Supporting Information

Nanostructured Cellulose II Gel Consisting of Spherical Particles

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Table S1. Comparison of the starting materials (pulp 1 and pulp 2) by GPC and x-ray scattering. M_w weight averaged molar mass, C_{WAXS} crystallinity determined by WAXS, D_{hkl} WAXS crystallite dimension, h_c/h_a solid state-NMR crystalline-amorphous ratio.

Samples	M_w (kg/mol)	Carbonyl content (µmol/g)	C_{WAXS} (%)	D_{110} (nm)	D_{020} (nm)	h_c/h_a
Pulp 1	233.9	9.9	68	3.6	4.9	1.18
Pulp 2	188.1	7.5	55	4.2	6.1	1.01

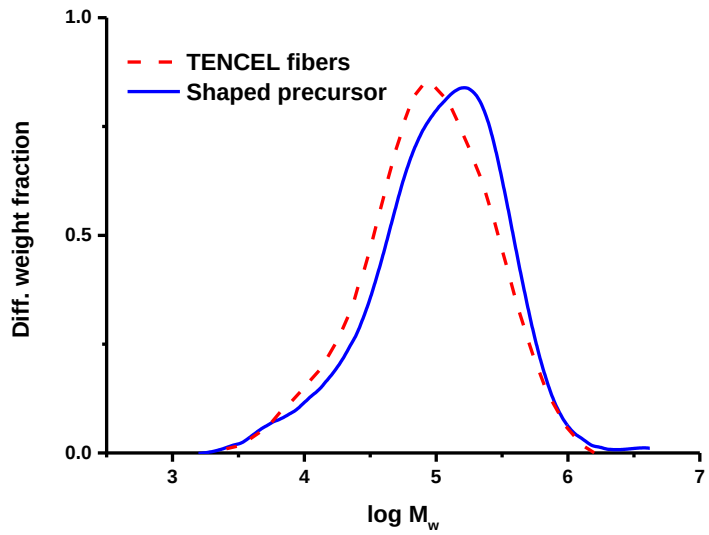

Figure S1. MW distribution of the shaped precursor and Lyocell fibers. Both were obtained from the Lyocell process and the shaped precursor is part of a high MW fraction in this process.

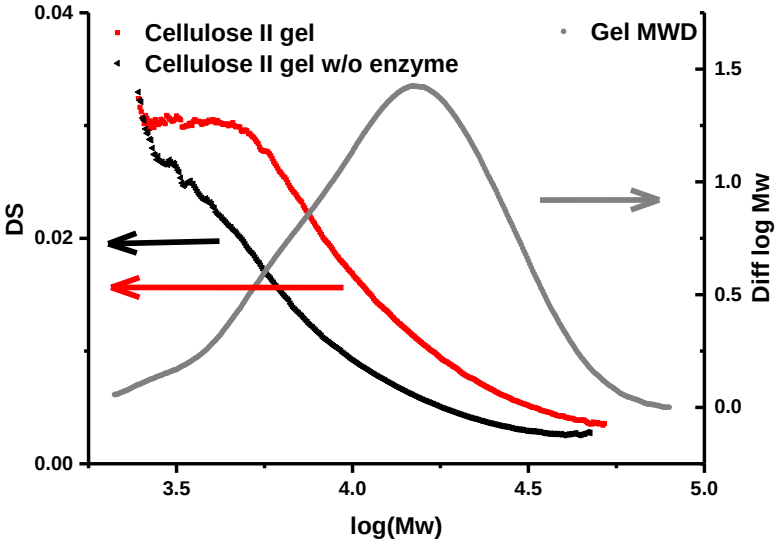

Figure S2. Relation of the carbonyl content to the molecular weight of the cellulose II gel before (red line) and after (black line) heating in 0.1 M aqueous NaOH solution for 30 min at 80°C. After the treatment, remaining residues from the enzymatic treatment were successfully removed.

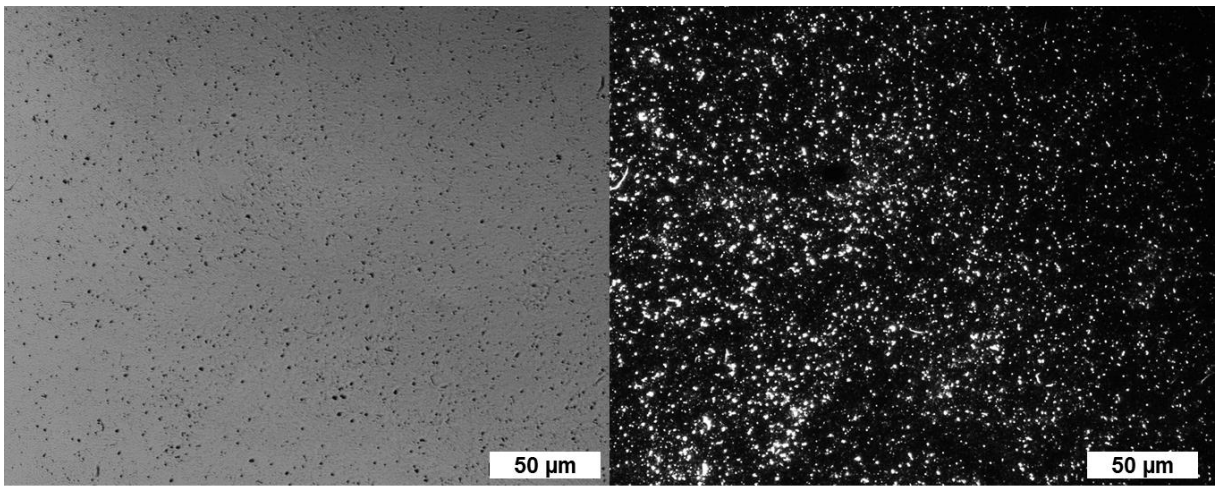

Figure S3. Appearance of a drop of aqueous cellulose II gel (approx. 0.02 wt%) dried on a glass (left). The particles were stained beforehand with calcofluor white stain to increase the contrast of the small particles to the background as shown in the fluorescence image on the right side.

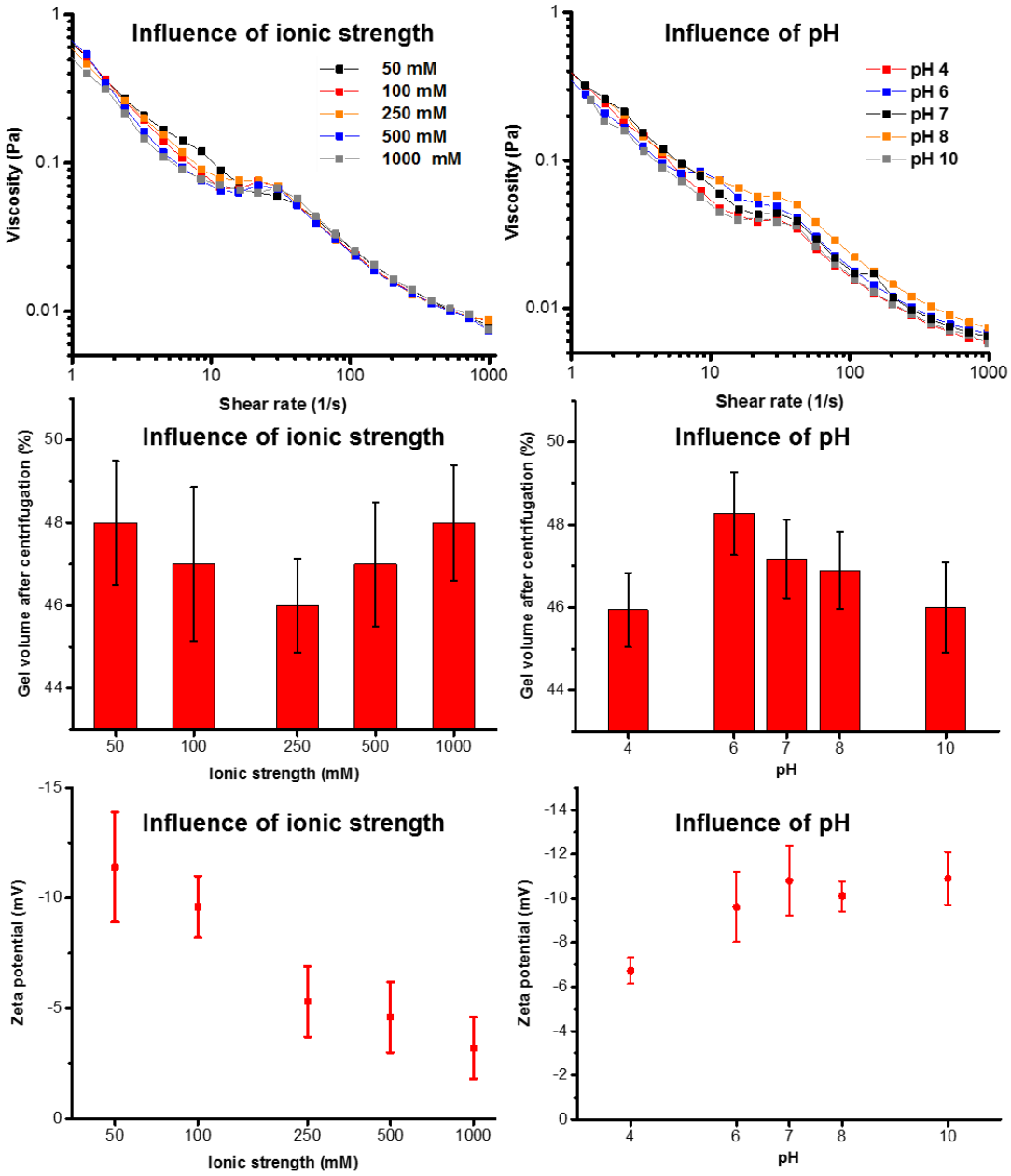

Figure S4. Influence of ionic strength (50 mM – 1000 mM NaCl) and pH in the range of 4 to 10 (100 mM buffer) on the viscosity and stability of the cellulose II gel (3.2 wt%). Without applying centrifugal force the prepared suspensions were all stable at RT. Centrifugation at 2000 RCF for 2 min resulted in a phase separation into a supernatant water and a concentrated gel phase. Measurement of the volume of the gel phase was used to estimate the stability of gel. Zeta potential was measured at 1.6 wt%.

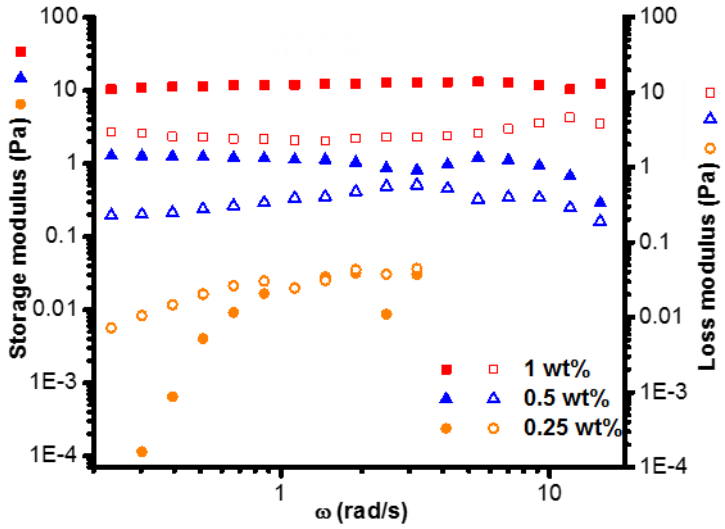

Figure S5. Frequency dependence of storage (G') and loss modulus (G'') of cellulose gels with different solid contents ranging from 0.25 wt% to 1 wt%. Suspensions with solid contents higher than 0.25 wt% show a dominant elastic behavior. In contrast to that, the suspension with a solid content of 0.25 wt% does not behave as gel and features dominant viscous behavior.

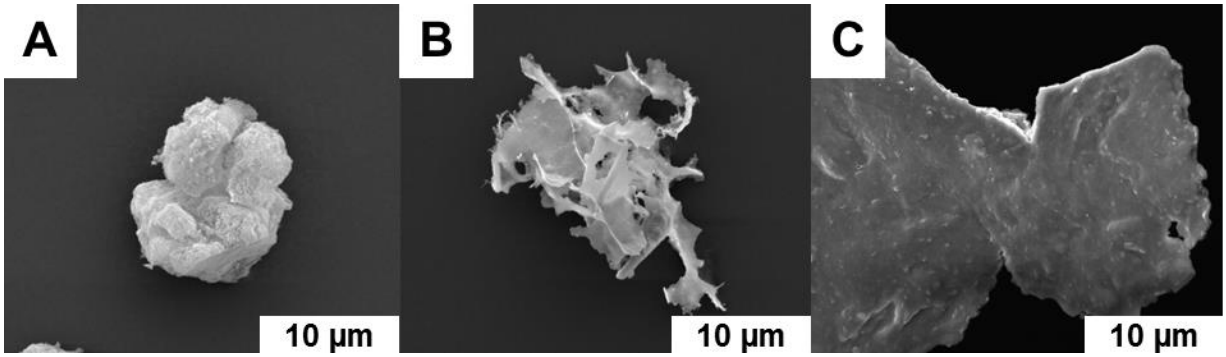

Figure S6. Comparison of cellulose II gel freeze-dried under different conditions. **A** freeze-dried from the *t*BuOH alcogel with pre-freezing in liquid nitrogen. **B** and **C** freeze-dried from the hydrogel, whereas **B** was pre-frozen in liquid nitrogen and **C** in a freezer at -20°C.

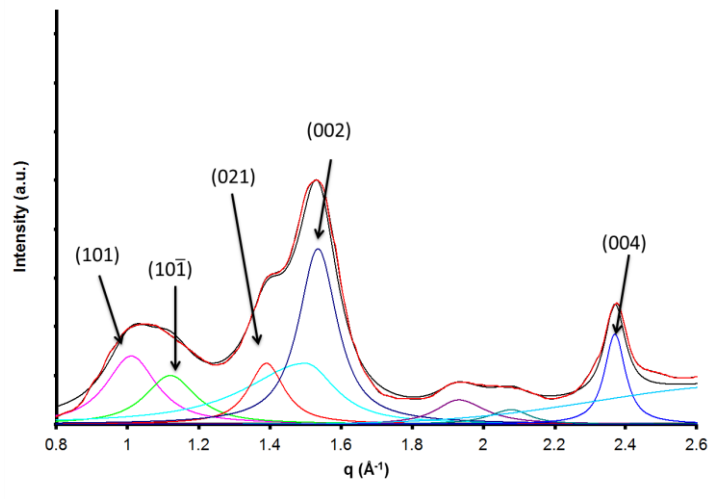

Figure S7. Diffractogram of pulp 2 (red line). The black line shows the fitted curve of the cellulose I sample.

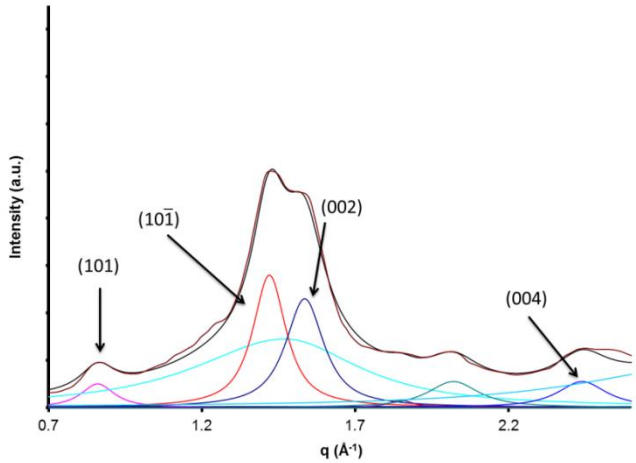

Figure S8. Diffractogram of TENCEL gel (red line). The black line shows the fitted curve of the cellulose II sample.

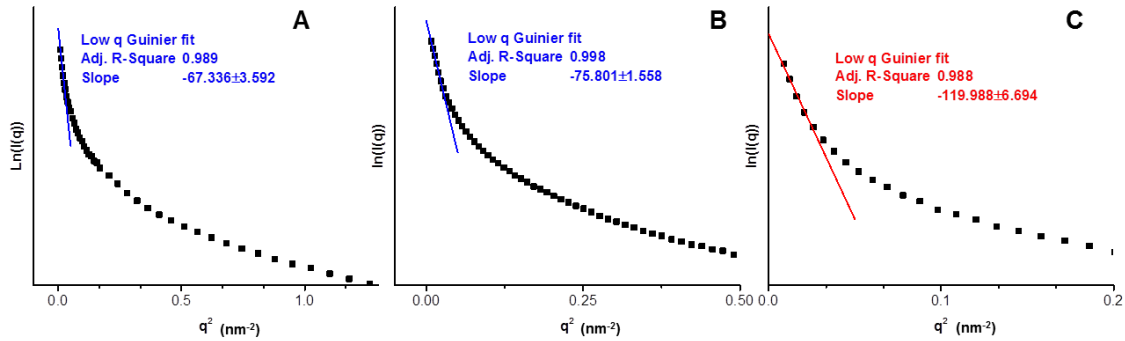

Figure S9. Calculation of the radii of gyration from the low q Guinier region of the scattering curve. A-C show the Guinier plots, q^2 against ln[I(q)], of the sample never-dried, freeze-dried from *t*BuOH and freeze-dried from water, respectively.

Materials and Methods

Sample preparation for gel stability

TENCEL gel (4 wt%) was diluted to 3.2 wt% and the ionic strength of the samples was adjusted by addition of NaCl to 50 mM, 100 mM, 250 mM, 500 mM and 1000 mM. For pH dependency solutions of the gel (3.2 wt%) were prepared with a buffer concentration of 100 mM (pH 4 acetate buffer, pH 6 citrate buffer, pH 7 and pH 8 phosphate buffer, pH 10 ammonium buffer). The prepared samples were used for rheological measurements. In addition to that, the stability of the colloidal suspensions was estimated by centrifugation at 2000 RCF for 2 min. The upper water phase was decanted and its volume was measured ($V_{supernatant}$). The gel volume after centrifugation (V_{gel}) was determined using Eq. S1 (Figure S4).

$$V_{gel} = 1 - \frac{V_{supernatant}}{V_{total}} \qquad \text{Eq. S1}$$