Supporting Information for

Cellulose Nanofibril Hydrogel Tubes as Sacrificial Templates for Freestanding Tubular Cell Constructs.

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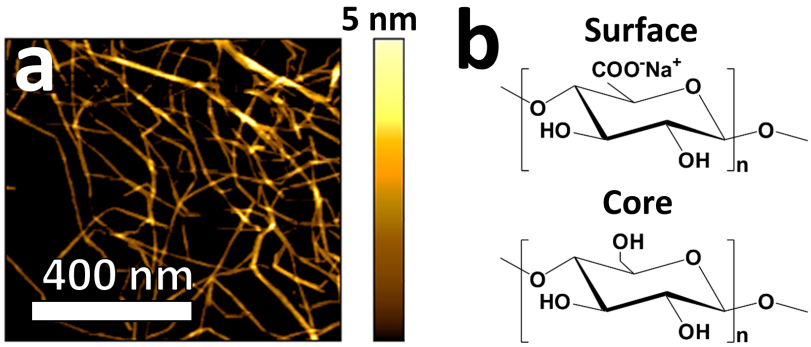

Figure S1. AFM height micrograph of the utilized CNF (a) and chemical structures of the core and surface of the CNFs (b).

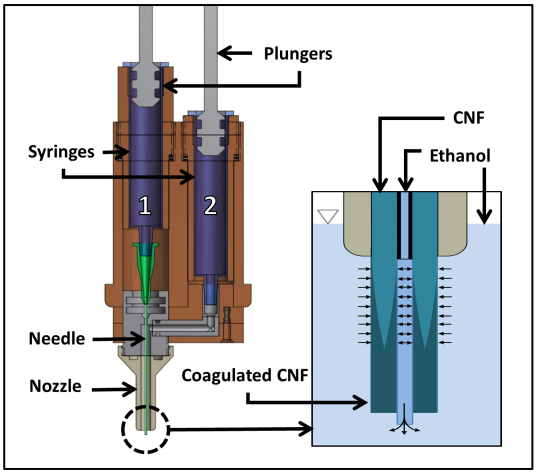

Figure S2. Inner components of the bioextruder and coagulation gradient happening in the coagulation bath (inset).

FTIR studies

We performed FTIR studies to support the GA crosslinking. The reduction of intensity in the -OH bands (ν = 3330-3350 cm^{-1}) can be used as an indication that GA reacts with the hydroxyl groups by correlating the -OH band at 3345 cm^{-1} with the near constant band at 1371 cm^{-1}, which is characteristic for carbohydrates and assigned to the C-H bending in cellulose and hemicellulose.[1] This consideration follows Mansur et al., who demonstrated the direct relationship between the ratio of poly(vinyl alcohol) (PVA)/GA and the concentration of hydroxyl groups in PVA crosslinked hydrogels.[2] Indeed the ratio decreases by ca. 15 % as shown in Figure S3a. The FTIR spectrum of a CNF-GA (Figure S3b) have the characteristic bands of native celluloses and TEMPO-oxidized celluloses.[1, 3, 4] Notice that the band at 1726 cm^{-1} represents the protonated carboxyl groups created by the addition of HCl during GA treatment

process. For comparison we show CNF and CNF-$CaCl_2$ (Figure S3c), in which no change of the COO^- band can be observed.

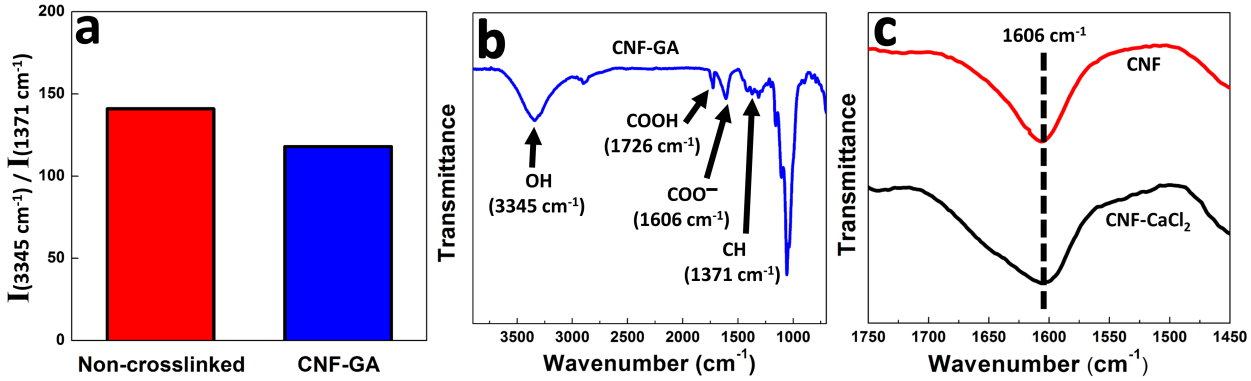

Figure S3. (a) Changes of the ratio of the peaks at 3345 cm^{-1} and 1371 cm^{-1}. (b) FTIR spectrum of a CNF-GA sample with assigned bands (used in this study). (c) FTIR spectra of non-crosslinked (CNF) and CNF-$CaCl_2$ samples in the region of 1450 to 1750 cm^{-1}.

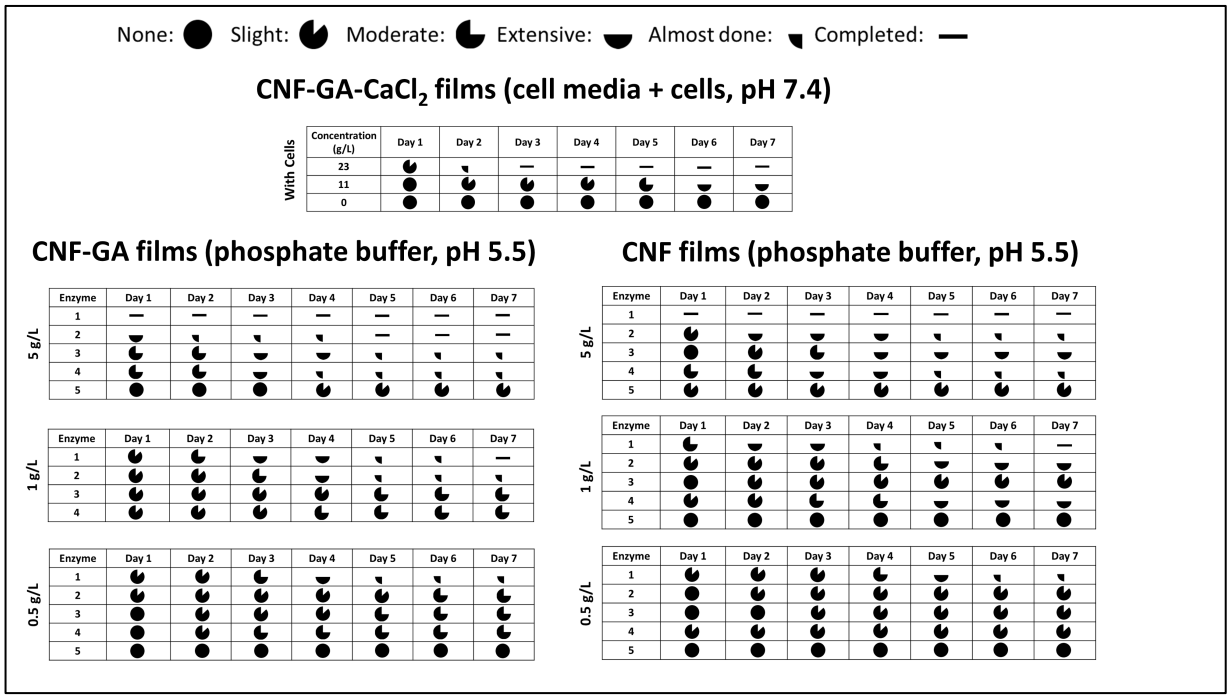

Figure S4. Enzymatic degradation observed at 37 °C of crosslinked (CNF-GA, CNF-GA-$CaCl_2$) and non-crosslinked CNF films.

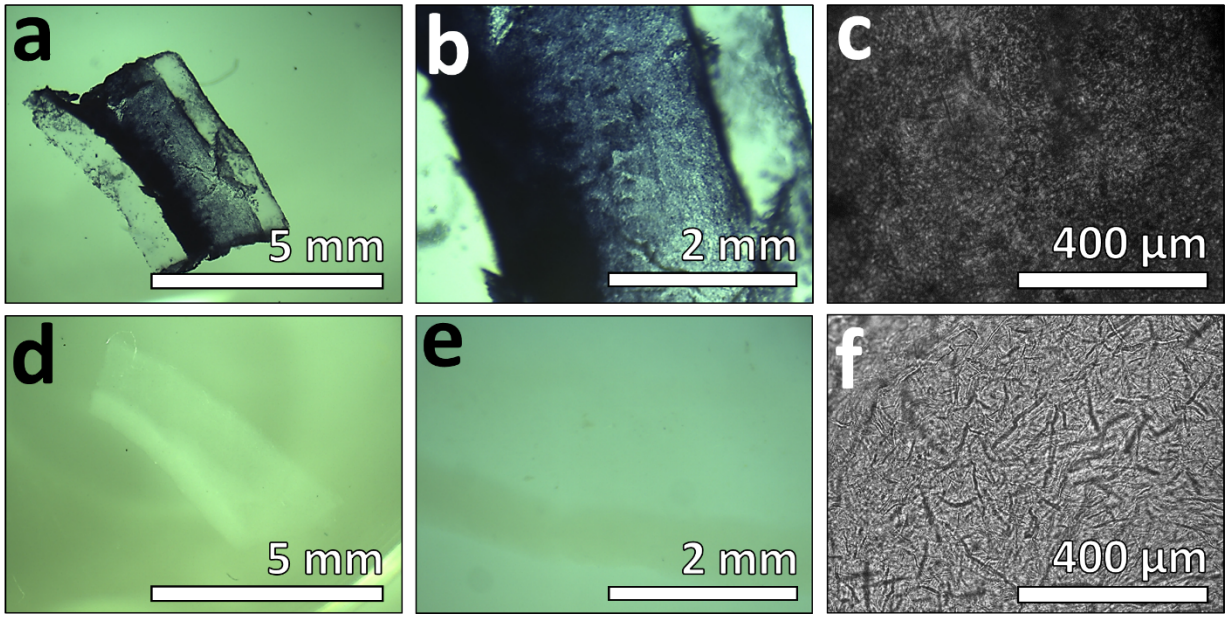

Figure S5. Multiscale characterization of cell cultured CNF-GA-$CaCl_2$ hollow tubes (500000 cells seeded and negative control). (a-c) Bright-field micrographs of a MTT stained CNF-GA-$CaCl_2$ tubes stained 3 days after seeding of 500000 cells. Cells are more inhomogeneously distributed. (d-f) Negative control: Bright-field micrographs of a MTT stained CNF-GA-$CaCl_2$ tube (no cells seeded). All samples are cut in half.

REFERENCES

1. Liang, C. Y.; Marchessault, R. H., *J. Polym. Sci.* **1959,** *39*, 269-278.
2. Mansur, H. S.; Sadahira, C. M.; Souza, A. N.; Mansur, A. A. P., *Mater. Sci. Eng. C* **2008,** *28*, 539-548.
3. Habibi, Y.; Chanzy, H.; Vignon, M. R., *Cellulose* **2006,** *13*, 679-687.
4. Ifuku, S.; Tsuji, M.; Morimoto, M.; Saimoto, H.; Yano, H., *Biomacromolecules* **2009,** *10*, 2714-2717.