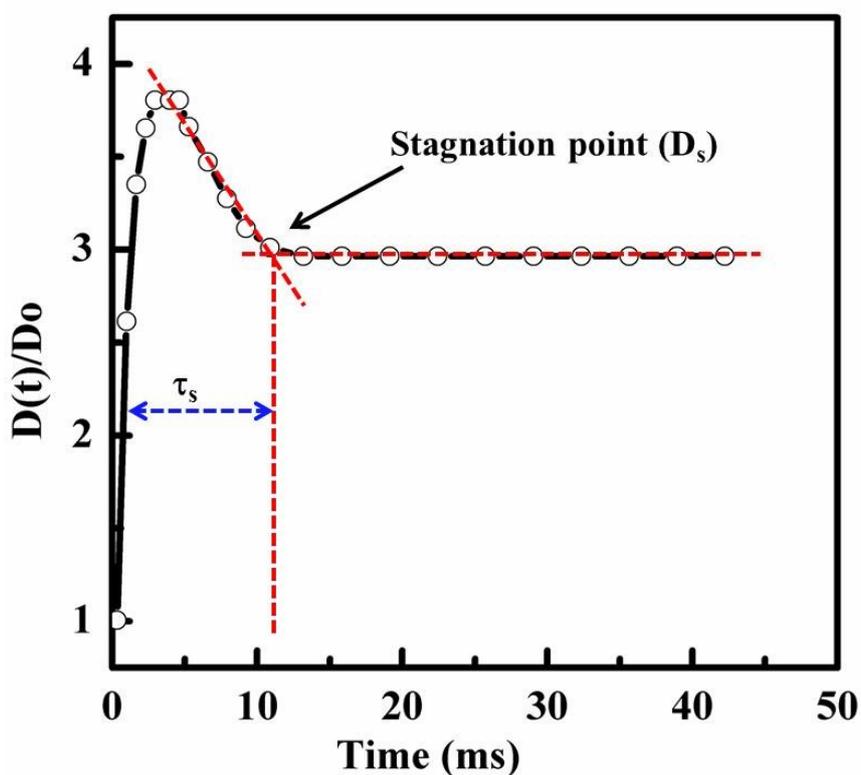
### **Ellipsometry**

Ellipsometry was performed using a 1cm x 1cm silicon wafer as a substrate. This wafer was etched with a piranha solution and subsequently modified with octyl silane, to render it hydrophobic. On the modified hydrophobic surface, we impinged a 1% cubosome dispersion using a drop of size  $\sim 2.2$  mm. Immediately after drop spreading, the substrate was rinsed with DI water and then air dried.

Multi angle spectroscopic ellipsometry measurements were performed on the hydrophobic silicon substrate before and after the drop impact experiment. We used a commercial spectroscopic ellipsometer, M2000 from J. A. Woollam Co, Lincoln, USA. The experiment was conducted in reflection mode at incident angles between  $60^\circ$  to  $80^\circ$  and using incident wavelengths of 200-1000nm. The amplitude ratio,  $\psi$  and phase difference,  $\Delta$  obtained from our experiments were analysed using WASE software, supplied with the ellipsometer. Ellipsometry was initially performed on the hydrophobic silicon substrate and was fitted with a two layer model (silicon substrate/hydrophobized oxide layer) Figure S6. The substrate after drop impingement could not be fitted with a two layer model. Therefore, we used a three layer model: silicon substrate/hydrophobized oxide layer/lipid film. The lipid layer was modeled using a Cauchy form ( $n = A + B\lambda^{-2} + C\lambda^{-4}$ ), since the lipid film does not absorb light in the wavelength range used. We used mean square error minimization to obtain the best fit to our data using the following parameters:  $A = 1.45$ ,  $B = 0.01$ ,  $C = 0$  and refractive index,  $n = 1.480$ . Our data can be fit with a lipid layer thickness of approximately 2 nm, in all our experiments.

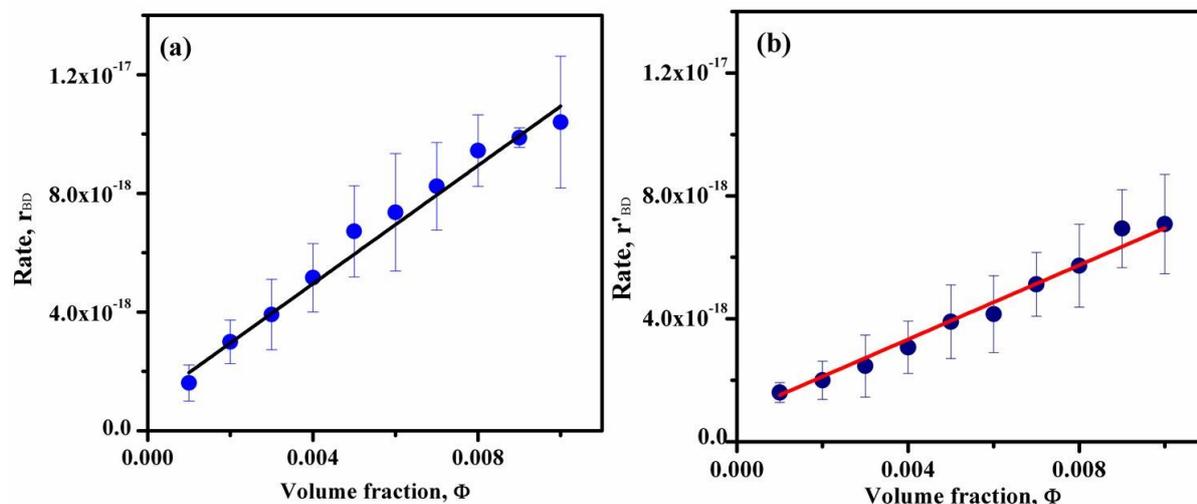


**Figure S6:** Silicon substrate modified using silanization and fitted using a two layer model.



**Figure S7:** The plot shows the retraction of lipid nanoparticle drop impinged on a hydrophobic surface. The point where retraction stops is termed as stagnation point and is characterized by a drop size  $D_s$ , and stagnation time,  $\tau_s$ .

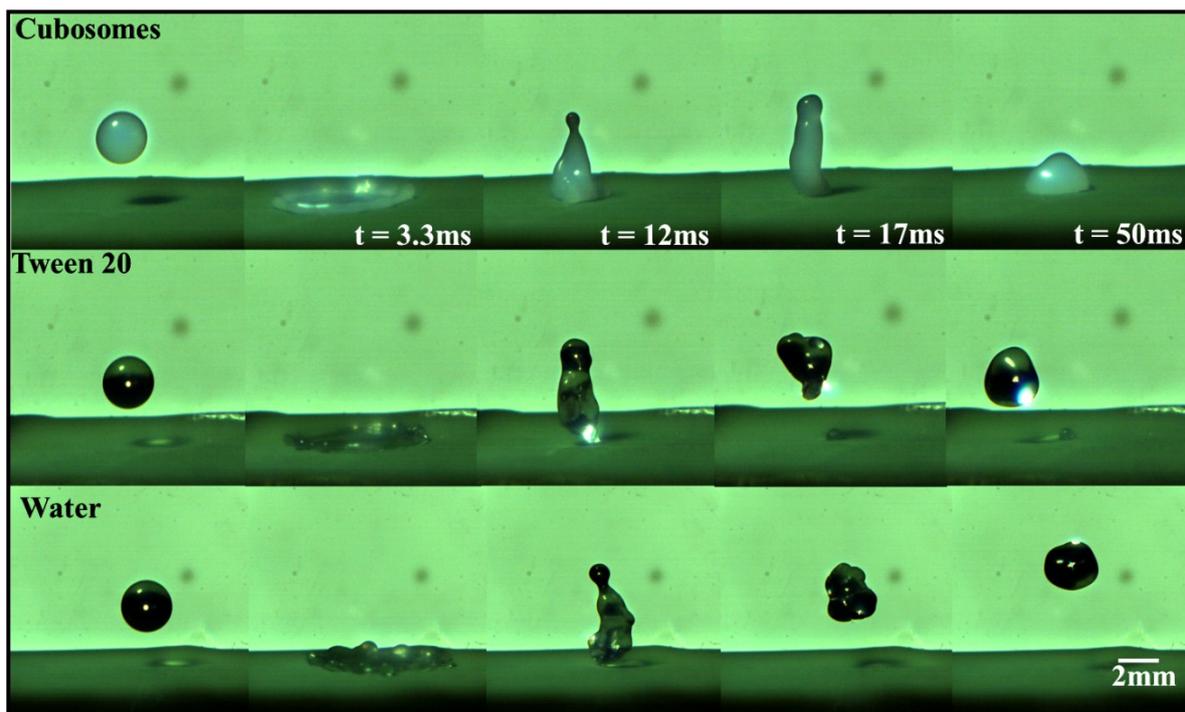
## Simulations



**Figure S8:** (a) The rate of nanoparticle diffusion across the bottom face,  $r_{BD}$  is plotted for different nanoparticle concentration,  $\Phi$ . We observe that  $r_{BD}$  is linear in  $\Phi$ . (b) We obtain the rate for nanoparticle adsorption to form a film, as described in the Simulation Methods,  $r'_{BD}$ . We adjust the fitting parameter,  $k$ , so that the  $\Phi$ -dependence of  $r'_{BD}^{-1}$  matches that of  $\tau_s$ , obtained from experiments.

Liquid drop, volume= $10\mu\text{l}$	Receding contact angle (RCA), degrees	Advancing contact angle(ACA), degrees
Water	$144.3^\circ \pm 3^\circ$	$146.3^\circ \pm 3^\circ$
Tween 20	$130.6^\circ \pm 3^\circ$	$144.3^\circ \pm 3^\circ$
Cubosomes	$106.7^\circ \pm 3^\circ$	$133^\circ \pm 3^\circ$

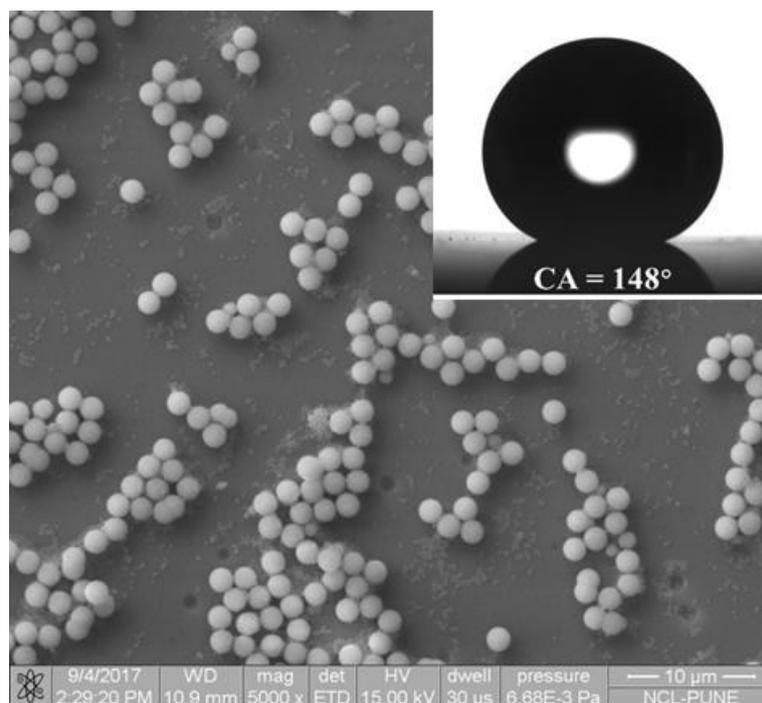
**ST1:** Table shows the receding (RCA) and advancing contact angle (ACA) for the drops of water, tween 20, and lipid nanoparticle dispersions on the lotus leaf inclined at angle  $15^\circ$  with the horizontal. The lotus leaf was supported with the help of a glass slide.



**Figure S9:** Sequence of images shows the spreading of a drop of water (bottom layer), 1% Tween 20 (middle layer), and 1% cubosomes (lipid nanoparticle dispersion) when impinged on a lotus leaf. The images show the behaviour of the drop before impact (first panel,  $t = 0$ ;  $D_0 = 2.20 \pm 0.02$  mm) and at  $t = 3.3, 12, 17$  and  $50$  ms (after impact).

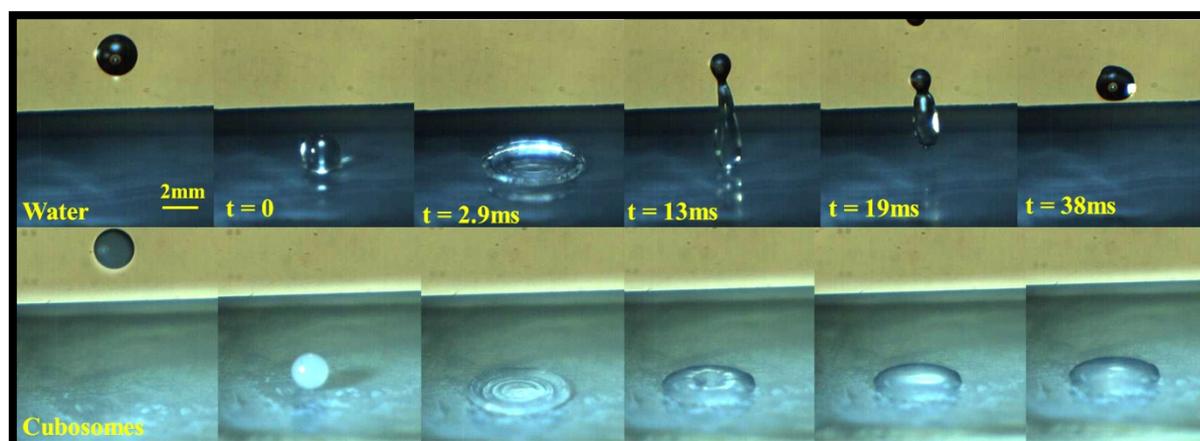
#### Preparation of Artificial Superhydrophobic Surface:

We prepared a 2ml solution of silica particles dispersed in ethanol. Solution was prepared by adding 50mg of 2 $\mu$ m size silica particles to that we add 5 $\mu$ l of 30% PEI (polyethylenimine) solution. Solution was vortexed and then to that added 200 $\mu$ l of 200nm size silica particles solution. A glass slide etched with HF (hydrofluoric) acid was dried under inert N<sub>2</sub> atmosphere. We coat the glass slide with 10 $\mu$ l of particle solution and dried with hot air gun. To burn the polymer and fuse the particles on the surface we stored the coated glass slide in high temperature oven at 600 °C for 4 hours. On the particle coated glass slide we perform silanization reaction using octadecylsilane.



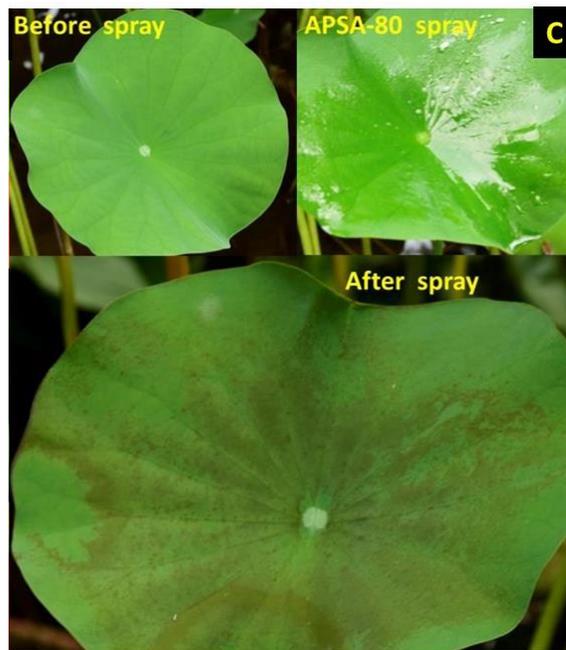
**Figure S10:** SEM of artificial superhydrophobic surface, prepared as describe in the main manuscript. Both 2  $\mu$ m and 0.2  $\mu$ m particles are observed on the substrate surface.

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**Figure S11:** Sequence of images shows the spreading of a drop of water (top layer), and 1% cubosomes (lipid nanoparticle dispersion) when impinging on an artificial superhydrophobic surface. The images show the behaviour of the drop before impact (first panel,  $t = 0$ ;  $D_0 = 2.20 \pm 0.02$  mm) and at  $t = 2.9, 13, 19$  and  $38$  ms (after impact).

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**Figure S12:** Photographs of lotus leaf before and 24 hours after spraying with APSA-80.

SV1: Water drop impacted on hydrophobic glass slide.

SV2: Tween 20 (1% aqueous solution) drop impacted on hydrophobic glass slide.

SV3: Cubosomes (1% aqueous dispersion) drop impacted on hydrophobic glass slide.

SV4: Water drop rolling off inclined Lotus leaf

SV5: Tween 20 (1% aqueous dispersion) drop rolling off inclined Lotus leaf

SV6: Cubosomes (1% aqueous dispersion) drop placed on inclined Lotus leaf

SV7: Water drop impacted on horizontal lotus leaf

SV8: Tween 20 (1% aqueous dispersion) impacted on horizontal lotus leaf

SV9: Cubosomes (1% aqueous dispersion) impacted on horizontal lotus leaf

## References:

1. Deshpande, S.; Venugopal, E.; Ramagiri, S.; Bellare, J. R.; Kumaraswamy, G.; Singh, N., Enhancing Cubosome Functionality by Coating with a Single Layer of Poly- $\zeta$ -Lysine. *ACS Appl. Mater. Interface* **2014**, *6*, 17126-17133.
2. Gray, J. J.; Bonnecaze, R. T., Adsorption of Colloidal Particles by Brownian Dynamics Simulation: Kinetics and Surface Structures. *J. Chem. Phys.* **2001**, *114*, 1366-1381.