Supplementary Information

Tunable dialdehyde/dicarboxylate nanocelluloses by stoichiometrically optimized sequential periodate-chlorite oxidation for tough and wet shape recoverable aerogels

Gabriel Patterson and You-Lo Hsieh[a]

Biological and Agricultural Engineering, University of California, Davis, California 95616, United States.

[a] *E-mail: ylhsieh@ucdavis.edu; Tel. +1 530 752 0843*

Table S1 Reaction variables and structures of PC-nanocelluloses from the literature.[16-20]

	periodate oxidation		chlorite oxidation			PC-nanocelluloses			
cellulose source; concentration (g/mL)	$NaIO_4$/	temp. time	$NaClO_2$/	CH_3COOH	temp. time	carboxyl (mmol/g)	Yield (%)	Shear force equipment, centrifugation	Thickness (T) by AFM; Width (W) & Length (L) by TEM, unless specified
bleached SKP (1.5 w/v%)[16]	1.9/3 g/g dry pulp[a]	RT, NR	2.8/3.5 g/g P-cell [a'] ($NaClO_2$ 80 % pure)	NA; pH 5, NaOH	RT, 20 h	1.0 2.0 2.5 3.5	15 30 50 50	blender (Braun 4191, 0–3.5 kWh/kg) NA	T: 10 – 20 nm
bleached birch SKP (1 w/v%)[17]	4.8/6 g/g dry pulp[b]	55 ºC, 0.25 h 0.5 h 1 h 2 h 3 h	4:1 mol/mol $NaClO_2$/HCO[b']	1 M	RT, 48 h	0.38 0.69 0.75 1.2 1.75	91 100 91 86 85	high-pressure homogenizer (APV-2000, 250-950 bar) 7.5kg, 20 min	25 6 nm (n50) by SEM
dissolving pulp (1 w/v%)[18]	8.2:10 g/g dry pulp[c]	55 ºC, 0.5 h 2 h 2.5 h	4:1 mol/mol $NaClO_2$/HCO 4 g P-cell (0.4 w/v%)[c']	1 M	RT, 48 h	0.44, 0.89, 1.16	84 88 104	Microfluidizer (Microfluidics M-110EH-30) NA	T: 2.6 nm; L: 807 nm 2.9 nm; L: 844 nm 3.6 nm; L: 656 nm n=200; n=350 by AFM
bleached hardwood pulp (1 w/v%)[19]	46 mmol/g pulp (12 g) [d]	50 ºC, 2 h 3.75 h 4.5 h	12/12 g/g P-cell (1 w/v%)[d']	1 M	RT, 40 h	0.78, 1.74, 2.0	ND	Homogenizer (APV 1000, SPX Flow Technology, 60 MPa) 4.83kg, 1 h	T: 2.5 nm, L: 375 nm T: 2.7 nm, L: 127 nm T: 2.7 nm, L: 96 nm (n=30)
sulfite pulp (1 w/v%)[20]	0.23 M/24 g pulp (50 w/v%)[e]	50 ºC, 3 h	2.013/2.0 g/g P-cell (1 w/v%)[e']	1 M	20 ºC, 16.5 h	1.02	ND	Homogenizer (maker not specified, 2x 50 MPa, 2x 80 MPa) 4.83kg, 1 h	T: 2.1 0.4 nm (n=35) L: 525±160 nm (n=6) by AFM
RS cellulose (1 w/v%) this work	0.25:1, 0.5:1, 0.75:1 mol:mol AGU	55 ºC, 4 h	1:1 (1 w/v% P-cell)	0.5 M	RT, 0.5 – 72 h	0.64 – 1.35	96±2 n=8	Blender (Vitamix 5200, 37.5k rpm) 4.83kg, 15 min	T: 1.3 nm (n=101) W: 3.8 nm (n=100) L: 1.01 μm (n=45)

SKP = softwood kraft pulp; P-cell = periodate oxidized cellulose; RS = rice straw;
NA = not applicable; ND = not determined; NR = not reported.

[a] 0.5:1 mol/mol $NaIO_4$/AGU; [a'] 1:1 mol/mol $NaClO_2$; 2.3 wt% P-cell; 30 wt% H_2O_2

[b] 0.82:1 mol/mol $NaIO_4$/AGU; [b'] 4:1 $NaClO_2$:HCO; 2:1 mol/mol $NaClO_2$/AGU

[c] 0.82:1 mol/mol $NaIO_4$/AGU; [c'] 4:1 $NaClO_2$:HCO; 2:1 mol/mol $NaClO_2$/AGU

[d] 0.82:1 mol/mol $NaIO_4$/AGU; [d'] 2:1 mol/mol $NaClO_2$/AGU

[e] 0.4:1 mol/mol $NaIO_4$/AGU; [e'] 2:1 mol/mol $NaClO_2$/AGU

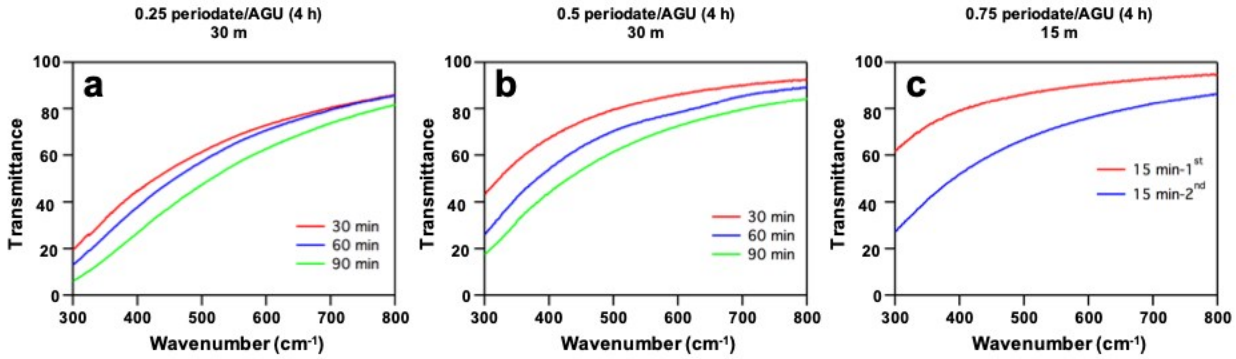


Fig. S1 UV/Vis transmittance of PC-NC from varied $NaIO_4$/AGU (55 C, 4 h): (a) 0.25:1; (b) 0.5:1; (c) 0.75:1.

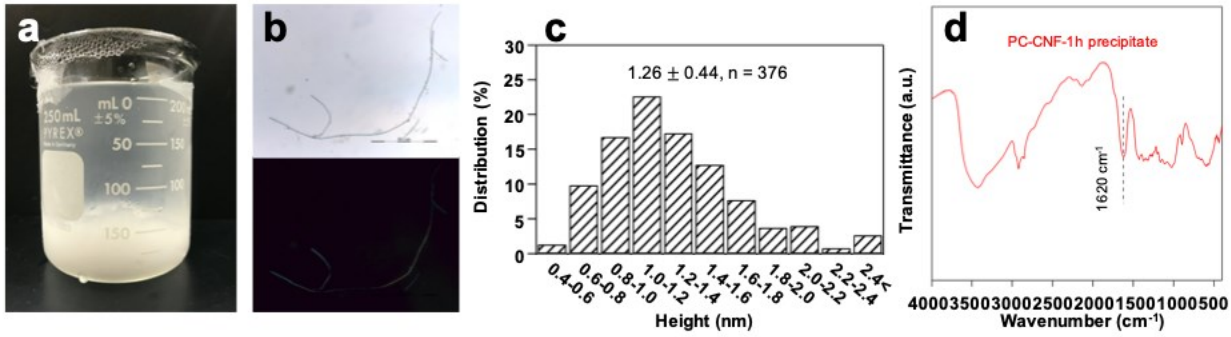


Fig. S2 (a) Non-aqueous dispersible P-cell upon blending and storage at 4 ºC overnight with (b) optical image (top) and birefringence (bottom). (c) Cumulative AFM height distribution of all PC-CNF 0.5–72 h. (d) FTIR spectrum of PC-CNF-1h air-dried precipitate fraction.

Table S2 PC-CNF properties from varied secondary sodium chlorite (1:1 $NaClO_2$/AGU) oxidation reaction time of optimally sodium periodate oxidized (0.5:1 $NaIO_4$/AGU) cellulose, followed by 30 m blending.

PC-CNF-h	yield (%)	carboxylate content (mmol/g)	aldehyde content (mmol/g)	height (nm)	width (nm)	length (μm)
-0.5h	93.7	0.64	0.71	1.2 ±0.38	ND	ND
-1h	93.8	0.86	0.69	1.26 ± 0.51	3.83 ± 1.12	1.01 ± 0.16
-2h	95.5	0.89	0.66	ND	ND	ND
-4h	94.1	0.93	0.62	1.24 ± 0.39	ND	ND
-6h	98.6	0.99	0.56	ND	ND	ND
-8h	95.9	0.99	0.56	ND	ND	ND
-12h	94.3 ± 1.2	1.18	0.17	1.30 ± 0.49	ND	1.01 ± 0.14
-18h	97.9 ± 0.6	1.29	0.06	1.26 ± 0.40	ND	1.01 ± 0.16
-72h	98.0	1.35	0.0	ND	ND	ND
Cumulative	95.6 ±1.6	NA	NA	1.26 ± 0.44	3.83 ± 1.12	1.01 ± 0.16

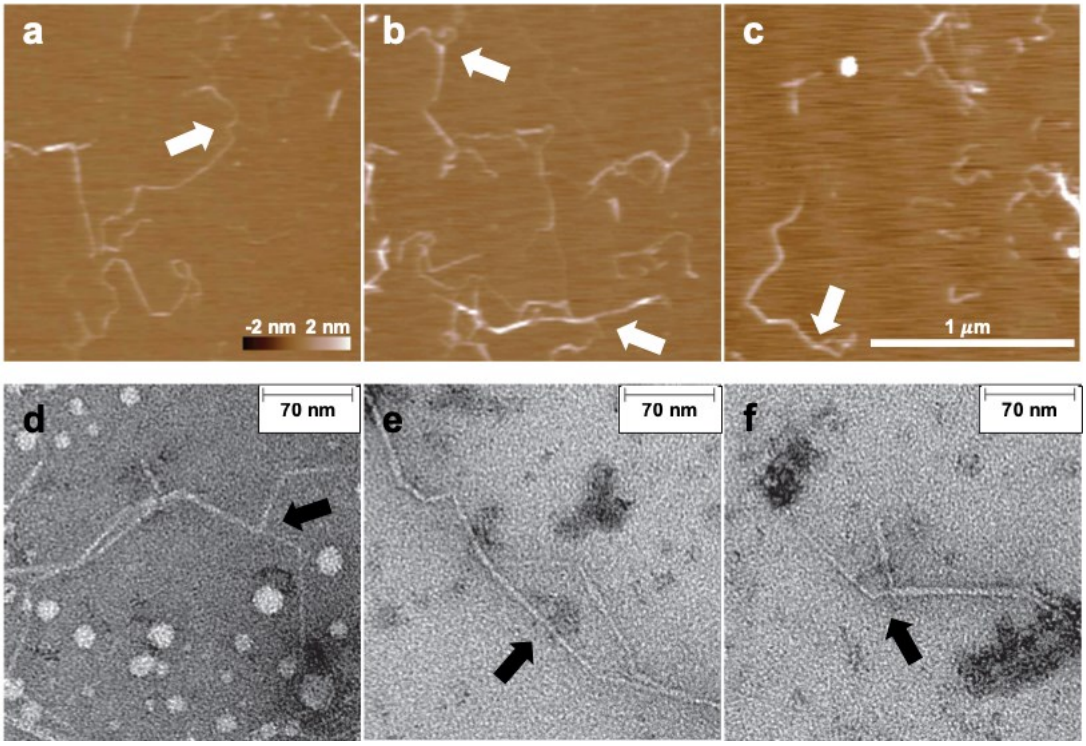


Fig. S3 Kinks and splitting of PC-CNFs: (a–c) AFM images, (d–f) TEM images. Possible splitting event at the end of PC-CNFs (a, b, c, d, f), as well as along the lengths (b, f).

Table S3 Further optimized secondary chlorite oxidation: reduced 0.5:1 $NaClO_2$ molar ratio and blending time. All at fixed 0.5:1 mol/mol $NaIO_4$/AGU (55 ºC, 4 h).

$NaClO_2$/AGU (mol/mol)	$NaClO_2$ reaction time (h)	Deprotonation	Blending time (min)	Yield (%)	Carboxyls (mmol/g)
1:1	4	Yes	15	72.0	1.16
	12		15	85.7	0.92
	18		15	88.3	1.15
1:1	4	No	30	31.5	1.86
	12		30	30.8	1.03
	48		30	47.6	1.48
0.5:1	4	No	15	15.7	1.12
			+15	6.1	0.54
			+30	4.1	0.44
0.5:1	8	No	15	18.9	1.59
			+15	5.6	0.89
			+30	7.0	0.56

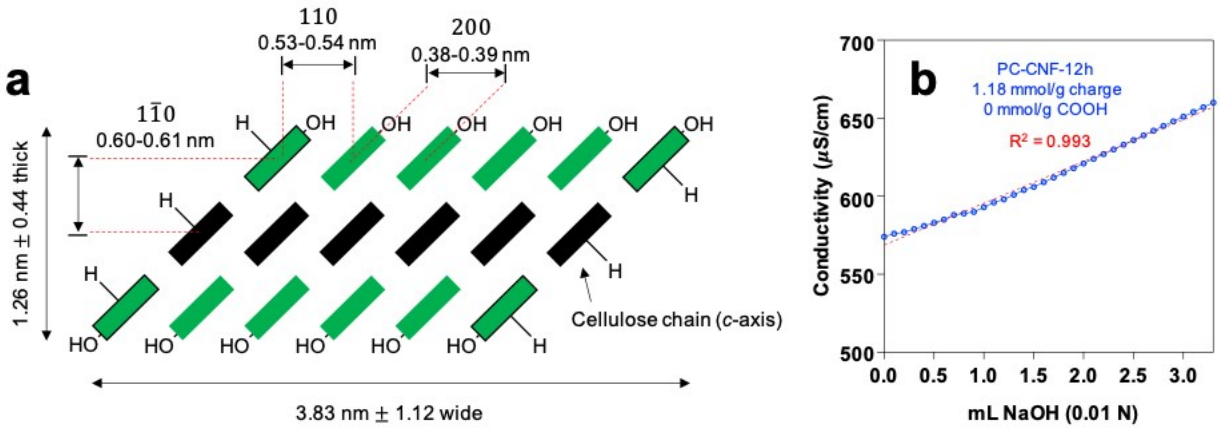


Fig. S4 PC-CNF properties: (a) schematic of PC-CNF-1h two-directional cross-section; (b) titration without HCl of aq. PC-CNF-12h (0.05 %).

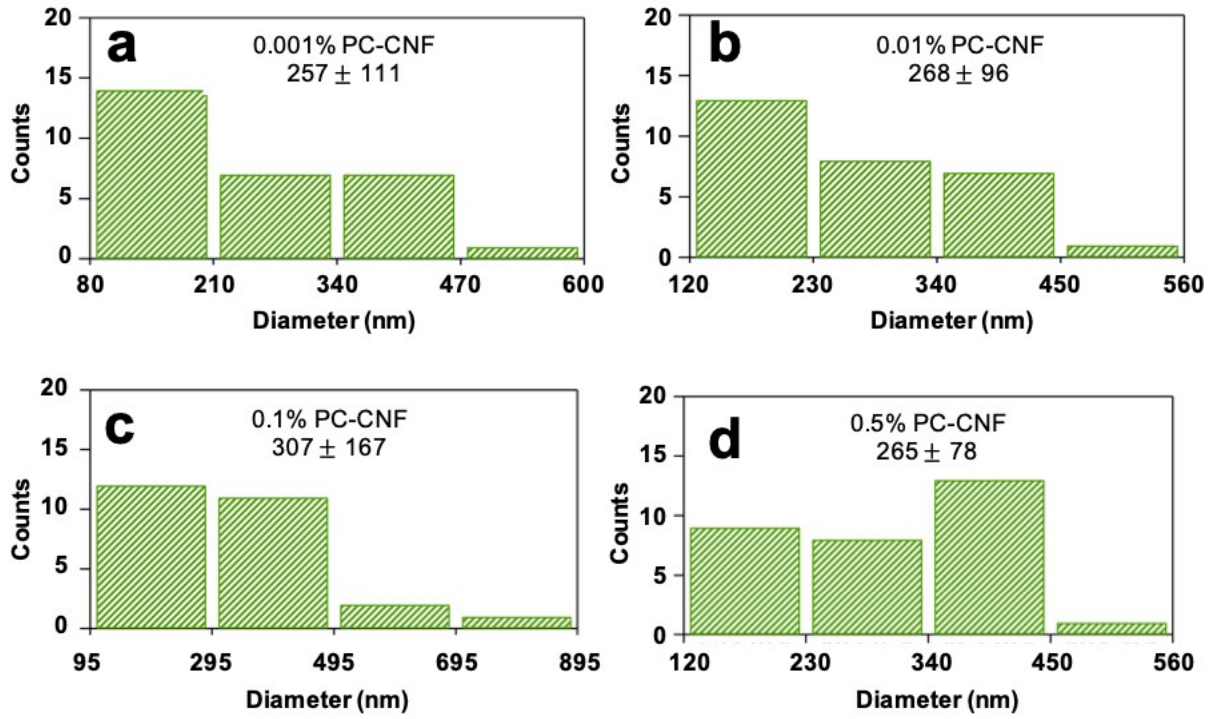


Fig. S5 Characterization of assembled PC-CNFs-72h: (a-d) fibril diameter distributions (*n=30*).

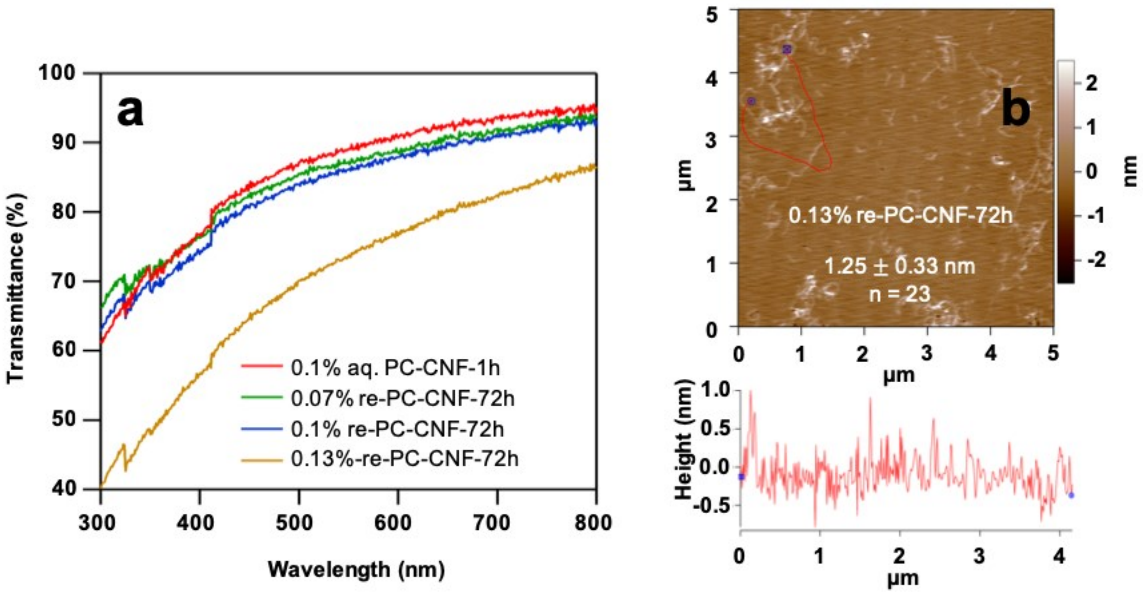


Fig. S6 Water redispersions of PC-CNFs-72h (1.0 %): (a) UV/Vis transmittance; (b) AFM phase image (0.0005 %, mica substrate) and corresponding height trace of aqueous redispersion (0.13 %).

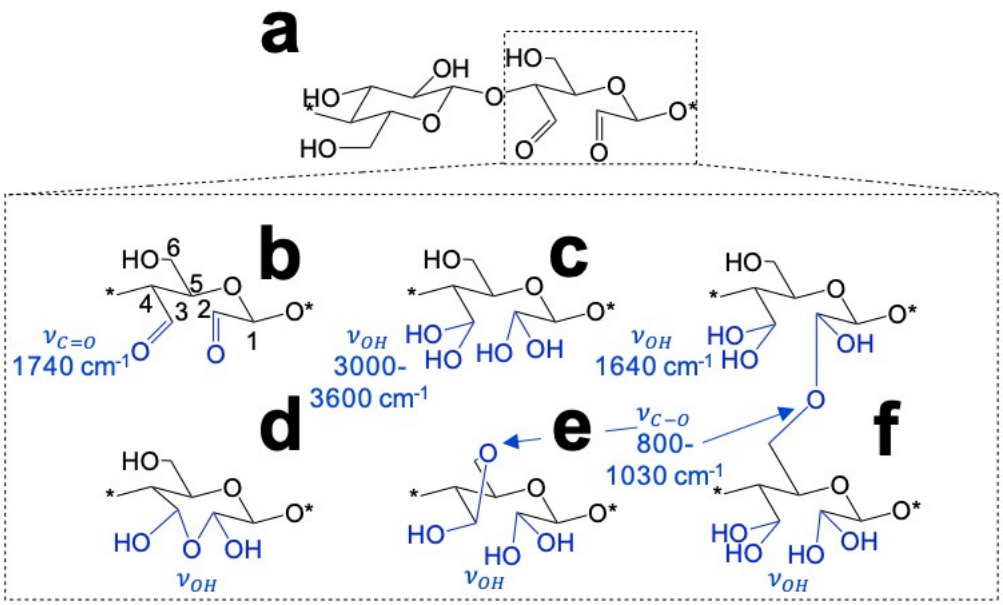


Fig. S7 Periodate oxidized cellulose (P-cell): (a) periodate oxidized cellobiose; (b) aldehydic carbonyl at ca. 1740 cm^{-1};[1-3] (c) possible hydrated aldehyde at ca. 3400 cm^{-1} and 1640 cm^{-1} –OH;[1-3] (d) hemialdol;[1-3] and (e) intramolecular and/or (f) intermolecular hemiacetal ca. 875 cm^{-1} band.[3]

1. H. Spedding, *J. Chem. Soc.*, 1960, 3147–3152.

2. Q. G. Fan, D. M. Lewis and K. N. Tapley, *J. Appl. Polym. Sci.*, 2001, **82**, 1195–1202.

3. L. Münster, J. Vícha, J. Klofáč, M. Masař, P. Kucharczyk and I. Kuřitka, *Cellulose*, 2017, **24**, 2753–2766.

Table S4 PC-CNF aerogel properties from varied secondary sodium chlorite (1:1 $NaClO_2$/AGU) oxidation reaction time of optimally sodium periodate oxidized (0.5:1 $NaIO_4$/AGU) cellulose, followed by 30 m blending, freezing (-20 °C) and freeze-drying at 0.6 and 1.0 % PC-CNF and compared to TEMPO-CNF aerogel,[4,5] all from rice straw.

4. F. Jiang and Y.-L. Hsieh, *J. Mater. Chem. A Mater. Energy Sustain.*, 2014, **2**, 350–359.

5. F. Jiang and Y.-L. Hsieh, *ACS Appl. Mater. Interfaces*, 2017, **9**, 2825–2834.

aerogel	charge (mmol/g)	diameter (mm)	density (mg/cm^3)	porosity (%)	pore volume (cm^3/g)	water (mL/g)	decane (mL/g)	chloroform (mL/g)
TEMPO-CNF 0.6 w%	1.15	12.0 ± 0.1	8.0 ± 0.6	99.5 ± 0.0	125.1 ± 9.8	103.4 ± 7.2	78.0 ± 4.3	85.9 ± 10.9
PC-CNF-12h 0.6 w%	1.18	14.0 ± 0.1	6.2 ± 0.3	99.6 ± 0.0	160.3 ± 7.0	103.3 ± 9.4	129.0 ± 10.7	ND
PC-CNF-1h 1.0 w%	0.86	13.8 ± 0.1	10.9 ± 0.3	99.3 ± 0.0	91.2 ± 2.7	82.4 ± 4.6	ND	72.1 ± 2.8
PC-CNF-4h 1.0 w%	0.93	13.6 ± 0.1	10.6 ± 1.0	99.3 ± 0.1	94.3 ± 8.2	65.3 ± 0.0	ND	67.0 ± 5.8
PC-CNF-8h 1.0 w%	0.99	13.6 ± 0.2	10.3 ± 0.9	99.4 ± 0.1	97.0 ± 8.2	62.7 ± 10.7	ND	60.8 ± 5.3
PC-CNF-12h 1.0 w%	1.18	13.6 ± 0.3	10.2 ± 1.3	99.4 ± 0.1	99.4 ± 13.5	69.7 ± 5.7	89.8 ± 7.7	ND
PC-CNF-18h 1.0 w%	1.29	14.0 ± 0.0	9.1 ± 0.1	99.4 ± 0.0	109.0 ± 0.9	87.1 ± 4.9	86.6 ± 7.4	ND

ND = note determined. PC-CNFs in supernatant following constant blending (37.5k rpm, 30 min) and centrifugation (5k rpm, 15 min). Fixed were 1.0 cm thick aerogels casted in 1.4 cm inner diameter borosilicate glass tubes.

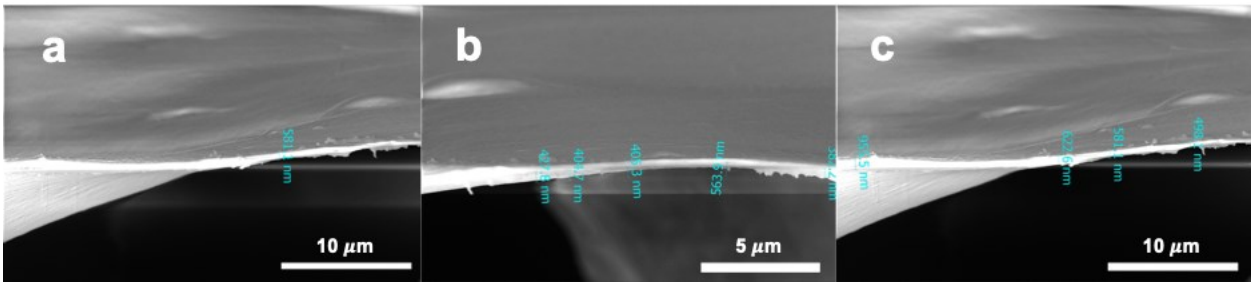


Fig. S8 SEMs of 0.6 % PC-CNF-12 h (1.30 nm thick, 1.01 m long, with 1.18 mmol/g surface charge, at 95 % yield) aerogel radial cross-section showing cell wall thickness. Images showing measurements of three samples made in SEM QUATTRO software.

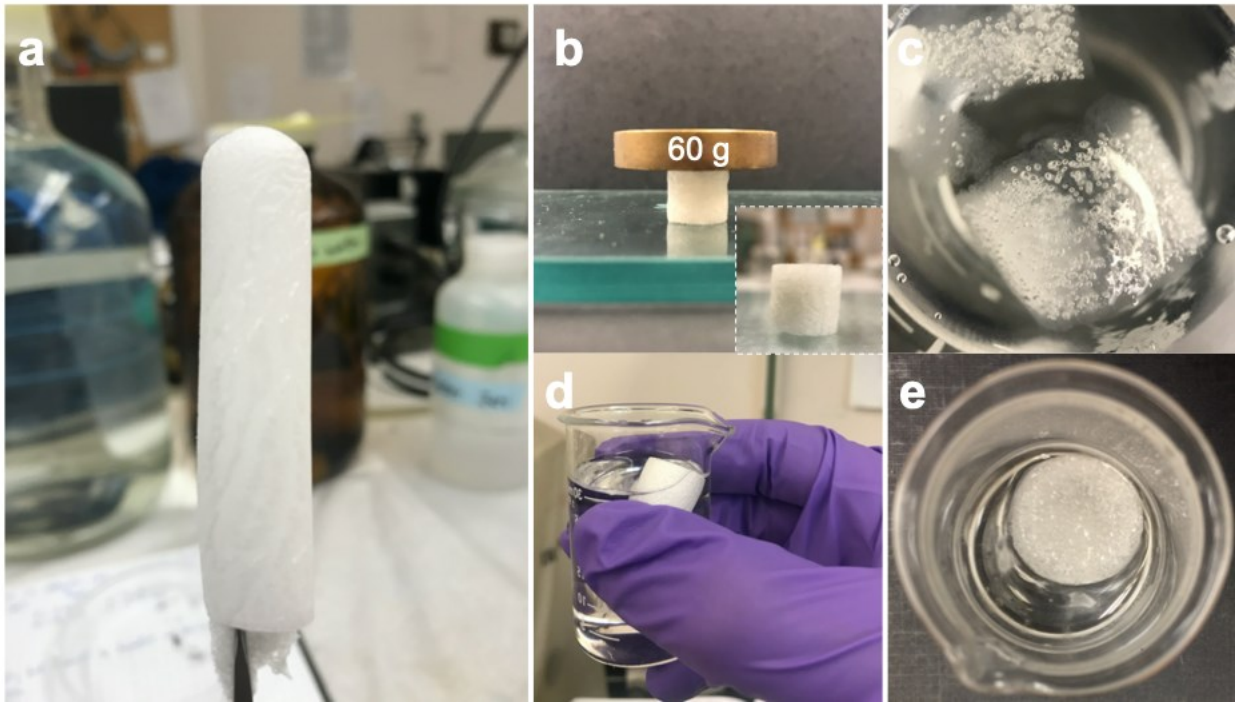
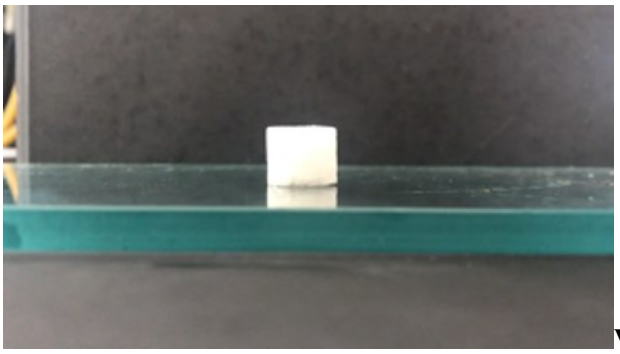
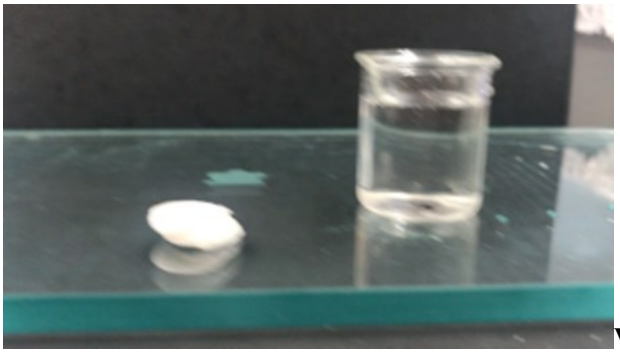


Fig. S9 PC-CNF-8h (0.99 mmol/g) aerogel (1 %): (a) as is; (b) 20 mg (1-cm section as is inset) under 60 g weight in air; (c) wet gel saturated in water for 15 m and pressed against the glass surface with a spatula; (d) chloroform; (e) decane.



Video S1 Dry recovery of PC-CNF-8h (1 %) aerogel (1.4 cm diameter, 1.0 cm height, 17.3 mg, 1.7 cm^3, 10.3 mg/cm^3, 99.4% porosity) under 14 kg weight.



Video S2 Water-activated 100 % shape recovery of PC-CNF-8h (1 %) compressed to 80 % strain in air, showing full return to = 0.0 upon immersion.