Supplementary material for

Self-assembly of cellulose nanocrystals confined to square capillaries

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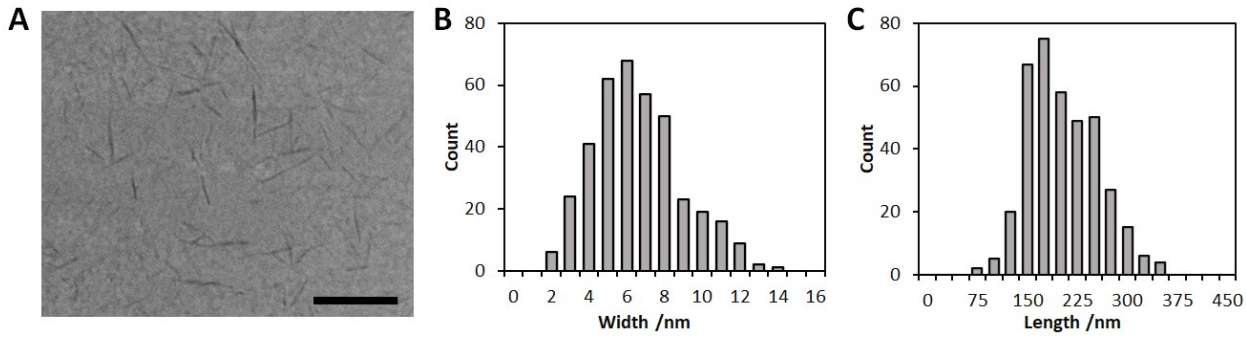

Fig. S1. TEM image and measurements of the CNCs**.** (**A**) Transmission electron microscopy (TEM) image of CNCs (scale bar, 500 nm). Distribution of CNC widths (**B**) and lengths (**C**) for *N* = 379 nanoparticles.

Table S1. TEM measurements for the lengths and widths of CNCs from final *ChN* suspensions; *N*, x̄, SD, SE, and CI refer to the number of measurements, average, standard deviation, standard error, and confidence interval to 95%

	N	**x̄ (µm)**	**SD (µm)**	**SE (µm)**	**CI (µm)**
Length	379	191.0	51.8	2.66	5.21
Width	379	6.13	2.71	0.14	0.27

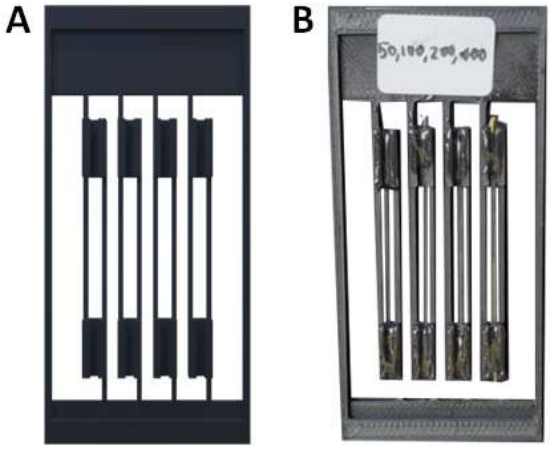

Fig. S2. 3D printed holder for the CNCs confined to capillaries. (**A**) 3D model of the holder and (**B**) 3D-printed holder with capillary tubes fixed. To image by POM, the thin connecters were cut to allow for 90° rotation on a glass slide.

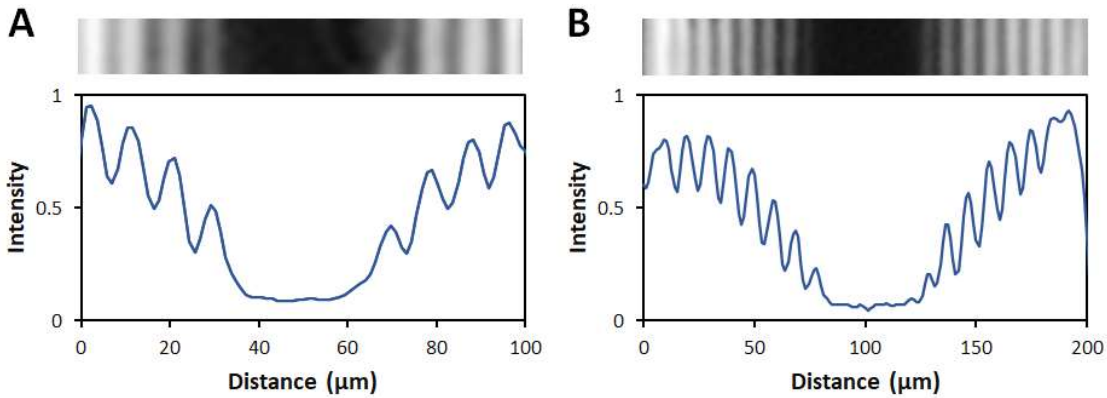

Fig. S3. Method used to measure the *ChN* pitch and central dark bands of the capillaries. POM images and their corresponding intensity profiles for the (**A**) 100 µm and (**B**) 200 µm capillaries after 24 h.

Table S2. Measurement of the *ChN* CNC *P*/2 formed within the capillaries after 24 h and 72 h; *N*, x̄, SD, SE, and CI refer to the number of measurements, average, standard deviation, standard error, and confidence interval to 95%

24 h					
Capillary	***N***	**x̄ (µm)**	**SD (µm)**	**SE (µm)**	**CI (µm)**
50	30	10.30	2.80	0.51	1.00
100	37	9.10	0.06	0.01	0.02
200	47	8.90	1.00	0.15	0.29
400	60	9.30	0.70	0.09	0.18
72 h					
Capillary	***N***	**x̄ (µm)**	**SD (µm)**	**SE (µm)**	**CI (µm)**
50	37	8.95	1.49	0.24	0.49
100	37	8.90	1.00	0.16	0.33
200	47	9.54	1.20	0.17	0.35
400	60	8.95	1.27	0.16	0.33

Table S3. Measurement of the central dark region width and ***R*** formed within the capillaries after 24 h and 72 h; *N*, x̄, SD, SE, and CI refer to the number of measurements, average, standard deviation, standard error, and confidence interval to 95%

24 h									
Capillary	***N***	**Width**				***R***			
		x̄ (µm)	**SD (µm)**	**SE (µm)**	**CI (µm)**	**x̄ (µm)**	**SD (µm)**	**SE (µm)**	**CI (µm)**
50	18	26.31	6.62	1.56	3.12	0.53	0.13	0.01	0.02
100	17	28.94	5.13	1.24	2.49	0.29	0.05	0.01	0.02
200	18	42.15	7.63	1.80	3.60	0.21	0.04	0.01	0.02
400	14	128.00	23.84	6.37	12.74	0.32	0.06	0.02	0.03
72 h									
Capillary	***N***	**Width**				***R***			
		x̄ (µm)	**SD (µm)**	**SE (µm)**	**CI (µm)**	**x̄ (µm)**	**SD (µm)**	**SE (µm)**	**CI (µm)**
50	14	19.99	1.53	0.41	0.82	0.40	0.03	0.01	0.02
100	16	28.37	5.70	1.43	2.85	0.28	0.06	0.01	0.03
200	15	45.67	4.68	1.21	2.42	0.23	0.02	0.01	0.01
400	11	115.79	18.18	5.48	10.96	0.29	0.05	0.01	0.03

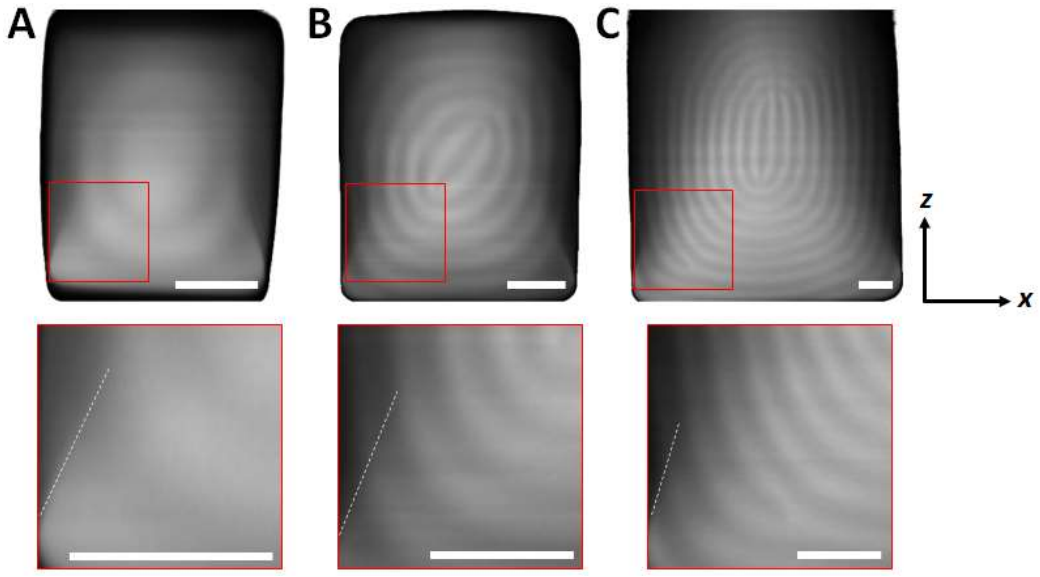

Fig. S4. Artifacts in the confocal laser scanning microscopy (CLSM) characterization. **A** to **C** correspond to the 50, 100 and 200 µm width capillaries, respectively. Areas inside the red boxes are expanded beneath to show the darkened regions at the corners, which persist up the walls of the capillary. Scale bars, 25 µm.

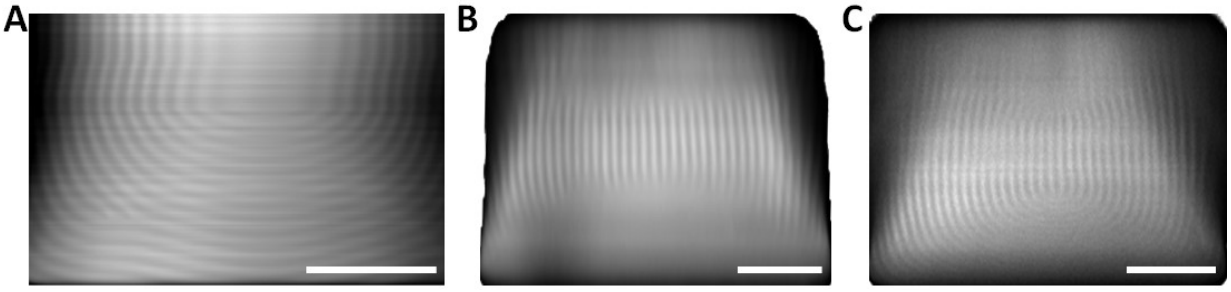

Fig. S5. Distortions in CLSM caused by objective working distance and Z-stack interval limitations. Images refer to 40×, 10×, and 20× objectives, respectively (**A** to **C**). The 400 µm (200 µm wall thickness) capillaries exceed the size limit for CLSM as a characterization technique. Scale bars, 100 µm.

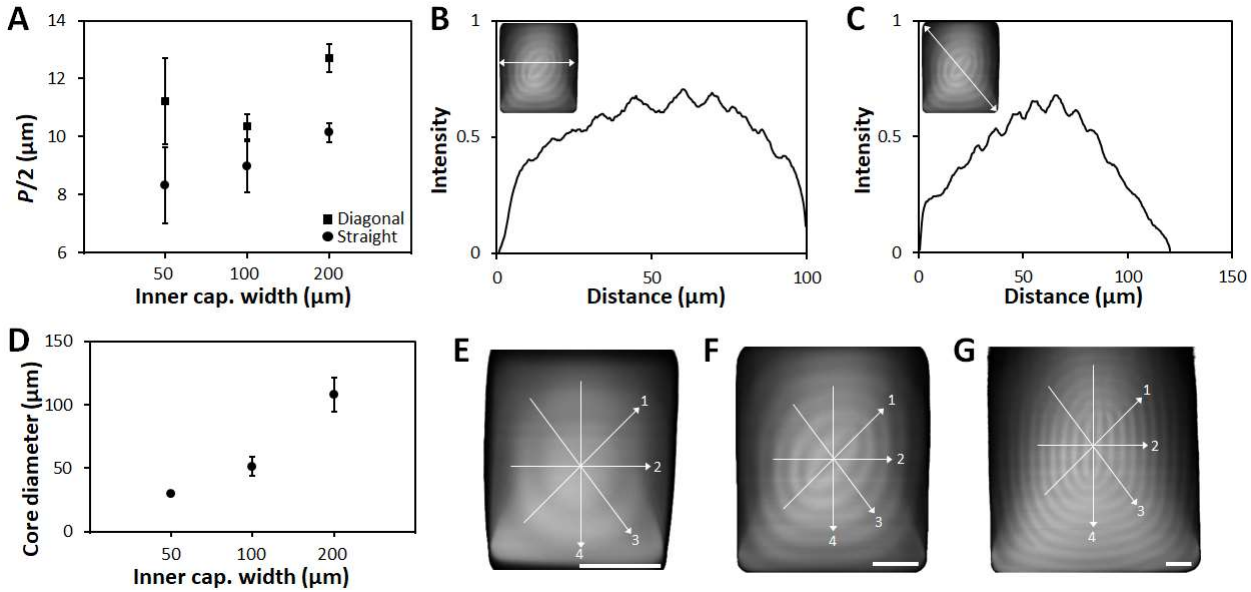

Fig. S6. Measurements from CLSM of CNC suspensions doped with 0.0001% rhodamine B dye imaged for the 50, 100 and 200 µm capillaries after 72 h. (**A**) Average *P/2* measurements; square and circle markers correspond to diagonal and planar measurements across the width of the capillary cross-section, respectively. (**B**) and (**C**) are intensity profiles of the dye emission intensity across the widths of the capillary from the planar and diagonal measurements, respectively, from images of the 100 µm width capillary. (**D**) Diameters of the cylindrical structures observed in the cross-section taken by averaging four measurements in the (**E**) 50, (**F**) 100, and (**G**) 200 µm capillaries. Scale bars, 25 µm.

Table S4. Measurement of *P*/2 for CNC suspensions doped with 0.0001% rhodamine B dye imaged with CLSM for the 50, 100 and 200 µm capillaries after 72 h; "diagonal" and "planar" measurements refer to corner-to-corner and edge-to-edge measurements across the width of the capillary cross-section, respectively. *N*, $\bar{x}$, SD, SE, and CI refer to the number of measurements, average, standard deviation, standard error, and confidence interval to 95%. *N* measurements include both peak-to-peak and valley-to-valley measurements.

	50 µm		**100 µm**		**200 µm**	
	Diagonal	**Planar**	**Diagonal**	**Planar**	**Diagonal**	**Planar**
N	16	16	33	33	58	58
$\bar{x}$ (µm)	11.22	8.32	10.35	8.97	12.71	10.14
SD (µm)	3.03	2.68	1.28	2.58	1.92	1.25
SE (µm)	0.76	0.67	0.22	0.45	0.25	0.16
CI (µm)	1.49	1.32	0.44	0.88	0.49	0.32

Table S5. Average diameters of *ChN* cylindrical core structures from the CLSM *xz* cross-sectional images. *N*, $\bar{x}$, SD, SE, and CI refer to the number of measurements, average, standard deviation, standard error, and confidence interval to 95%

Capillary	***N***	**$\bar{x}$ (µm)**	**SD (µm)**	**SE (µm)**	**CI (µm)**
50	4	29.65	1.07	0.53	1.05
100	4	51.32	7.46	3.73	7.31
200	4	107.75	16.62	6.81	13.35

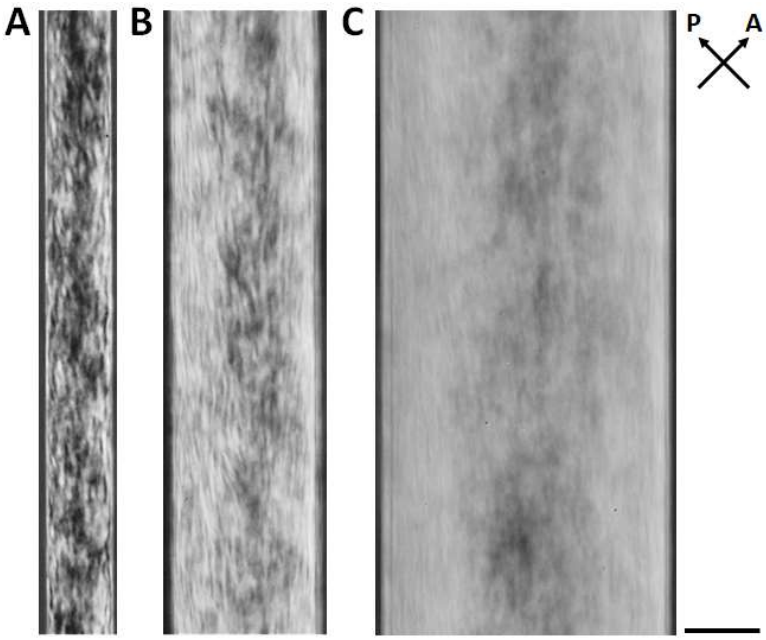

Fig. S7. POM images of CNC suspensions inside square capillaries after 15 min equilibration time. (**A** to **C**) are capillaries with IDs of 50, 100, 200 µm, respectively, viewed between crossed polarizers. Scale bar, 50 µm.

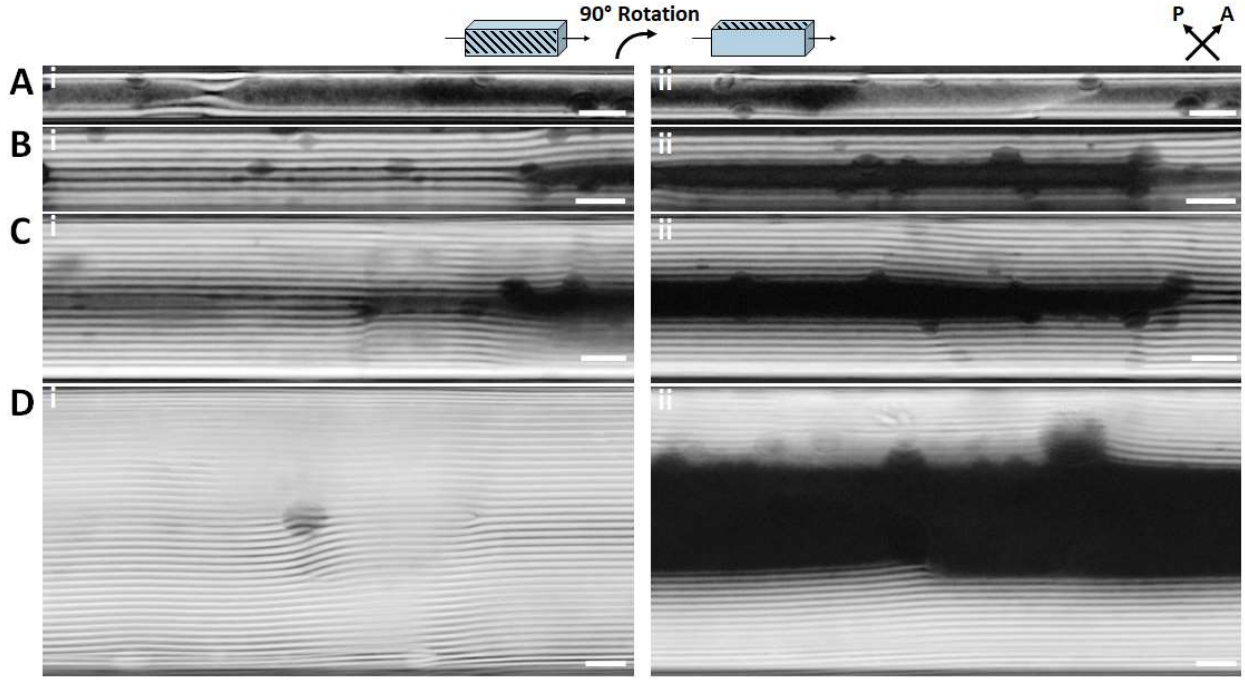

Fig. S8. POM images of CNC suspensions inside square capillaries after 72 h equilibration time. (**A** to **D**) are capillaries with ID = 50, 100, 200 and 400, respectively, viewed between crossed polarizers. The laying capillaries (i) were rotated 90° with respect to the centre of the capillary (ii). Scale bars, 50 µm.

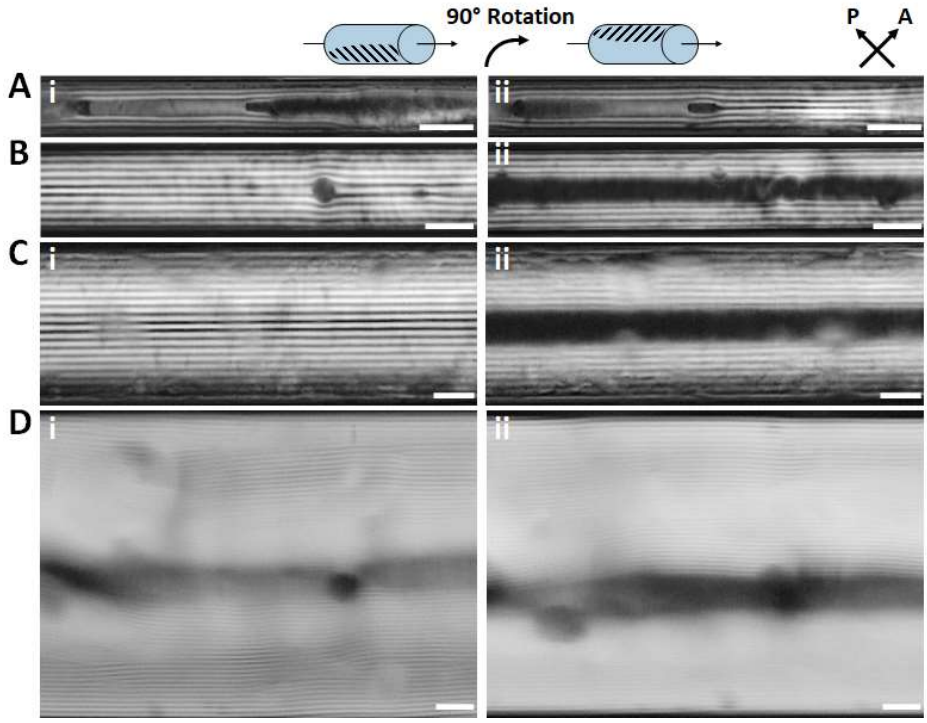

Fig. S9. POM images of CNC suspensions inside cylindrical capillaries after 7 d equilibration time. (**A** to **D**) are capillaries with ID = 50, 100, 200 and 400, respectively, viewed between crossed polarizers. The horizontal capillaries (i) were rotated 90° with respect to the centre of the capillary (ii). Scale bars, 50 µm.

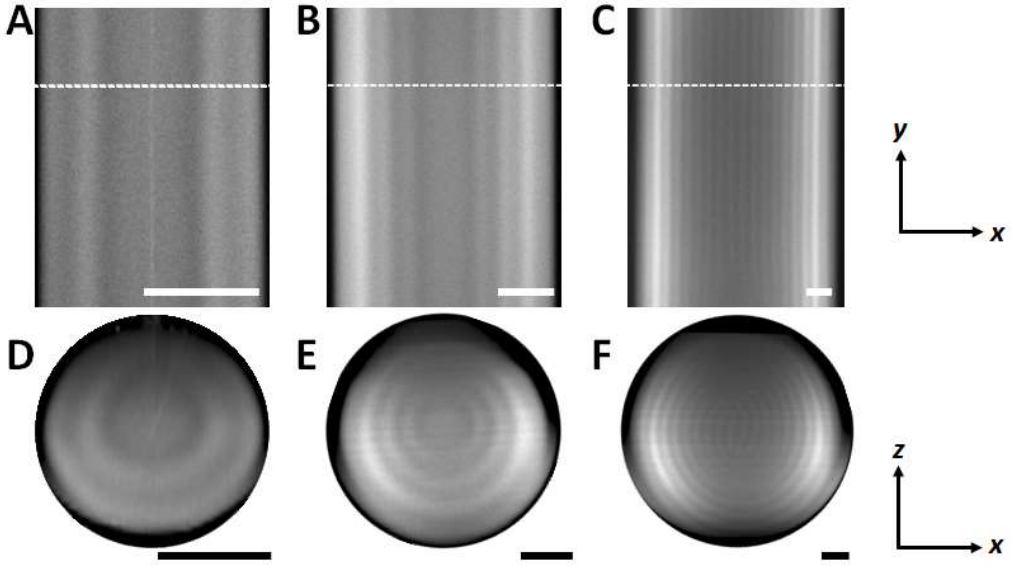

Fig. S10. Cross sections of CNC/rhodamine B suspensions in cylindrical capillaries. CLSM images of *xy* cross-sections (half-way through capillary in the ***z*** direction) for capillaries equilibrated for 72 h with inner diameters of (**A**) 50, (**B**) 100, and (**C**) 200 µm, respectively. The dashed lines in **A** to **C** correspond to the *xz* cross-sectional images of the (**D**) 50, (**E**) 100, and (**F**) 200 µm capillaries, respectively. Scale bars, 25 µm.

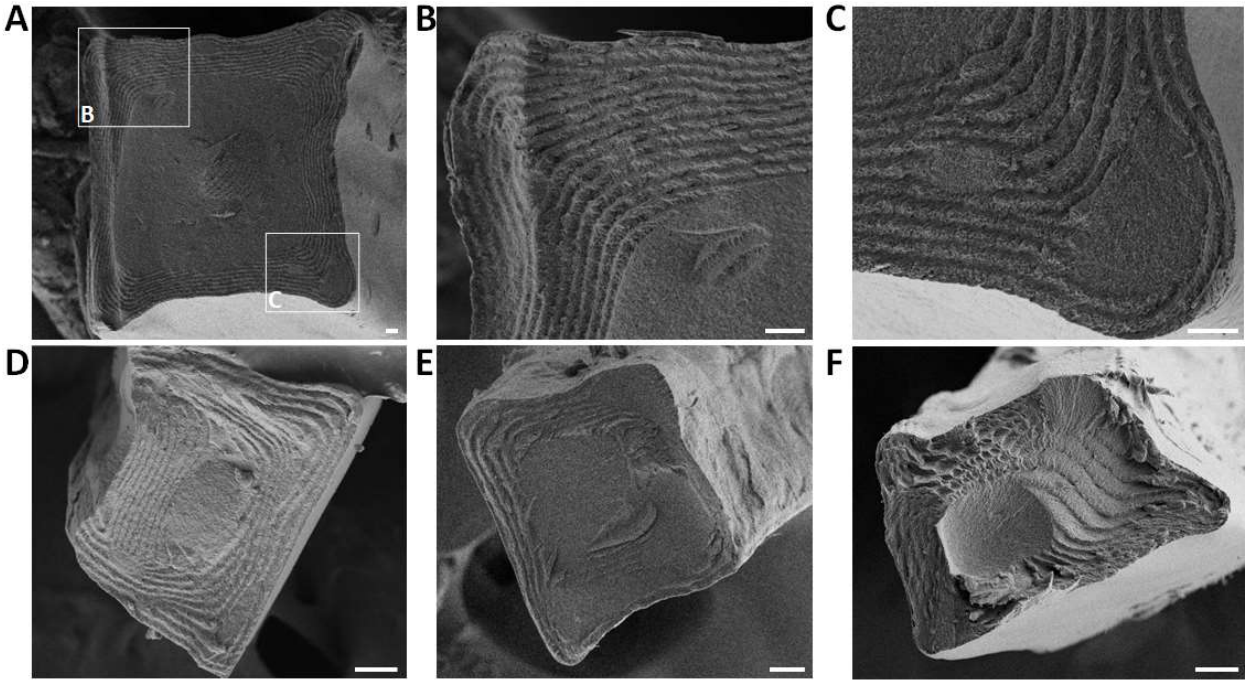

Fig. S11. SEM images of composite silica/CNC aerogel cross-sections. SEM images of cross-sections formed from square capillaries with an inner diameter of (**A** to **C**) 400 µm and (**D** to **F**) 200 µm. (**B** and **C**) correspond to the corners shown in (**A**), while (**D** to **F**) are different silica/CNC cross-sections from a 200 µm capillary. Scale bars, 10 µm.

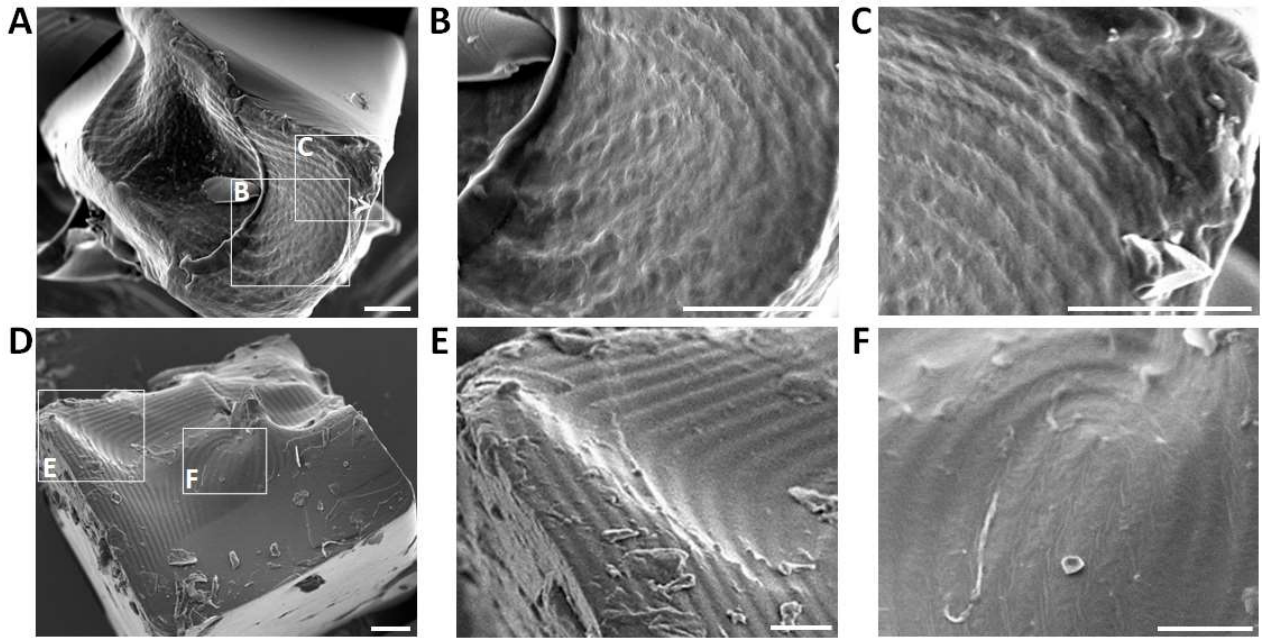

Fig. S12. SEM images of composite CNC/pHEA/pHEMA cross-sections. The samples were formed in square capillaries with an inner diameter of (**A**) 100 µm. (**B** and **C**) correspond to the insets shown in (**A**). (**D**) is the cross-section from a capillary that had a 200 µm cross-section, and (**E** and **F**) correspond to the insets of (**D**). Scale bars, 25 µm.