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Electronic Supplementary Information: Process-morphology scaling relations quantify self-organization in capillary densified nanofiber arrays

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S1 Carbon Nanotube Cell Area Quantification

To evaluate the carbon nanotube (CNT) cell area (A) from experimentally obtained top-view optical microscope images, we first processed the raw optical microscope images with the built-in threshold and color inversion filters in ImageJ (see Fig. S1), similar to the approach used in a recent study.[1] First, the contrast of the optical images was enhanced to obtain a clear color difference between the bare substrate and the tops of the cell walls (*i.e.* the wall thickness). Then, the color threshold was set to fill the area of each cell in the image, excluding the area of the cell walls. As illustrated in Fig. S1, processed optical microscope images were then analyzed using ImageJ's particle size analysis function, which calculates the area of each cell as dictated by the color threshold and produces a corresponding image of the cell area outlines. The resulting area distributions were analyzed using log-normal statistics (see exemplary histogram in Fig. S1) as discussed in the main text.

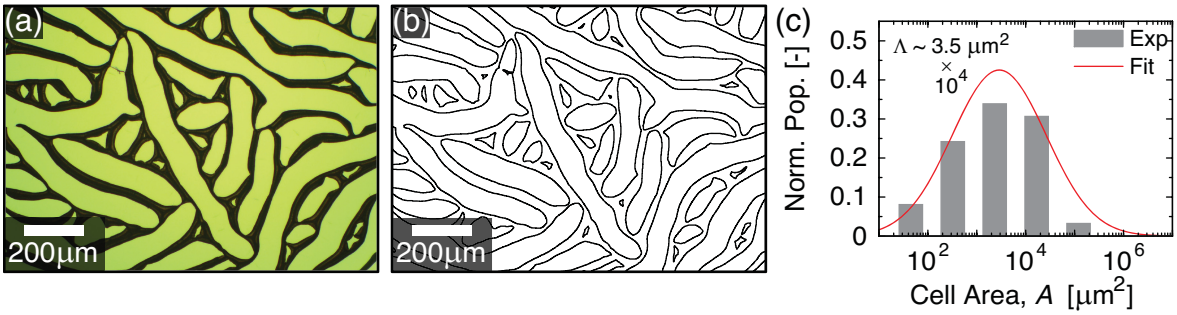

Fig. S1 Exemplary optical microscope images and plot illustrating how the carbon nanotube (CNT) cell area (A) was estimated. To approximate A, (a) raw optical microscope images were first processed in ImageJ using the built-in threshold and color inversion filters, and then (b) ImageJ's particle size analysis function was used to outline and measure the voids that comprise the two-dimensional CNT cellular network, which leads to (c) histograms of the cell area distribution for each sample. As further discussed in the main text, these histograms are then analyzed *via* log-normal statistics to yield the arithmetic mean (Λ).

S2 Cell Geometry Modeling Details

To model the capillary-mediated densification of nanofiber arrays, here carbon nanotubes (CNTs), one can start from the maximum bundle size ($N_{\max}$) that was previously derived for fibers that self-organize due to capillary forces,[2–4] and has the following form:

$$N_{\max} = \left(\frac{\gamma}{E}\right)^{2/3} \left(\frac{4h^{8/3}}{D_{\text{cnt}}^2 \Gamma_{\text{i}}^{4/3}}\right) \tag{S1}$$

where γ is the surface tension of the solvent, E is the effective (axial) elastic modulus of the cell wall, h is the cell wall height, D_{cnt} is the CNT outer diameter (~ 8 nm here),[5] and Γ_{i} is the as-grown inter-CNT spacing ($\sim 60-80$ nm here).[5–7] While eqn S1 was derived by assuming that frictional effects between adjacent fibers can be neglected, which leads the bending stiffness of the bundles to scale linearly with the number of fibers (*i.e.* N) that comprise them,[4] CNTs undergoing densification processing were found to exhibit non-negligible CNT-CNT frictional effects.[8] This means that the bending stiffness scaling for CNT cell walls is expected to scale as N^3 given a one-dimensional geometry, and leads the relation proposed in eqn S1 to correspond to $N_{\max}^3$. Given an estimate for $N_{\max}$, the CNT cell wall thickness (t) can now be approximated as follows:

$$t = N_{\max}\Gamma_{\text{f}} \tag{S2a}$$

$$\hookrightarrow t = \Gamma_{\text{f}} \left(\left(\frac{\gamma}{E}\right)^{2/3} \left(\frac{4h^{8/3}}{D_{\text{cnt}}^2 \Gamma_{\text{i}}^{4/3}}\right)\right)^{1/3} \tag{S2b}$$

where Γ_{f} is the final inter-CNT spacing within the CNT wall. Since Γ_{f} depends on the degree of densification of the CNTs in the cell wall, and assuming that the total area of the cellular network is about the same as the area of the original CNT array, the densification factor Ξ can be defined as follows:

$$\Xi^{\beta} = \frac{w+t}{t} \tag{S3}$$

where w is the cell width, $t+w$ is defined as the average characteristic size of the repeat unit (see Fig. S2 for illustration), and β is a factor that accounts for the dimensionality of the densification, *i.e.* $\beta \sim 1$, $1/2$, and $1/3$ for one-, two-, and three-dimensional densification, respectively. Using Ξ and the as-grown CNT volume fraction ($V_{\text{f}} \sim 1\%$),[5,6] the previously developed functional forms for the inter-CNT spacing scaling as a function of the CNT waviness and V_{f} can be used to estimate Γ_{f} as follows:[6,7,9]

$$\Gamma_{\text{f}} = \Omega D_{\text{cnt}} \left((11.77(3.2(\Xi V_{\text{f}})^{0.6}+4.1)^{-3.042}+0.9496)\sqrt{\frac{\sqrt{3}\pi}{6\Xi V_{\text{f}}}}-1\right) \tag{S4a}$$

$$\Omega = -0.002\Xi V_{\text{f}} + 1.072 \tag{S4b}$$

where Ω is the waviness correction factor, and originates from a three-dimensional stochastic simulation of the packing morphology of wavy CNTs.[7] Using the evaluated Ξ, the scaling of w with h can also be approximated from eqn S3 as follows:

$$w = t(\Xi^{\beta}-1) \approx t\Xi \tag{S5}$$

The reduced form of eqn S5 is reproduced in the main text as eqn 2, and is valid when w originates from one-dimensional densification ($\beta \sim 1$), *i.e.* when the CNT array is not pre-patterned into pillars or another repeating structure.

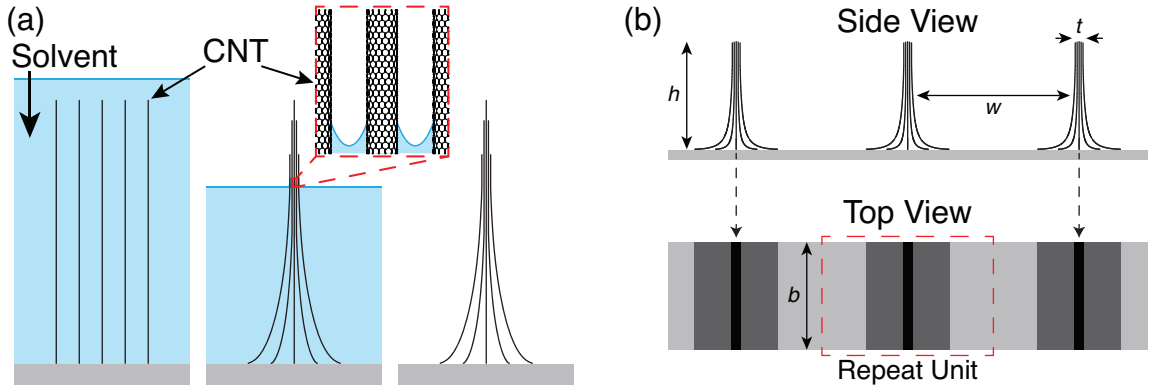

Fig. S2 Overview of carbon nanotube (CNT) cellular network modeling geometry. (a) One-dimensional schematic illustrating CNT self-organization as the solvent's meniscus recedes due to evaporation. (b) Side view illustration defining the CNT cell height (h), width (w) and wall thickness (t), and top view illustration showing the CNT cell wall length (b) and repeat unit (2D size of $(w+t)\times b$) used in eqns S3−S5.

To predict how the cell area (A) scales with w, we start with the definition of cell circularity (O) as follows:

$$O = \left(\frac{4\pi}{P_c^2}\right) A \tag{S6}$$

where P_c is the cell perimeter. Since the cells are not perfectly circular, a factor accounting for the aspect ratio of the cells (ζ) can be integrated into P_c, and the approximately elliptical shape of the cells can be used to estimate A as follows:

$$P_c = \pi\zeta w \tag{S7a}$$

$$\hookrightarrow A = O\left(\frac{\pi}{4}\right)(\zeta w)^2 \approx O(\zeta w)^2 \tag{S7b}$$

One straightforward way to approximate ζ is to evaluate it directly from the major and minor diameters of the ellipse (d_1 and d_2, respectively). See Fig. S3 for illustration. Defining the ellipse aspect ratio as d_1/d_2, and since w is a one-dimensional approximation, specific information about how w compares to d_1 and d_2 for any specific cell is not available. Also, since the real two-dimensional shapes of the cells that form are irregular and only very roughly approximated by ellipses, we propose that ζ^2 is of the same order of magnitude as the ellipse aspect ratio, which leads to the following functional form:

$$\zeta^2 \propto \frac{d_1}{d_2} \tag{S8}$$

To estimate d_1/d_2, a perfect ellipse's area ($\rightarrow A_{\bigcirc} = \pi d_1 d_2$) and O ($\rightarrow O_{\bigcirc}$) can be used in conjunction with Ramanujan's approximation of an ellipse's perimeter ($P_{\bigcirc}$) that has the following form:[10]

$$P_{\bigcirc} \approx \pi(d_1+d_2)\left(1+\frac{3\lambda^2}{10+\sqrt{4-3\lambda^2}}\right) \tag{S9a}$$

$$\lambda = \frac{d_1-d_2}{d_1+d_2} \tag{S9b}$$

Numerical approximations of d_1/d_2 as a function of O obtained by plugging in $O_{\bigcirc}$, $A_{\bigcirc}$, and $P_{\bigcirc}$ (from eqn S9) into the non-reduced version of eqn S7b and can be found in Fig. S3 and Table S1. As Fig. S3 and

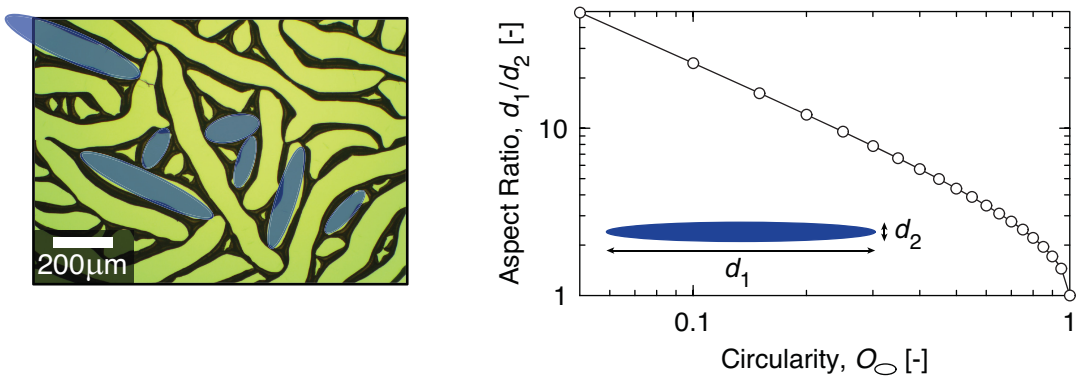

Fig. S3 Illustration of elliptical estimate of CNT cell geometry and plot of an idealized ellipse's aspect ratio (d_1/d_2) vs. its circularity ($O_{\bigcirc}$).

Table S1 illustrate, since O is experimentally determined as $O \approx 0.60 \pm 0.04$ here (see Sec. S3 for details), this leads to $d_1/d_2 = \zeta^2 \approx 3.5 \pm 0.3$ as discussed in the main text.

Table S1 Numerical approximations of a perfect ellipse's aspect ratio (d_1/d_2) as a function of its circularity ($O_{\bigcirc}$). See Fig. S3 for a plot of d_1/d_2 vs. $O_{\bigcirc}$ and an illustration of ellipses with various values of d_1/d_2.

$O_{\bigcirc}$ [-]	d_1/d_2 [-]
1.00	1.00
0.95	1.45
0.90	1.71
0.85	1.96
0.80	2.21
0.75	2.47
0.70	2.77
0.65	3.09
0.60	3.45
0.55	3.87
0.50	4.37
0.45	4.96
0.40	5.69
0.35	6.62
0.30	7.84
0.25	9.54
0.20	12.06
0.15	16.22
0.10	24.51
0.05	49.27

S3 Cell Geometry as a Function of Carbon Nanotube Array Height

Table S2 and Table S3 present the raw data that was evaluated experimentally (*i.e.* 'Measured'), and the predictions that result from the eqns S1−S9 in Sec. S2 (*i.e.* 'Evaluated'). This data is also presented in Fig. 3 in the main text.

Table S2 Experimentally determined carbon nanotube (CNT) cell height (h), width (w), area (A), circularity (O), and wall thickness (t) in addition to the evaluated cell wall effective elastic modulus (E, estimated from eqn S2b), densification factor (Ξ, estimated from eqn S5), and the cell aspect ratio factor (ζ^2, estimated from eqns S7−S9) for non-cemented CNTs (*i.e.* nc-CNTs in the main text). This data originates from paper-based densification with acetone and ethanol, as discussed further in the main text.

	Measured					**Evaluated**		
	h [μm]	t [μm]	w [μm]	$A\times10^3$ [μm^2]	O [-]	E [MPa]	Ξ [-]	ζ^2 [-]
Acetone	9 ± 1	2.9 ± 0.7	36.5 ± 4.4	7.6 ± 5.3	0.66 ± 0.10	280 ± 140	12.9 ± 4.8	3.1 ± 0.7
	12 ± 1	2.7 ± 0.5	53.9 ± 7.5	9.1 ± 1.6	≈0.54	130 ± 70	20.4 ± 7.0	≈4.0
	35 ± 3	3.7 ± 0.2	82.8 ± 12	9.9 ± 1.7	0.70 ± 0.08	360 ± 150	21.1 ± 2.5	2.8 ± 0.5
	50 ± 5	3.8 ± 0.4	88.4 ± 18	9.9 ± 1.2	0.64 ± 0.15	960 ± 360	22.2 ± 2.4	3.4 ± 1.1
Ethanol	10 ± 1	≈2.3	43.3 ± 4.4	7.3 ± 4.4	0.63 ± 0.08	29 ± 10	17.9 ± 1.8	3.3 ± 0.6
	15 ± 3	1.8 ± 0.1	59.6 ± 1.8	13 ± 1.9	0.54 ± 0.05	38 ± 17	32.4 ± 2.3	4.0 ± 0.5
	40 ± 3	3.5 ± 0.3	65.7 ± 14	12 ± 6.3	0.57 ± 0.01	2800 ± 1300	17.7 ± 4.4	3.7 ± 0.1
	52 ± 2	4.4 ± 0.7	74.6 ± 7.1	13 ± 0.9	0.52 ± 0.05	2300 ± 900	16.3 ± 1.1	4.2 ± 0.5

Table S3 Experimentally determined carbon nanotube (CNT) cell height (h), width (w), area (A), circularity (O), and wall thickness (t) in addition to the evaluated cell wall effective elastic modulus (E, estimated from eqn S2b), densification factor (Ξ, estimated from eqn S5), and the cell aspect ratio factor (ζ^2, estimated from eqns S7−S9) for cemented CNTs (*i.e.* c-CNTs in the main text). This data originates from paper-based densification with acetone and ethanol, as discussed further in the main text.

	Measured					**Evaluated**		
	h [μm]	t [μm]	w [μm]	$A\times10^3$ [μm^2]	O [-]	E [MPa]	Ξ [-]	ζ^2 [-]
Acetone	11 ± 1	3.6 ± 0.4	88.4 ± 14	18.9 ± 6.2	0.57 ± 0.04	1.3 ± 0.6	24.1 ± 3.1	3.7 ± 0.3
	18 ± 1	3.8 ± 0.5	106 ± 7.7	25.4 ± 4.5	0.51 ± 0.03	7.0 ± 3.0	28.0 ± 2.8	4.3 ± 0.3
	25 ± 2	4.8 ± 0.4	149 ± 17	52.3 ± 13	0.55 ± 0.06	5.1 ± 2.1	30.3 ± 2.8	3.9 ± 0.6
	50 ± 15	6.6 ± 0.4	147 ± 19	48.2 ± 23	0.65 ± 0.01	300 ± 150	21.4 ± 4.3	3.1 ± 0.1
	300 ± 20	7.1 ± 1.1	291 ± 82	242 ± 13	0.64 ± 0.01	2700 ± 1000	39.2 ± 5.4	3.2 ± 0.1
Ethanol	9 ± 1	2.1 ± 0.4	81.0 ± 16	29.4 ± 1.4	0.59 ± 0.07	2.2 ± 1.1	37.6 ± 5.1	3.6 ± 0.6
	20 ± 3	2.9 ± 0.2	90.3 ± 4.3	18.4 ± 3.7	0.65 ± 0.02	14 ± 6	30.7 ± 1.0	3.1 ± 0.1
	39 ± 6	5.1 ± 1.0	147 ± 21	83.1 ± 59	0.54 ± 0.03	110 ± 50	30.7 ± 7.8	4.0 ± 0.3
	85 ± 10	6.4 ± 0.6	172 ± 11	63.9 ± 23	0.56 ± 0.07	540 ± 250	26.1 ± 3.9	3.9 ± 0.6
	260 ± 60	9.2 ± 1.4	223 ± 45	105 ± 19	0.62 ± 0.02	12000 ± 5400	24.4 ± 8.7	3.3 ± 0.1

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