Supplementary Information

Inducing Nematic Ordering of Cellulose Nanofibers using Osmotic Dehydration

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1. Additional experimental details

1.1 Morphological characterization

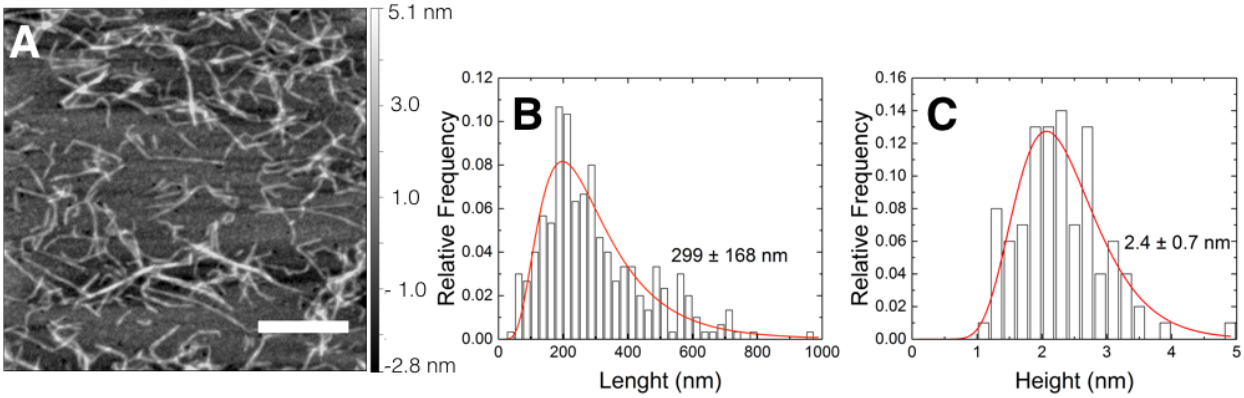

Figure S1. (A) AFM picture of the CNF (scale bar 500 nm). (B) and (C) show the histogram of the height and length distribution of the CNF, respectively measured from 100 and 300 individual nanofibers. The corresponding log-normal distribution is shown in red solid lines.

Figure S1 shows the morphological characterization of the CNF. The CNF suspension (concentration 0.01 wt%) was deposited on freshly peeled mica substrate, which has been functionalized with 3-aminopropyl triethoxysilane (Sigma Aldrich, 99 %) to ensure electrostatic adhesion of the CNF on the mica substrate. After removing the excess of suspension by a stream of air, the sample was ready for the analysis. The height and length of the nanofibers were obtained directly from the images acquired by atomic force microscope Veeco Dimension 3100 SPM (tapping mode). A lognormal function $y = \frac{A}{\sqrt{2\pi}\cdot w\cdot x}\exp\frac{-\left(\ln\left(\frac{x}{x_c}\right)\right)^2}{2w^2}$ was fitted to the data from which the mean, $\bar{x}$, and standard deviation, σ, were calculated according to $\bar{x} = e^{\left(x_c+\frac{w^2}{2}\right)}$ and $\sigma = \bar{x}\cdot\left(e^{w^2}-1\right)^{\frac{1}{2}}$, respectively. The CNF used in this study have a mean length $\bar{L}$ = 299 ± 168 nm and mean height $\bar{h}$ = 2.4 ± 0.7 nm, giving a mean nominal aspect ratio $\bar{a}_0$=125 ± 88.

1.2 Osmotic dehydration setup

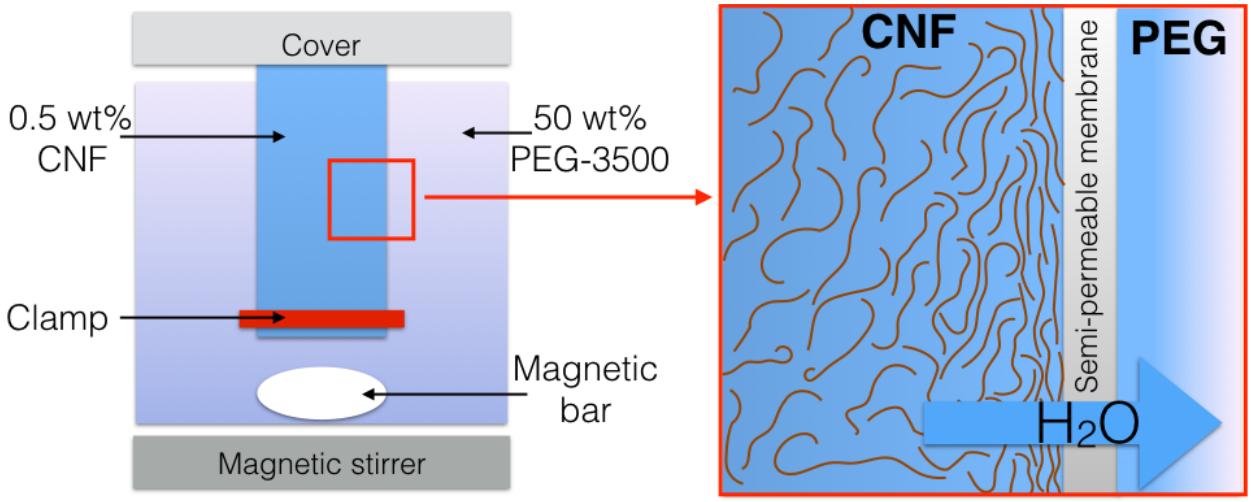

Figure S2. The schematic shows the CNF gel inside the semipermeable membrane, immersed in the PEG solution which is stirred by a magnetic bar.

As shown in Fig. S2, a semipermeable bag containing 30 g of carboxylated CNF suspension (0.5 wt%, prepared according to a previous report[1]) is immersed in 200 g of a 50 wt% poly(ethylene glycol) solution (M_w ≈ 35 kDa). The dialysis bag (cutoff of 14 kDa) is sealed in the bottom by a clamp, while the top is accessible. In the expanded figure (Figure S2 right) the upconcentration and alignment of the CNF is promoted by the removal of water and the osmotic pressure applied by the PEG solution. The clamp closes the membrane in the bottom and lets it accessible from the top, which is closed by a lid.

1.3 Rheological characterization

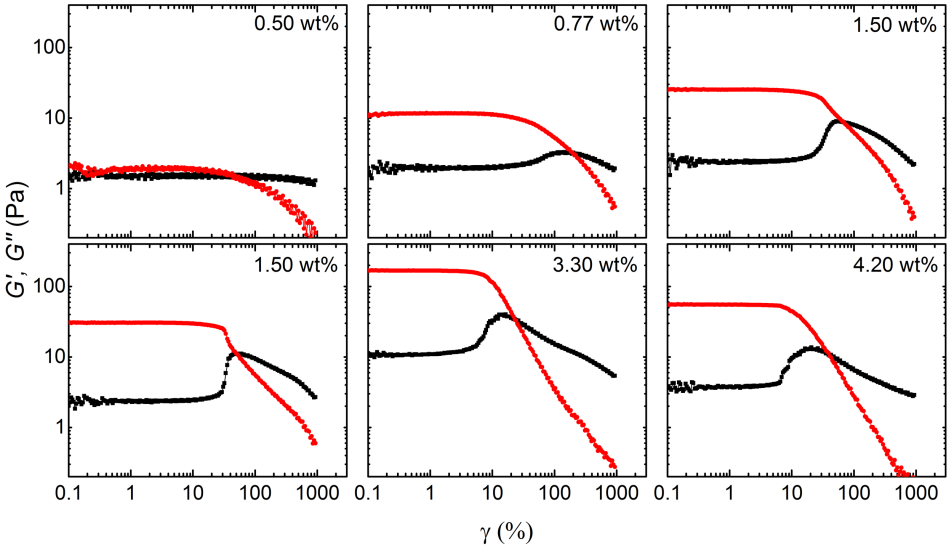

Figure S3: The storage modulus, G', (red) and loss modulus, G'', (black) of the CNF suspensions plotted as a function of strain, . The linear viscoelastic region can be seen from ≈ 0.1 to 10 % In all the samples G' is higher than G'', indicating that the CNF suspensions behave like a viscoelastic solid, with a more predominate character as the concentration increases.

1.4 Critical concentration as function of aspect ratio. Excluded volume and arrested states.

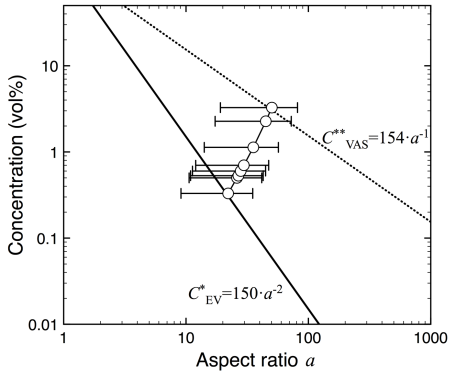

Figure S4. Diagram of concentration as function of aspect ratio, a. The experimental symbols are obtained considering the effective aspect ratio a_{eff} obtained from the constant length of CNF and its variable thickness, i.e., $h_{\text{eff}} = \bar{h} + 2 \cdot \kappa^{-1}$ where κ^{-1} is the Debye length. The error in a_{eff} is obtained using the derivative of the expression for the effective aspect ratio, i.e., $\delta_{a_{\text{eff}}} = \frac{\delta L}{h_{\text{eff}}} + \frac{1}{2}\frac{L \cdot \delta h_{\text{eff}}}{h_{\text{eff}}^2}$ where δL and δh_{eff} are the standard deviations of the length and height of CNF, respectively. The dotted line corresponds to the empirical formula for volume arrested states (C_{VAS}^{**}) obtained by Nordenström et al. for a number of CNF suspensions[2] whereas the continuous line corresponds to the excluded volume calculation of fibers (C_{EV}^{*}) as defined by Mason.[3]

1.5 Small-angle X-ray scattering

Table S1. SAXS fitting parameters of Eq. 1, see main text for details.

C [wt%]	Scale ($\times 10^{-3}$)	n	$I_G(0)$ ($\times 10^{-2}$)	Ξ [nm]	$I_L(0)$ ($\times 10^{-2}$)	ξ [nm]
0.5	0.26	2.54	5.17	10.16	4.48	3.95
0.75	2.00	2.21	8.14	8.70	4.70	2.87
0.8	3.16	2.10	7.87	8.52	4.14	2.58
0.9	3.67	2.07	5.06	7.05	4.33	2.49
1.05	3.08	2.16	9.78	6.22	9.31	2.47
1.6	2.03	2.28	10.61	5.00	11.20	2.38
1.7	2.07	2.28	8.00	4.56	11.13	2.42
3.4	2.39	2.25	11.54	3.25	9.89	1.98
4.9	4.22	2.28	21.10	2.85	11.00	1.59

2. Additional references

1. H. Lu, V. Guccini, H. Kim, G. Salazar-Alvarez, G. Lindbergh, and A. Cornell, *ACS Appl. Mater. Interfaces*, 2017, **9**, 37712–37720.
2. M. Nordenström, A. Fall, G. Nyström, and L. Wågberg, *Langmuir*, 2017, **33**, 9772–9780.
3. S. G. Mason, *Pulp Pap. Mag. Canada*, 1950, **51**, 94–98.