Electronic Supplementary Material (ESI) for Soft Matter.

Electronic Supporting Information:
Increasing aspect ratio of particles suppresses buckling in shells formed by drying suspensions

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EXPERIMENTAL DETAILS

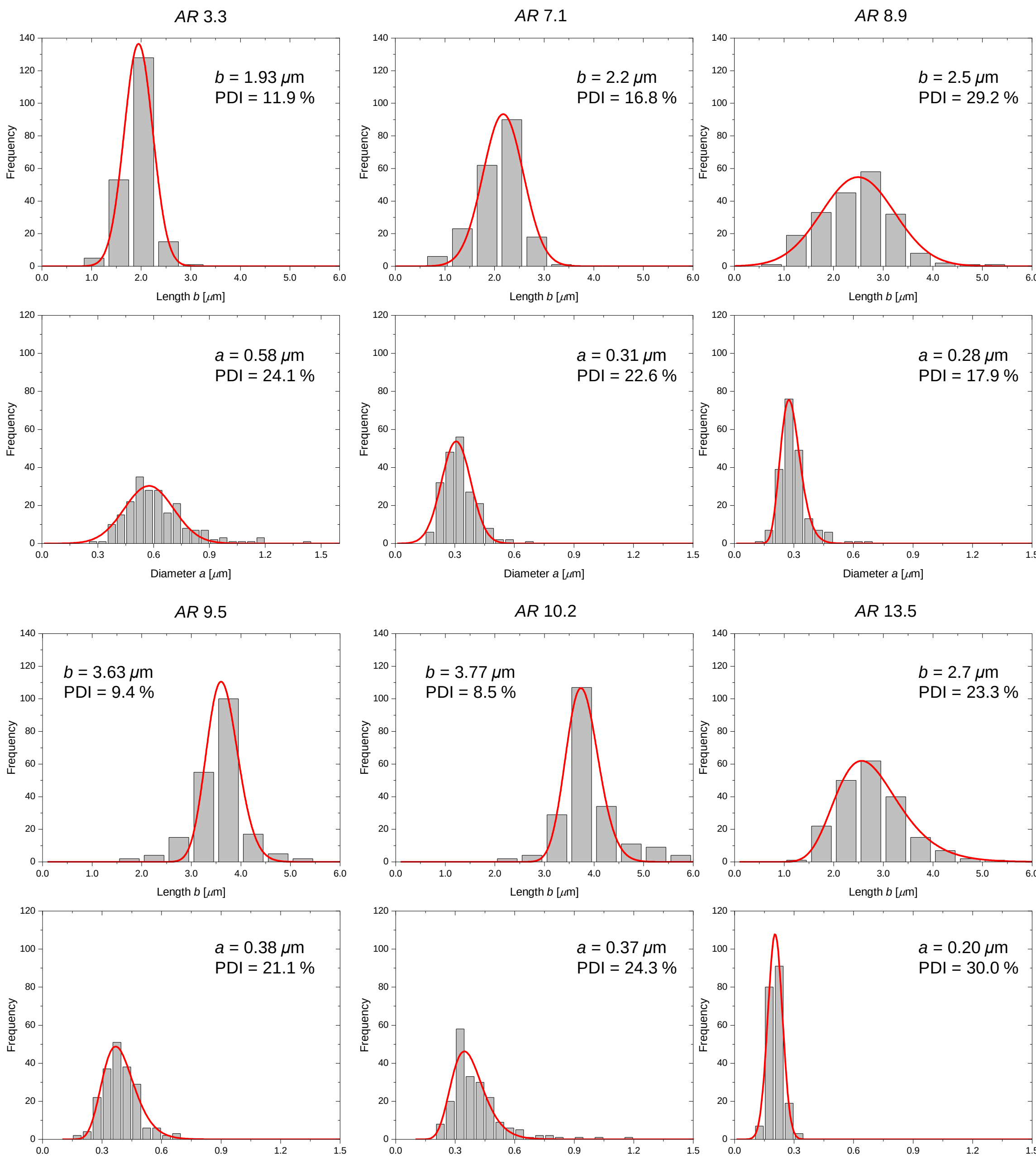

Fig. S1 Size distribution for all aspect ratio rods synthesized, defined as *AR* = *b*/*a* where *b* is the length and *a* is the diameter of the rod particle. All lengths are measured from analysis of scanning electron microscope images containing more than 200 particles per sample. The bars represent the measured data, and lines are fits to the data using log-normal distribution function. The polydispersity index (PDI) values given in the plots are determined using standard deviation of the distribution.

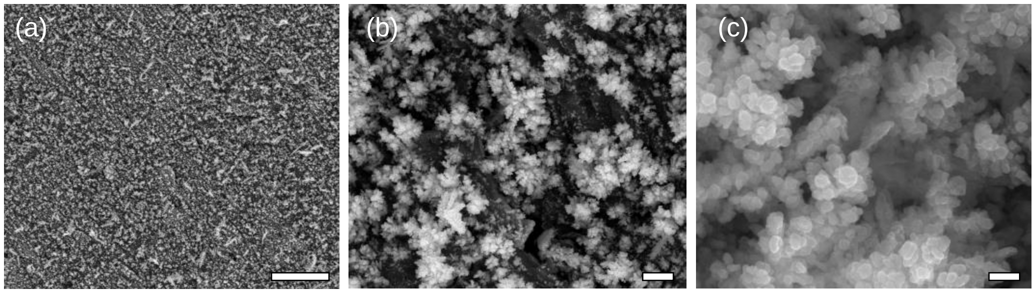

Fig S2 Scanning electron micrographs of the copper plate with electrochemically deposited silver crystals at three magnifications: (a) 500x with scale bar representing 50 μm, (b) 6500x with scale bar representing 2 μm and (c) 65000x with scale bar representing 200 nm. The air pockets on the nanostructured surface render the substrate superhydrophobic.

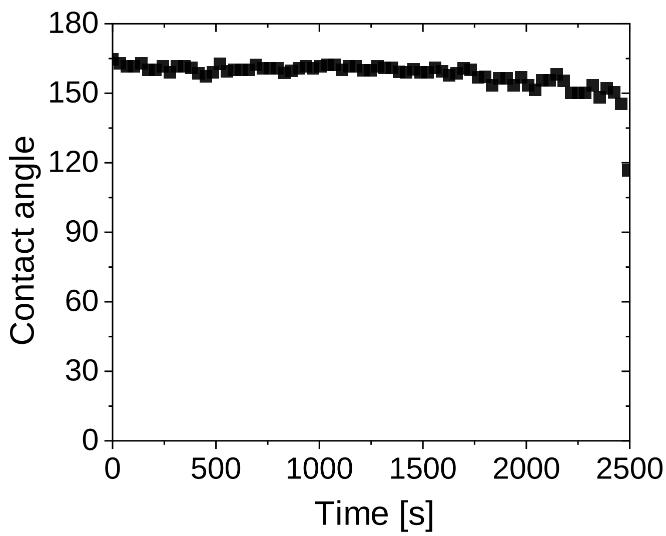

Fig S3 Measured contact angle between water droplet and the superhydrophobic substrate, throughout drying. The initial droplet volume was 3 μl.

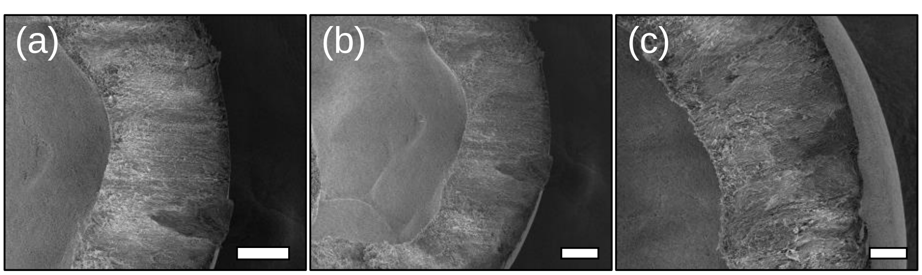

Fig. S4 Scanning electron micrographs of shells packed with rods of aspect ratio (a) 9.5, (b) 10.2 and (c) 13.5. All scale bars represent 50 μm.

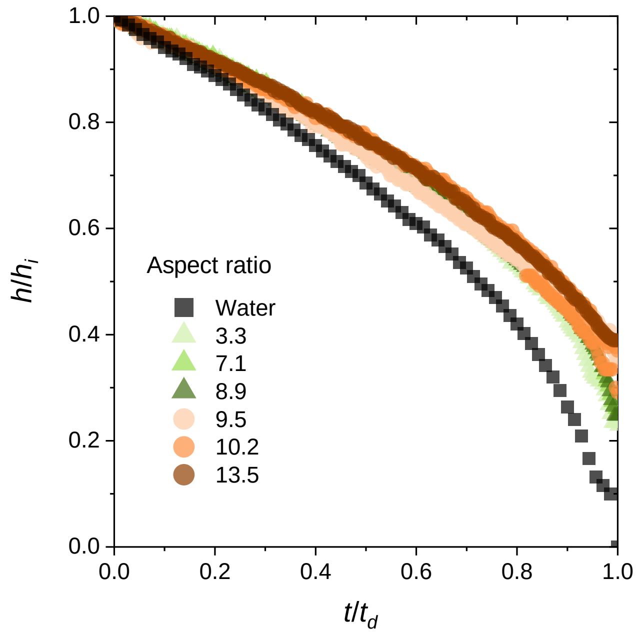

Fig. S5 Change in the normalized height of drying aqueous droplets in the absence and presence of rods with increasing aspect ratio.

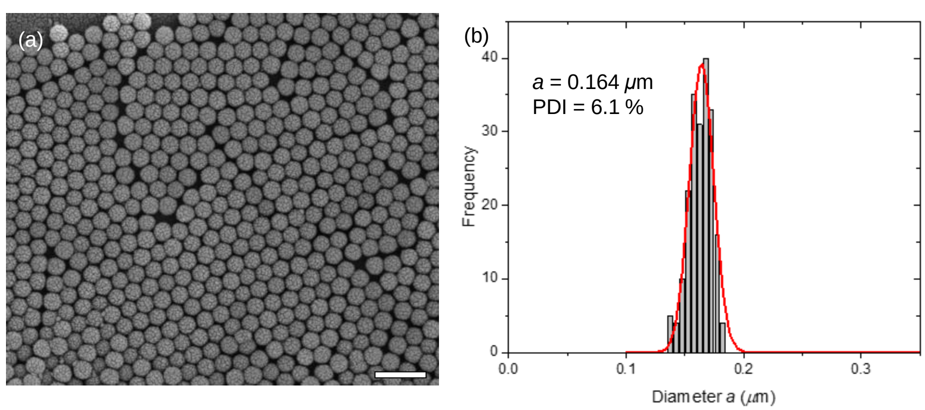

Fig. S6 (a) Scanning electron micrograph and (b) size distribution of silica nanoparticles used in tests to reduce shell permeability. The bars are the experimental data obtained by image analysis and line is the fit to the data using log-normal size distribution. Scale bar in (a) is 500 nm.

CALCULATIONS

Timescale for diffusion of rods

The timescale for translation diffusion of rods within the droplet volume is calculated as $t_{mix} = R^2/D$ where R is the radius of the droplet and D is the diffusion coefficient of a single rod-like particle. Tirado, Martinez and de la Torre[1] derived an expression of D for a cylinder of length b and aspect ratio AR:

$$D = \frac{k_B T}{3\pi\eta b}[\ln(AR) + \nu] \quad (1)$$

where k_B is Boltzmann's constant, T is temperature and η is the solvent viscosity. Their model includes a correction for end-effects ν which is a function of AR. This was interpolated from empirical values valid between $2 < AR < 30$ as follows[2,3]: $\nu = 0.312 + \frac{0.565}{AR} - \frac{0.100}{AR^2}$.

Karman-Cozeny relationship for rod particles

The base form of the Karman-Cozeny scaling is as follows[4,5]:

$$k = \frac{(1-\phi)^3}{C\,\phi^2}\, l^2 \quad (2)$$

where k is the liquid permeability, ϕ is the volume fraction of solid in the packing, l is the characteristic length-scale of the particles and C is a constant dependent on the particle size and ordering and determined to be 5.6 by Thies-Weesie et al.[6].

The characteristic length-scale is expressed for rod-like particles as the volume of a spherocylinder V_{rod} of length b and diameter a, divided by its surface area S_{rod}:

$$l = \frac{V_{rod}}{S_{rod}} = \frac{a(3b+2a)}{12(b+a)} \quad (3)$$

Thus, the Karman-Cozeny relationship for rods of aspect ratio $AR = b/a$ takes the following form:

$$k = \frac{(1-\phi)^3}{5.6\,\phi^2}\frac{a^2}{144}\left(\frac{3AR+2}{AR+1}\right)^2 \quad (4)$$

Shell mass balance

In the high Pe regime, a core exists with constant volume fraction ϕ_i, while a shell thickens throughout drying with volume fraction ϕ. The following results from mass conservation:

$$V_i\phi_i = V_c\phi_i + V_s\phi \quad (5)$$

where V_i and ϕ_i are respectively the volume and volume fraction of the droplet at $t = 0$. V_c is the volume of the core at $t = 0.9\ t_d$, whose volume fraction remains unchanged at ϕ_i. V_s and ϕ are the volume and volume fraction of the shell. The values of V_i, V_c and V_s can be estimated as:

$$V_i = \frac{4}{3}\pi[R_i^3] \quad (6)$$

$$V_c = \frac{4}{3}\pi[(R-\delta)^3] \quad (7)$$

$$V_s = \frac{4}{3}\pi[R^3 - (R-\delta)^3] \quad (8)$$

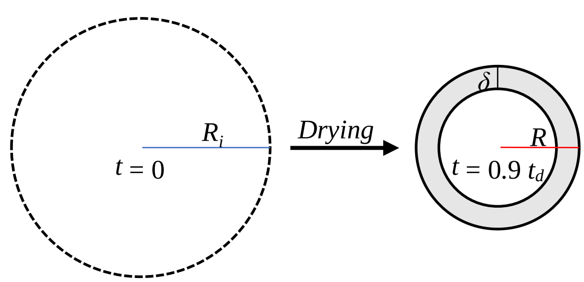

Fig. S7 Schematic of core-shell geometry evolving throughout drying.

where delta is the thickness of shell, R_i and R respectively are the droplet radii at its initial state and after time t (Fig. S7). Higher-order terms of δ may be ignored for $R >> \delta$ and $V_{s,i}$ and V_s may be rearranged into (5) to obtain an expression for the shell thickness:

$$\delta = \frac{1}{3}\left(\frac{R_i^3 - R^3}{R^2}\right)\left(\frac{\phi_i}{\phi - \phi_i}\right) \tag{9}$$

Pore diameter estimation

The pore diameter d is estimated as the characteristic length-scale of a pore defined as the void volume divided by the pore-particle interfacial area S_p:

$$d = \frac{V_p(1-\phi)}{S_p} \tag{10}$$

where V_p is the volume of the packing. Note that the previously discussed length-scale for particles is also defined as $l = \phi V_p / S_p$ such that (10) becomes:

$$d = \frac{(1-\phi)}{\phi}\, l \tag{11}$$

VIDEO CAPTIONS

Video S1 – Timelapse of buckling droplet containing rod particles of $AR = 3.3$

Video S2 – Timelapse of non-buckling droplet containing rod particles of $AR = 10.2$

REFERENCES

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