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*Antifogging abilities of model nanotextures*

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Nanometer-scale features with special shapes impart a broad spectrum of unique properties to the surface of insects. These properties are essential for the animal's survival, and include the low light reflectance of moth eyes, the oil repellency of springtail carapaces and the ultra-adhesive nature of palm tree bugs. Antireflective mosquito eyes and cicada wings are also known to exhibit some antifogging and self-cleaning properties. In all cases, the combination of small feature size and optimal shape provides exceptional surface properties. In this work, we investigate the underlying antifogging mechanism in model materials designed to mimic natural systems, and explain the importance of the texture's feature size and shape. While exposure to fog strongly compromises the water-repellency of hydrophobic structures, this failure can be minimized by scaling the texture down to nanosize. This undesired effect even becomes non-measurable if the hydrophobic surface consists of nanocones, which generate antifogging efficiency close to unity and water departure of droplets smaller than  $2 \mu\text{m}$ .

## Introduction

Although textured hydrophobic materials show spectacular water-repellency, which causes millimetre-size drops to bounce off such surfaces<sup>1,2</sup>, they generally get wet when exposed to fogs or to humid atmosphere<sup>3-9</sup>. Droplets of a size comparable to that of the surface features can nucleate and grow within – rather than atop – the texture, and this so-called Wenzel state destroys superhydrophobicity<sup>6-9</sup>. Water strongly pinned in this way remains stuck as dew accumulates, resulting in hydrophilic-like behaviour. A large drop contacting this infused solid will also be pinned, owing to the multiple bridges provided by the subjacent wet patches. In humid air, water drops of any size between mist and rain get captured on the previously repellent material, even when it is tilted<sup>3-5</sup>.

These considerations suggest that more effective anti-fogging might result from scaling the texture sizes to the submicrometer range<sup>10-11</sup>, which has other practical benefits such as rendering the coating robust against pressure<sup>12</sup>, or enhancing optical transparency<sup>13</sup> and heat transfer<sup>14-15</sup>. It has been reported that droplets of 10-100  $\mu\text{m}$  condensing on nanotextures can remain mobile enough to allow an efficient transfer of surface energy gained in coalescence to kinetic energy, causing them to sometimes jump off the surface<sup>15-18</sup>. This property has been observed on solids with two-tier roughness<sup>19-21</sup> or colloids<sup>22</sup>, and on cicadae wings covered with nanocones<sup>11</sup> – thus potentially self-cleaned by fogs.

## Model nanotextures

Inspired by these natural examples, we investigate how the anti-fogging properties of model patterned solids are impacted firstly by reducing the texture size, and secondly by changing the texture shape. A first series of substrates is uniformly decorated by pillars with accurately-controlled geometry, and long and dense enough to maintain Cassie configurations even for micrometric drops<sup>23-24</sup>. The pillars we designed have aspect ratios of 2-3 and spacing  $p$  comparable to their height  $h$ . Scanning electron microscope (SEM) viewgraphs show these pillar arrays (Figure 1a). Sample A has the smallest structures, yet large enough to neglect wetting anomalies<sup>25</sup> or structural effects in the liquid<sup>26</sup>. Posts have a radius  $a = 15 \text{ nm}$  and a height  $h = 88 \text{ nm}$ , and they are disposed on an array of rhombuses with side  $p = 52 \text{ nm}$ <sup>27</sup>. The roughness factor  $r$ , ratio of the total to apparent surface area of the solid, is  $r_A \approx 4.5$ . Textures B1, B2 and B3 are homothetic square lattices of posts with a pillar density around 10%, an

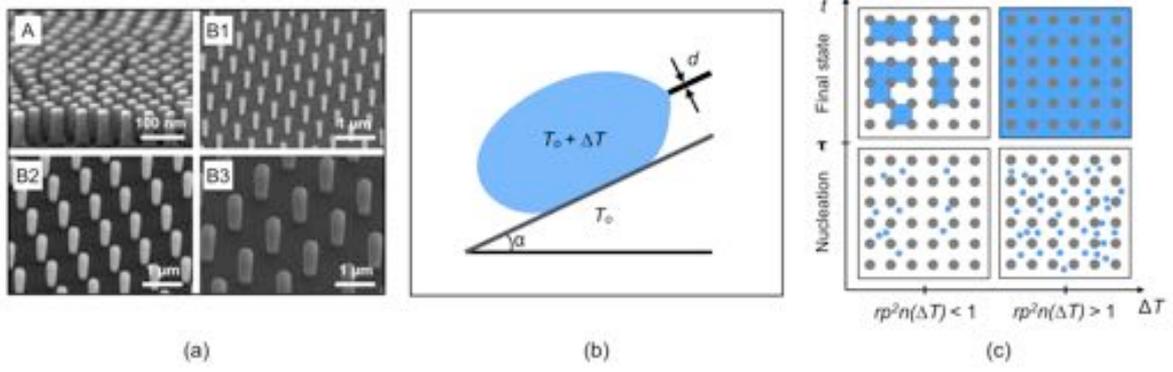
aspect ratio  $h/2a = 3$ , and a roughness  $r_B \approx 2.2$ . The periodicity  $p$  is 560 nm (B1), 840 nm (B2) and 1120 nm (B3), respectively. Surfaces A and B are rendered hydrophobic by vapour deposition of 1H,1H,2H,2H-perfluorodecyltrichlorosilane. This treatment on flat silicon provides an advancing angle for water of  $120^\circ \pm 2^\circ$ .

Roughness enhances hydrophobicity; for textures B1-3, of constant density, we expect<sup>28</sup> and observe comparable advancing and receding water contact angles  $\theta_a = 168^\circ \pm 2^\circ$  and  $\theta_r = 143^\circ \pm 3^\circ$ . Sample A has similar wetting characteristics, with  $\theta_a = 167^\circ \pm 2^\circ$  and  $\theta_r = 140^\circ \pm 2^\circ$ , despite its larger pillar density (which we discuss in the Supplementary Note 1). Anyway, the similarity in wettability allows us to compare materials with the same effective surface energy, but different structure size and periodicity.

### Condensation-induced adhesion

In order to quantify the water-repellency of surfaces exposed to fogs, we examined the adhesion of drops having a temperature  $T_d$  larger than that of the substrate,  $T_o$  (Figure 1b). Water evaporates and recondenses in the textures, and the parameter  $\Delta T = T_d - T_o$  allows us to continuously tune the atmosphere from relatively dry ( $\Delta T = 0$ ) to highly foggy ( $\Delta T > 0$ ). It has been reported that heated water often destroys superhydrophobicity<sup>8,29</sup>: at large  $\Delta T$ , many water nuclei form and grow beneath the drop, which eventually sticks it to its substrate (Figure 1c).

We affix the centimetre-size samples to a brass block anchored at room temperature ( $T_o = 24 \pm 1$  °C) and tilted by  $\alpha = 20^\circ$ . Water at a controlled temperature  $T_d = T_o + \Delta T$  is dispensed from a needle of diameter  $d = 210$   $\mu\text{m}$  at a rate  $Q = 0.25$  mL/min, so that millimetre-sized drops are inflated in a few seconds. We measure the drop mass  $m$  as it detaches from the needle, that is, when its projected weight  $mg \sin \alpha$  ( $g$  is the gravity acceleration) overcomes both the adhesion  $F$  on the surface and the capillary force  $\pi d \gamma$  of the needle, denoting  $\gamma$  as the surface tension of water. Hence we deduce the adhesion force:  $F = mg \sin \alpha - \pi d \gamma$ .



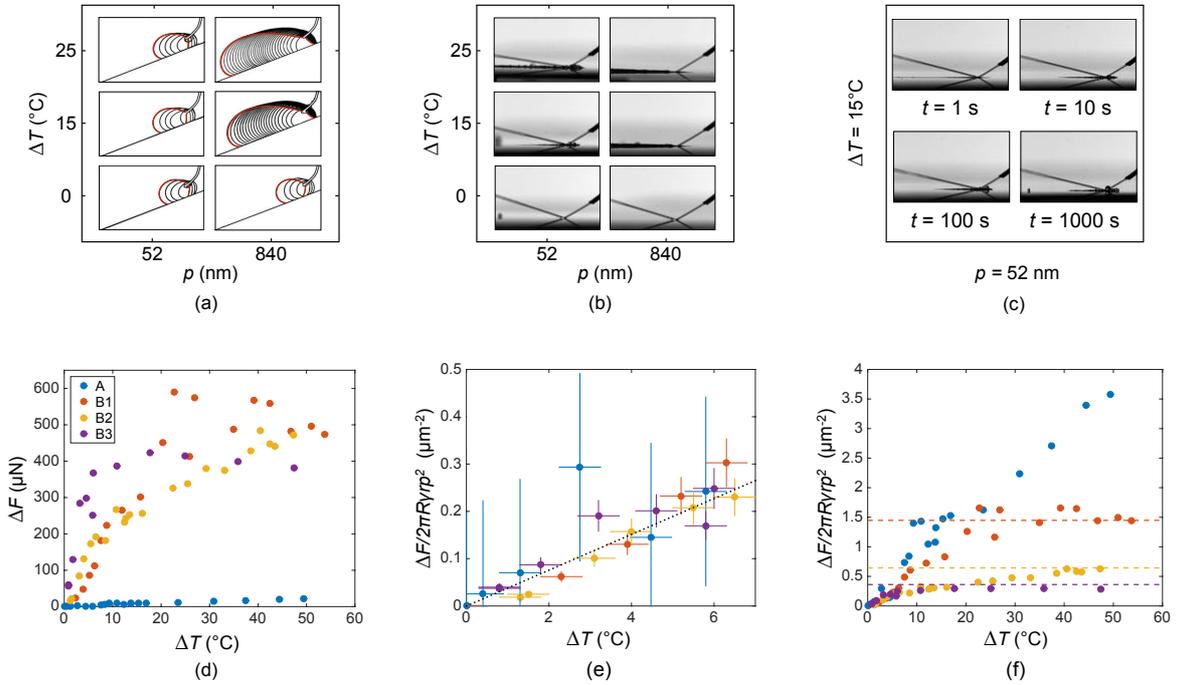
**Figure 1.** Hot drops on hydrophobic pillars. (a) Scanning electron microscope images of the pillar textures used in this study. On sample A, the pillars have a height  $h = 88$  nm, radius  $a = 15$  nm and spacing  $p = 52$  nm. Samples B are homothetic, with pillars of aspect ratio 3 on a square lattice with spacing  $p = 560$  nm (B1), 840 nm (B2) and 1120 nm (B3). (b) Experimental protocol: A needle of diameter  $d$  dispenses water at temperature  $T_d = T_o + \Delta T$  on hydrophobic textures at temperature  $T_o \approx 24^\circ\text{C}$ . The samples are tilted by  $\alpha = 20^\circ$ , and we measure the mass  $m$  of the drop when it detaches from the needle. (c) Schematic of the condensation steps in a cold texture beneath a hot drop, as a function of  $\Delta T$  (horizontal axis) and time (vertical axis). Grey and blue dots respectively show the lattice of pillars and the nuclei of water (of density  $n$ ) condensing on the substrate. At small  $\Delta T$ , there is on average less than one nucleus per cell, which generates disconnected patches when cells are filled ( $t > \tau$ ). At large  $\Delta T$ , there is at least one nucleus per cell, so that water later invades all the structures.

Two factors contribute to  $F$ . First, pinning of water on pillars generates an intrinsic adhesion  $F_o = F(\Delta T = 0)$ , as expressed by the contact angle hysteresis  $\Delta\theta = \theta_a - \theta_r$  (constant for all samples).  $F_o$  is assumed independent of temperature, owing to the modest variation of  $\gamma$  as  $T_d$  increases. Yu *et al.* indeed reported that water-repellency is maintained if both the substrate and water are heated, keeping  $\Delta T = 0$ <sup>29</sup>. Second, additional pinning will result from the nucleation and growth of droplets inside the texture for  $\Delta T > 0$  (Figure 1c). We assume the total adhesion  $F$  is the sum of these two contributions, so that the condensation-induced adhesion  $\Delta F = F(\Delta T) - F_o$  can simply be deduced from  $m$  and  $F_o$ .

Figure 2a shows successive contours of inflating drops (black profiles), until detachment (red profile). Surface A ( $p = 52$  nm) shows little change in the contour of detaching droplets with increasing  $\Delta T$ . In contrast, heating water dramatically amplifies adhesion on surface B2 ( $p = 840$  nm), where drops can become 10 times heavier without moving, even for  $\Delta T$  as modest as  $15^\circ\text{C}$  (Supplementary Movies 1-2). The receding angle in this case reduces significantly (while the advancing angle does not seem affected), which is indicative of stronger pinning.

The mass  $m$  of detaching drops is found to be roughly independent of the injection rate  $Q$  between 0.01 and 0.3 mL/min (as reported in the Supplementary Note 2). At higher flow rates,

inertia makes water come out of the needle as a jet, a regime that can also be tested. Figure 2b shows jets dispensed at  $Q = 1$  mL/min and impacting samples A and B2 (Supplementary Movies 3-4). The results are fully consistent with observations in Figure 2a: both samples exhibit a similar behaviour for  $\Delta T = 0$  (the hallmark of hydrophobicity being here jet rebound) whereas repellency is destroyed on B2 and preserved on A for  $\Delta T = 15^\circ\text{C}$  (or more). Hence repellency of hot water by sample A also holds under dynamic conditions (Supplementary Note 3). In addition, the reflection of hot jets on A is independent of the impact duration in the range 1-1000 s, as shown in Figure 2c.



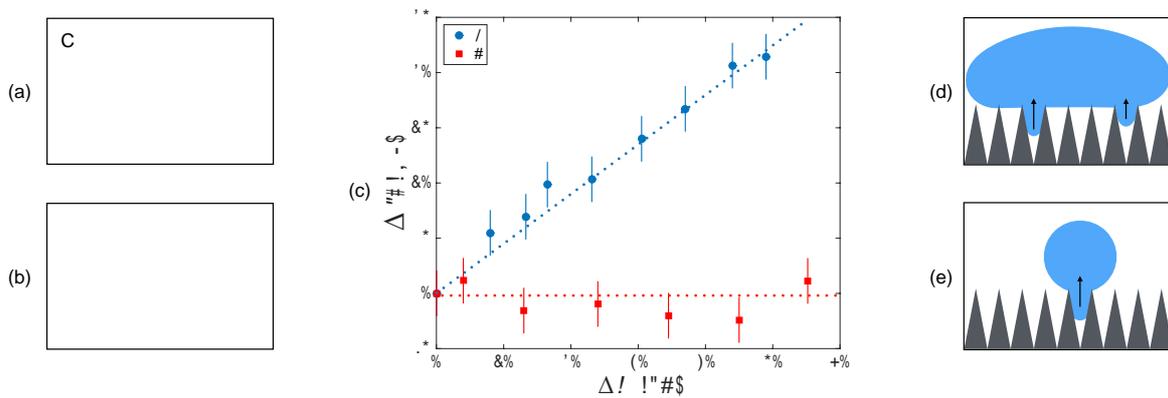
**Figure 2.** Adhesion of cold and hot water on materials A and B. **(a)** Successive profiles of water drops inflated either at the substrate temperature ( $\Delta T = 0$ ), or at a larger temperature ( $\Delta T = 15$  and  $25^\circ\text{C}$ ) on materials A ( $p = 52$  nm) and B2 ( $p = 840$  nm). Time interval between two contours is 0.75 s, and inflating flux  $Q$  is 0.25 mL/min. The red contour corresponds to the maximum mass  $m$  immobilised on the solid. **(b)** At higher flow rate (here  $Q = 1$  mL/min), water comes out of the needle as a jet, whose behaviour on samples A and B2 is shown as a function of temperature  $\Delta T$ . **(c)** For sample A, the rebound of a hot jet does not depend on the duration  $t$  of impact. **(d)** Increment of adhesion force  $\Delta F$  due to a temperature difference  $\Delta T$  between water and its substrate for the surfaces of Figure 1a. **(e-f)** Adhesion force  $\Delta F$  normalized by its maximum  $2\pi R\gamma$ , and presented per unit area  $rp^2$  of pillar cell, as a function of  $\Delta T$ . The colour code of the data points is the same as in (d). In (e), data at small  $\Delta T$  collapse on the same curve (the dotted line is a guide for the eyes). In (f), data separate at larger  $\Delta T$ , and coloured dashed lines are the plateaus  $1/rp^2$  predicted by Eq. 1, for each B-substrate. The parameter  $1/rp^2 = 82 \mu\text{m}^2$  for surface A is out of the scale.





## Feature shape effect

While the texture size impacts a hydrophobic surface's ability to resist fogging, its shape can further enhance the effect. Here, we compare the behaviour of cylindrical and conical nanopillars undergoing water condensation. A fifth model material used in this study (Sample C, Figure 3a) is designed with a texture similar to that on the wings of the cicada *Psaltoda claripennis* (Figure 3b), for which antifogging properties were reported<sup>11</sup>.



**Figure 3.** Comparison of the adhesion of hot drops on nanopillars and on nanocones. **(a)** SEM image of the nanocones (sample C) used in this study. They are 115 nm-high and disposed on a lattice with spacing  $p = 52$  nm. **(b)** Nanotextures on cicada (*Psaltoda claripennis*) wings shown by atomic force microscopy (picture adapted from ref. 11). **(c)** Adhesion force  $\Delta F$  due to condensation, as a function of temperature difference  $\Delta T$  between water and substrate. We compare the adhesion on substrate A (blue circles, see also Figure 2b) to that on substrate C (red squares). **(d)** Sketch showing the effect of geometry: droplets beneath a large drop can be reabsorbed. **(e)** Similarly, small droplets condensing in cones can reconfigure at the cone tops.

Surface C is covered by a dense array of nanocones with roughness  $r_C \approx 4.2$  and treated by the same silane as previous samples. The conical structures with height  $h = 115$  nm are created via the approach used for Sample A (Figure 1a), with slight changes to the etching conditions<sup>27</sup>. The spacing (or base diameter)  $p = 52$  nm is that of Sample A, allowing studies of structures which differ only in profile. The new design produces a high degree of hydrophobicity, with water angles  $\theta_a = 170 \pm 2^\circ$  and  $\theta_r = 163 \pm 2^\circ$ . Compared to Sample A, the advancing angle increases by  $10^\circ$  and the hysteresis decreases by  $10^\circ$ , due to the geometrical reduction of liquid contact.

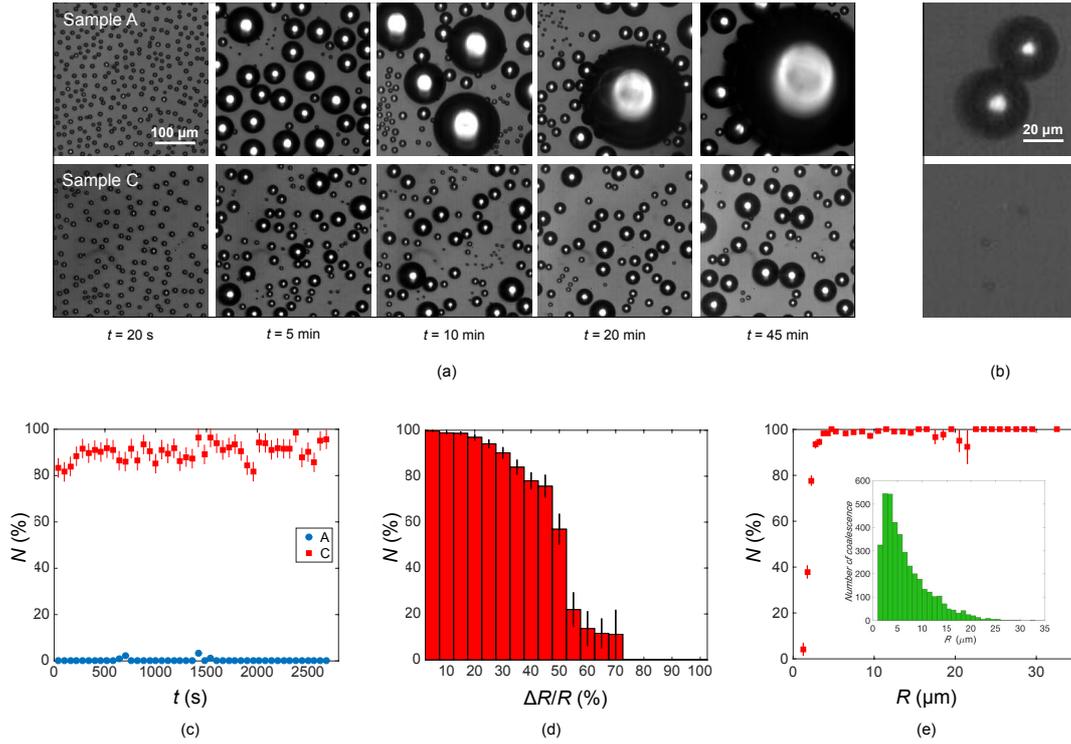
Nanocones are far less adhesive toward hot water (Figure 3c, red squares) than nanocylinders with the same spacing (Sample A, blue circles) – the surface that previously outperformed all

larger structures B1-3 (Figure 2d). Within the measurement uncertainty, surface C has nearly no variation of adhesion  $\Delta F$  with increasing condensation strength  $\Delta T$ , in contrast to substrate A where  $\Delta F$  increases linearly with  $\Delta T$ . The conical geometry influences water adhesion in two ways (Figure 3d): as suggested numerically in ref. 32, it impedes condensation at the bottom of the structures, where pillar spacing vanishes; and it provides a Laplace expulsion out of the texture, preventing formation of durable wet patches. These effects conspire to keep the liquid in a full Cassie state, with no increase of adhesion as condensation proceeds, even for isolated microdrops (Figure 3e).

### **Statistical analysis of the antifogging ability**

We evaluate the promising anti-fogging behaviour of nanocones under the more realistic conditions of dew formation. Samples are placed upside down on a Peltier module and brought to a temperature such that the supersaturation  $S$  (ratio between vapour pressure at laboratory temperature and saturated vapour pressure at surface temperature) is kept constant for all experiments, at a value  $S = 1.7 \pm 0.1$ . We observe the breath figures with an inverted microscope over the course of 45 minutes and take one image every 2 s.

Breath figures on nanocylinders (Sample A) markedly differ from those on nanocones (Sample C) (Figure 4a). At short times ( $t = 20$  s), both substrates are similarly covered by a large number of microdroplets (radius  $\sim 5 \mu\text{m}$ ), but differences become readily apparent after 5 minutes: the cylindrical texture then forms large droplets, while conical structures show only a few of intermediate size and a new generation of microdroplets. This population can be understood from movies (Supplementary Movie 5): growing droplets coalescing with their neighbours irreversibly jump from conical nanotexture, as shown in Figure 4b, with an average size of  $9 \mu\text{m}$ . As a consequence, the breath figure on Sample C does not evolve with time, while drops keep growing on Sample A. Thus, the volume of water adhered to the solid after 45 minutes falls from  $\sim 50 \text{ nL/mm}^2$  on A to only  $\sim 5 \text{ nL/mm}^2$  on C.



**Figure 4.** Condensation of water from a supersaturated atmosphere on nanoscale cones and pillars. **(a)** Breath figures on samples A and C under an optical microscope after 20 seconds, 5 minutes, 10 minutes, 20 minutes and 45 minutes. The scale bar indicates  $100\ \mu\text{m}$ . **(b)** Snapshots of surface C before (top) and after (bottom) two drops coalesce and jump off. **(c)** Time evolution of the percentage  $N$  of coalescences resulting in droplet jumps for samples A (blue circles) and C (red squares). Each point is obtained by averaging the proportion of jumps over one minute, from a total number of 5500 coalescences for sample C and 2000 for sample A. **(d)** Antifogging ability  $N$  on material C as a function of  $\Delta R/R$ , the relative difference between coalescing drops' radii larger than  $4\ \mu\text{m}$ .  $N$  decreases sharply around  $\Delta R/R = 0.5$ , which corresponds to droplet volumes differing by a factor 10. **(e)** Antifogging ability  $N$  as a function of  $R$ , the common radius ( $\Delta R/R < 0.2$ ) of drops coalescing on sample C.  $N$  reaches a constant value of 99% independent of  $R$ , down to a sharp cutoff value  $R_{\text{min}} = 1.5 \pm 0.2\ \mu\text{m}$ . The insert shows the size distribution of drops coalescing on sample C with  $\Delta R/R < 0.2$ .

We quantify in Figure 4c the antifogging efficiency by measuring the proportion  $N$  of drops jumping after coalescence. After observing  $\sim 7500$  coalescences (5500 for the cones, 2000 for the pillars), we plot  $N$  versus time; each data point represents an average over one minute, corresponding to typically 150 coalescences on cones, and 50 on pillars. The difference between these numbers arises from the difference in breath figures, which produce more coalescences on cones. For both textures,  $N$  is constant in time, but its value dramatically differs. In a cylindrical texture,  $N$  is essentially zero (only 5 droplets were observed to take off), while more than 90% of droplets leave conical features. Jumping droplets have been reported on cicada wings<sup>11</sup>, nanoneedles<sup>18</sup>, Glaco nanobeads<sup>22</sup> or hierarchical surfaces<sup>20-21,33</sup> – the only case where  $N$  was reported<sup>33</sup> and found to be around  $\sim 30\%$ . We show in Supplementary Note 7 that statistics for Glaco under similar conditions gives  $N \approx 6\%$ .

Hence nanocones provide remarkable antifogging abilities: the rare events of coalescence without jump correspond to asymmetric merging, as shown in Figure 4d where the probability of jump  $N$  is plotted as a function of the relative difference in radius  $\Delta R/R$ , for drops larger than  $4\ \mu\text{m}$ . For similar sizes ( $\Delta R/R < 0.2$ , 2300 events in a total of 3200 two-body coalescences), we measure  $N \approx 99\%$ , producing the impression of extensive departure observed in the accompanying Supplementary Movie 5. However,  $N$  falls to  $\sim 20\%$  around  $\Delta R/R \sim 0.5$ , corresponding to a 10-fold volume difference between droplets. For such marked asymmetries, the smaller drop does not communicate enough momentum to generate takeoff. Error bars and fluctuations also increase, due to the rarity of asymmetric events (100 for  $\Delta R/R > 0.5$  compared to 3100 for  $\Delta R/R < 0.5$  in Figure 4d).

The antifogging ability  $N$  for similar drops ( $\Delta R/R < 0.2$ ) is finally plotted in Figure 4e as a function of the average drop size  $R$ . Antifogging is found to keep its full efficiency ( $N \approx 99\%$ ) in a very broad range of radii (from  $\sim 3\ \mu\text{m}$  to  $32\ \mu\text{m}$ , corresponding to drop volumes differing by a factor 1000), which confirms that the 10% probability of having no jump in Figure 4c is mostly due to size contrast between merging drops. The insert shows the coalescence distribution used to perform this statistics. It peaks at small size ( $R = 2\text{-}3\ \mu\text{m}$ ), and the statistics for  $R < 3\ \mu\text{m}$  is based on 870 events. In this range, we observe a modest decrease of  $N$  as  $R$  decreases, followed by a sharp fall, which defines a cut-off radius  $R_{min}$  for departing. Quantifying  $R_{min}$  as the radius at  $N = 50\%$ , we measure  $R_{min} = 1.5 \pm 0.2\ \mu\text{m}$ . This quantity can be used as a metrics of water mobility on textures: the smaller  $R_{min}$ , the more fog-repellent the material. In the few cases where it was discussed, this distance was found to be typically  $10\ \mu\text{m}$ , a value attributed to the interactions with the substrate<sup>34-35</sup>. Our value is much smaller, which highlights the extreme mobility of droplets on nanocones, even at a microscale. The value of  $R_{min}$  might be understood by comparing the radius  $\ell$  of the contact line to the texture period. On a non-wetting material at small  $R$ , we have  $\ell \approx R(\pi - \theta_a)$ , taking the advancing angle as the relevant one for a growing drop. For  $R = R_{min} \approx 1.5\ \mu\text{m}$  and  $\theta_a \approx 170\pi/180$ , we obtain  $\ell \approx 250\ \text{nm}$ , a value comparable to  $90\ \text{nm}$ , the largest distance between neighbouring cone tops on sample C. Such droplets (or smaller) may sag between cones, which impedes their mobility.

Hence feature small size was found to improve anti-fogging abilities (as assumed for mosquitoes' eyes<sup>10</sup>), an effect maximized by shaping nanofeatures into cones (such as

observed on cicadae's wings<sup>11</sup>). The existence of an optimum of antifogging for dense nanocones could be discussed both by considering intermediate shapes between cylinders and cones, and by diluting nanofeatures. Departing drops also raise interesting questions of fluid dynamics: takeoff speeds can approach 1 m/s for micrometric drops, a value much smaller than predicted by a transfer of surface energy in kinetic energy, which remains to be understood. This speed might be sufficient in most natural systems to allow droplets to go with the wind, but what happens if they go back to the substrate remains to be described: at such microscales, air viscosity slows down these drops that can get stuck at impact – except in cases where they meet other condensing drops and participate to their evacuation. More generally, the remarkable water repellency of nanocones arrays, even for microdrops, yields a new kind of platform for manipulating such tiny quantities of cold, or even hot, water.

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## **3. Author contributions**

*Ti.M. and D.Q. conceived the project, Ti.M., G.L., Th.M., C.C. and D.Q. designed the project, G.L. and S.X. produced samples B1-3, A.C., A.T. and C.T.B. produced samples A and C, Ti.M. and A.C. performed experiments and analyses, Ti.M., C.C. and D.Q. discussed the models, Ti.M. and D.Q. wrote the manuscript with inputs from all other authors.*

## **4. Data availability statement**

*The datasets generated during current study are available from the corresponding author on reasonable request.*

## **5. Additional information**

*Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at [www.nature.com/reprints](http://www.nature.com/reprints). Correspondence and requests for materials should be addressed to Ti.M. or D.Q.*

## **6. Competing financial interests**

*The authors declare no competing financial interests.*

## 7. Methods

### Model nanotextures

Sample A: This surface is fabricated by combining block-copolymer self-assembly with anisotropic plasma etching in silicon, which provides large-area ( $\text{cm}^2$ ) textures with  $\sim 10$  nm feature size and long-range order as described in Checco *et al.* in ref 27. Posts on sample A have a radius  $a = 15$  nm and a height  $h = 88$  nm, and they are disposed on a rhombus network with side  $p = 52$  nm. The roughness factor  $r$  is  $r_A \approx 4.5$ .

Sample B1, B2 and B3: These textures are square lattices of pillars fabricated by electron-beam lithography and anisotropic plasma etching in silica. These homothetic surfaces have a pillar density of about 10%, an aspect ratio  $h/2a = 3$ , and a roughness  $r_B \approx 2.2$ . The pillar sizes, heights and spacings  $a$ ,  $h$ ,  $p$  are respectively 100, 600, 560 nm (surface B1), 150, 900, 840 nm (B2), and 200, 1200, 1120 nm (B3).

Sample C: Nanocones are fabricated by using the exact same method as for sample A, and the only difference comes during the etching step. To obtain conical shape, etching is made more isotropic as described in Checco *et al.* in ref 27. Cones on sample C have a height  $h = 115$  nm, and a texture's spacing (or base diameter)  $p = 52$  nm, as for Sample A. Cones have a roughness factor  $r_C \approx 4.2$ , close to that of A.

Chemical vapour deposition is made by activating the surface in a plasma cleaner during 45 seconds. The activated surface is enclosed in a Petri dish close to a plastic well containing typically  $\sim 20$   $\mu\text{L}$  of 1H,1H,2H,2H-perfluorodecyltrichlorosilane and desiccants to avoid reaction between the silane and water contained in the air. The silane used is referenced as L16584.03 in VWR.

### Condensation induced adhesion

Immersing the syringe and the connecting tube in a thermostated liquid controls the drops' temperature. The thermostated water is contained in a cylindrical copper pipe closed with a brass plate where the needle is attached. We control the temperature via the voltage applied to a silicon heater mat (referenced as 245-534 on RS Components) glued to the copper container and precisely monitored with a temperature sensor.

### Condensation observations

We place the substrate on a Peltier module (referenced as 693-7043 on RS Components) whose hot side is cooled with a heat sink coupled to a fan (commonly used for CPU cooling). The samples are brought to a temperature such that the supersaturation  $S$  (ratio between vapour pressure at laboratory temperature and saturated vapour pressure at surface temperature) is kept constant for all experiments at a value  $S = 1.7 \pm 0.1$ . The samples are mounted upside down on the Peltier module's underside, so that any droplets jumping from the surface do not return. We observe the breath figures during 45 minutes using an inverted microscope (Amscope IN300-FL) connected to a high-resolution video-camera (Photron Fastcam SA3).