Calculation of condensation-based growth factor α

$$\alpha \equiv \left[\int_{t_{start}}^{t_{end}} f\left(T_{surface}(t)\right) dt \right]^{1/3} \tag{1}$$

The exact integral form of alpha can be approximated by the trapezoidal rule. The saturated vapor pressure difference is estimated using the Magnus approximation with recommended Alduchov-Eskeridge coefficients ($A = 17.625,\ B = 243.04$ °C).

$$\alpha \approx \left\{ \alpha_{corr} + \sum_{i=2}^{N} \frac{1}{2}\left[f(T_{i-1}) + f(T_i) \right]\left(t_i - t_{i-1}\right) \right\}^{1/3} \tag{2}$$

The dew point, T_{dew}, is calculated from the Magnus formula with the Alduchov-Eskeridge recommended coefficients ($A = 17.625,\ B = 243.04$ °C, RH = Relative Humidity/ %, T_{room} = Room Temperature/ °C):

$$T_{dew} = \frac{B\left[\ln\left(\frac{RH}{100}\right) + \frac{AT_{room}}{B + T_{room}} \right]}{A - \ln\left(\frac{RH}{100}\right) - \frac{AT_{room}}{B + T_{room}}} \tag{3}$$

The thermal data points (t_0, T_0) to (t_{N+1}, T_{N+1}) are such that they include the entire time where the liquid surface temperature is below that of the dew point:

$$\begin{aligned} &T_0 > T_{dew}, \\ &T_1, T_2, \ldots, T_N < T_{dew}, \\ &T_{N+1} > T_{dew} \end{aligned} \tag{4}$$

The term α_{corr} refers to the end-correction near the limits of the integration, and can be calculated as follows:

$$\alpha_{corr} = \alpha_{\text{corr, start}} + \alpha_{\text{corr, end}}, \tag{5}$$

$$\alpha_{\text{corr, start}} = \frac{1}{2}(t_1 - t_{start}) f(T_1), \tag{6}$$

$$\alpha_{\text{corr, end}} = \frac{1}{2}(t_{end} - t_N) f(T_N) \tag{7}$$

The times t_{start} and t_{end} refer to the times when the surface temperature reaches dew point during the decrease in temperature and increase in temperature respectively. These quantities are estimated by assuming a linear variation of temperature between the data points adjacent to the point of crossing the dew point.

$$t_{start} = \frac{T_{dew} + t_0\left(\frac{T_1 - T_0}{t_1 - t_0}\right) - T_0}{\frac{T_1 - T_0}{t_1 - t_0}}, \tag{8}$$

$$t_{end} = \frac{T_{dew} + t_N\left(\frac{T_{N+1} - T_N}{t_{N+1} - t_N}\right) - T_N}{\frac{T_{N+1} - T_N}{t_{N+1} - t_N}} \tag{9}$$

Calculation of Coordinational Entropy

The order of a Voronoi diagram (coordinational entropy) can be calculated by considering the value of $-\sum P_n \ln P_n$, where P_n refers to the probability of finding a polygon with n sides in the Voronoi diagram. The minimum value occurs when the sample is perfectly ordered. In such a sample, every polygon will have the same number of sides (i.e. $P_n = 1$ for a certain n), and hence the entropy will evaluate to zero. The value of coordinational entropy associated with a random distribution of particles depends on the number of particles (or in this case, pores) in the system, and tends to increase as the number of particles increases (**Figure S2**). The calculated entropy values for any Voronoi pattern can hence only be compared with the entropy value associated with a random distribution of the same number of points in the sample. The calculated value of 1.657 in our work is based on about 3000 random distributions of 229 points (same number of points used in the Voronoi analysis of our NCP array). This is close to the value of 1.71 commonly cited for a random distribution of points based on work by Limaye *et. al.*[1]

[1] A. V. Limaye, R. D. Narhe, A. M. Dhote, S. B. Ogale, *Phys. Rev. Lett.* **1996**, *76*, 3762.

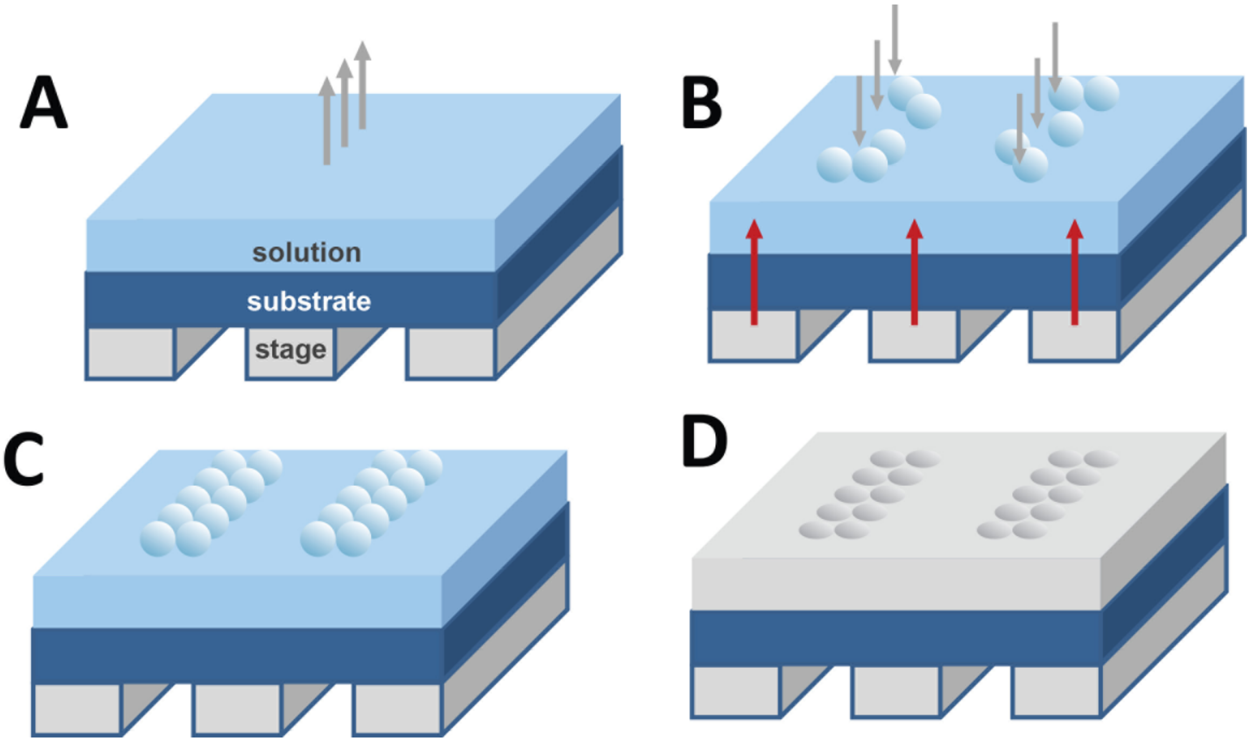

Figure S1 The spatio-thermal templating method works by modulating the solution surface temperatures by heat transfer from a thermally conductive stage. The stage reduces the effect of evaporative cooling **(A)** resulting in a localization of water droplet nucleation to specific regions above the air pockets **(B)**. Eventual packing and evaporation was expected to form CP arrays in these regions with sharply defined edges **(C-D)**. However, unexpectedly, instead of sharply defined edges as seen in **(D)**, we observed NCP BFAs forming around the periphery of the CP BFAs (see **Figure 1F**), something unexplained by current packing mechanisms.

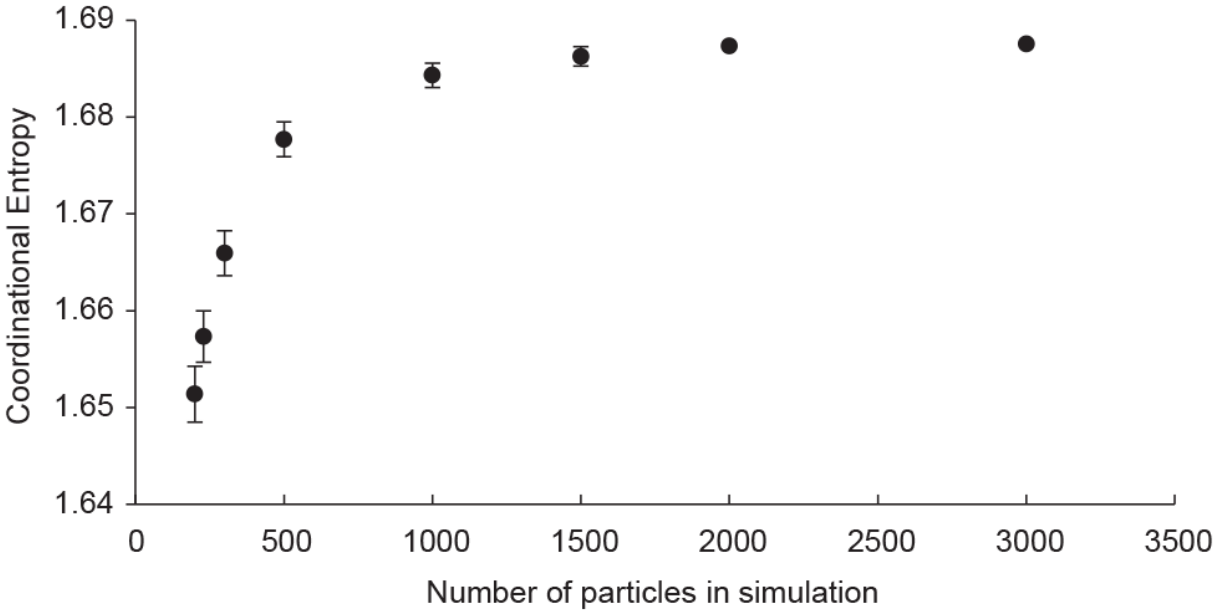

Figure S2 Plot of the mean coordinational entropy associated with random distributions of particles obtained by Monte Carlo simulation against the number of particles in the system. 99% confidence intervals around the mean are also plotted.

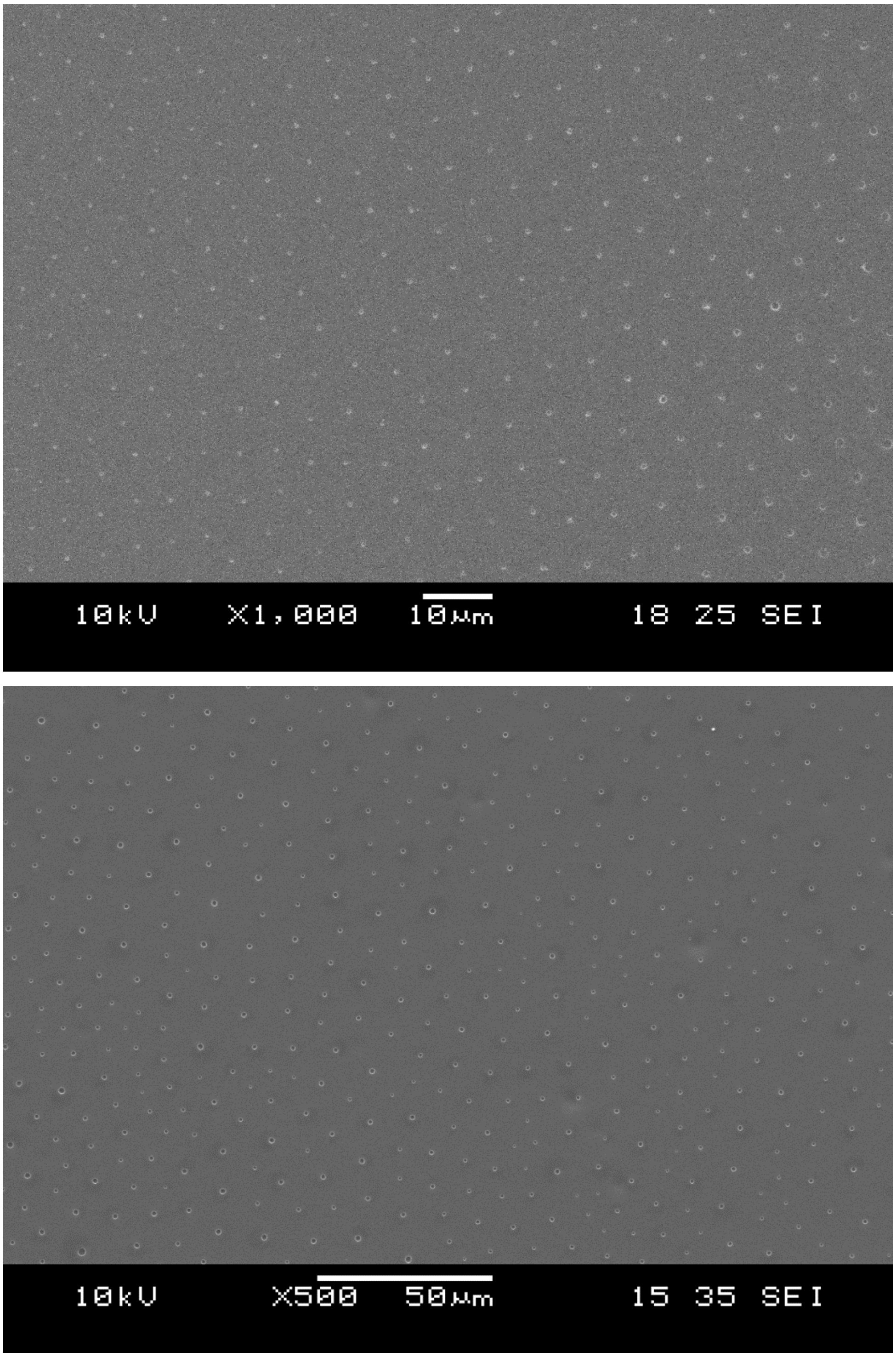

Figure S3 Low-magnification electron micrographs of NCP arrays formed using the original spatio-thermal templated method (**top**) and in our proof-of-concept (**bottom**).

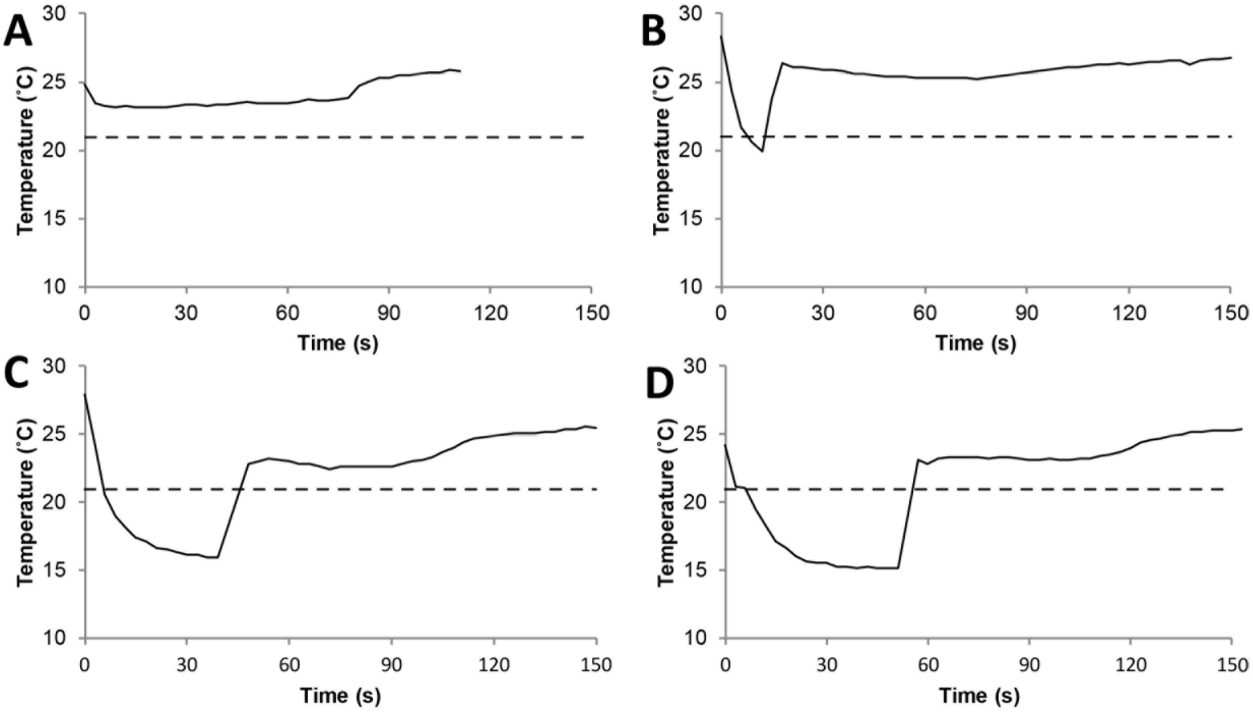

Figure S4 Representative local thermal profiles of the drying films when transferred at (**A**) 0 s (i.e. negative control), (**B**) 15 s, (**C**) 45 s, and (**D**) 60 s. Dotted lines represent the dew point of the sample.

Table S1 Table of the coordinational entropy values obtained by Monte Carlo simulation of a random distribution of points. The highlighted row reflects a random distribution of an equal number of particles as that of the BFA sample shown in **Figure 1F**.

Number of particles	Entropy mean	Entropy standard deviation	Number of trials
200	1.651384	0.06249	3103
229	**1.657342**	**0.058683**	**3236**
300	1.66594	0.05011	3103
500	1.677708	0.038791	3103
1000	1.684319	0.027136	3100
1500	1.686282	0.021669	3099
2000	1.687368	0.018733	717
3000	1.687565	0.015508	716

edge.mp4

Movie S1 Shrinking of floating water droplets at the edge of a drying volatile organic phase. Direction of movement of the liquid phase is towards the edge of the drying solvent front.