

Supplementary Information

Self-Aligned Integration of Native Cellulose Nanofibrils towards Producing Diverse Bulk Materials

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Preparation procedure for aqueous dispersions of cellulose nanofibrils

Supplementary figures, Figs. S1 to S9

References

Surface Carboxylation and Nanofibrillation of Cellulose

Cellulose (1 g) was suspended in distilled water (100 mL) containing TEMPO (0.016 g) and NaBr (0.1 g). A 1.8 M NaClO solution (2.1 mL) was added to the cellulose suspension, and the pH of the suspension was maintained to be 10 by adding 0.5 M NaOH with a pH stat. After 1 h, the oxidized cellulose was thoroughly washed with distilled water by filtration (recovery ratio > 95%). The TEMPO-oxidized cellulose was further treated with 1% NaClO₂ (100 mL) at pH 4.8 for 1 day to oxidize aldehyde groups remaining in the oxidized cellulose,¹ and washed with distilled water again. Carboxylate content of the oxidized cellulose was determined to be approximately 1.2 mmol per gram of the cellulose by an electric conductivity titration method.¹

A part of the oxidized cellulose was mechanically disintegrated in water to individual nanofibrils by the following procedure; a 0.11% w/v suspension of the oxidized cellulose (25 mL) was treated with a double-cylinder type homogenizer (Physoctron NS-56, Microtec) for 2 min, and then sonicated for 4 min using an ultrasonic homogenizer equipped with a 7 mm probe tip (US-300T, Nihon Seiki). Unfibrillated fraction (< 15%) was removed by centrifugation at 12,000g for 20 min, and the supernatant was used as the nanofibril dispersion. The nanofibril dispersions at ~0.1% w/v were evaporated up to a designed concentrations at 42 °C under reduced pressure.

Supplementary Figures

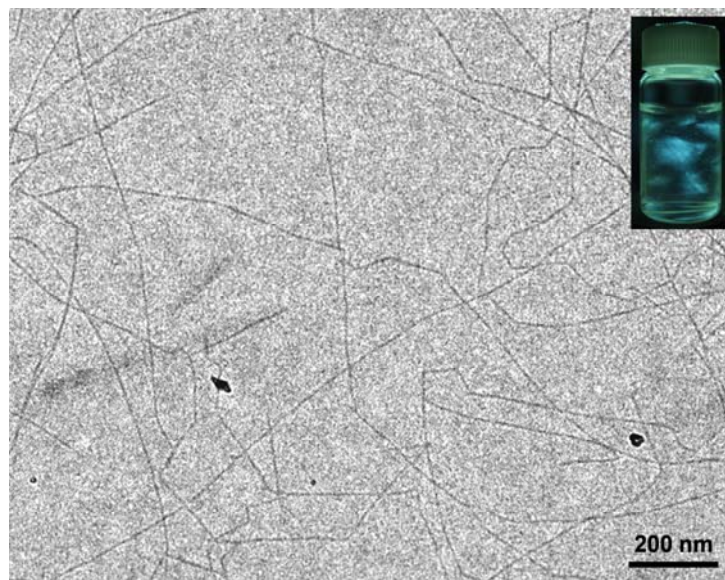


Figure S1. TEM image of wood cellulose nanofibrils dispersed in water. The image shows individualized cellulose nanofibrils with widths of 4 nm and lengths of more than 1 μm . The inset is a birefringence image of the 0.1% aqueous dispersion placed at rest between crossed polarizers.

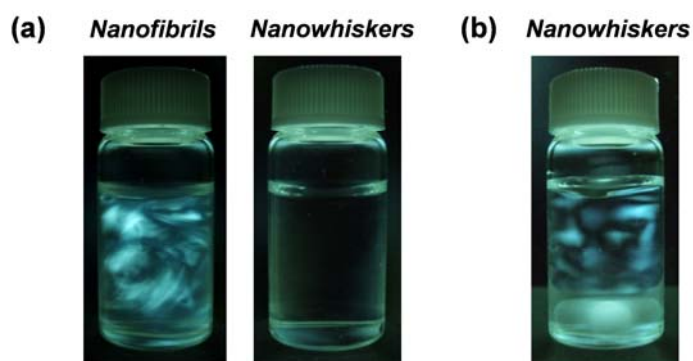


Figure S2. Anisotropic dispersion of cellulose nanofibrils in water. a) 0.2% aqueous dispersion of wood cellulose nanofibrils or nanowhiskers. Aspect ratios of the nanofibrils and nanowhiskers are over 250 (Fig. S1) and ~ 50 (length: 100–300 nm),² respectively. The images were taken for the dispersions placed at rest between crossed polarizers. The nanofibril dispersion shows a distinct birefringence, whereas the nanowhisker dispersion showed no birefringence even at the same concentration. This indicates that the nanowhiskers with low aspect ratios are isotropically dispersed in water. The nanowhiskers were prepared by the surface carboxylation of wood cellulose hydrolyzed beforehand with 2 M HCl at 105°C for 1 h. b) Flow-induced birefringence of the 0.2% nanowhisker dispersion stirred between crossed polarizers, indicating orientation of the nanowhiskers in water by flow.³

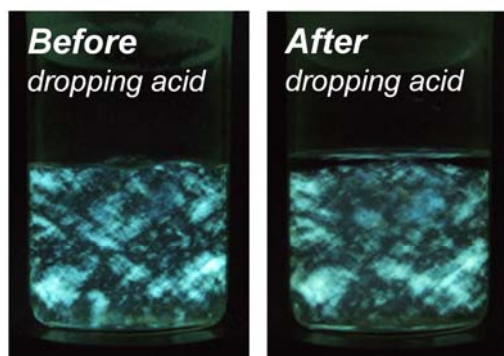


Figure S3. Fixation of anisotropic alignment of cellulose nanofibrils dispersed in water. Birefringence texture of the 0.4% dispersion was nearly unchanged before and after dropping 0.1 M HCl. The images were taken for the dispersion placed at rest between crossed polarizers.

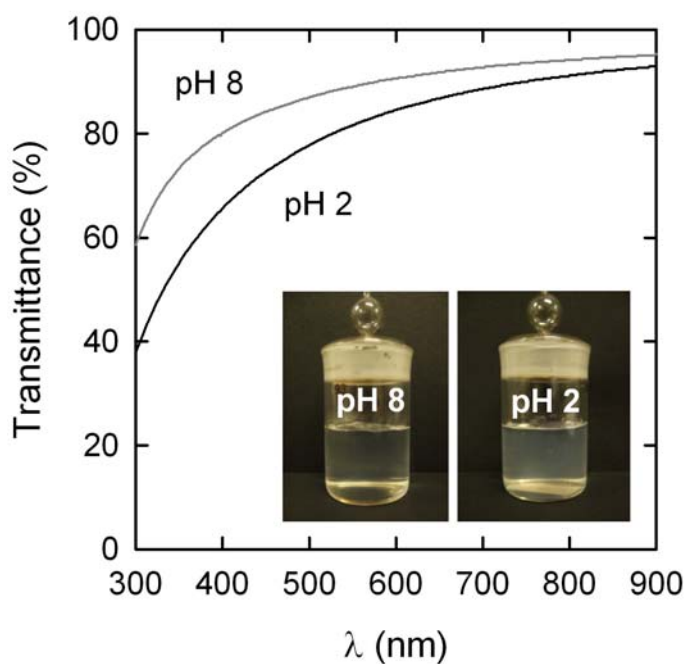


Figure S4. Optical transmittances of hydrogels. The spectra were measured for the 0.4% nanofibril dispersion before (pH 8) and after (pH 2) dropping 0.1 M HCl onto the dispersions. The light-path length is 1 cm. The insets are their appearances.

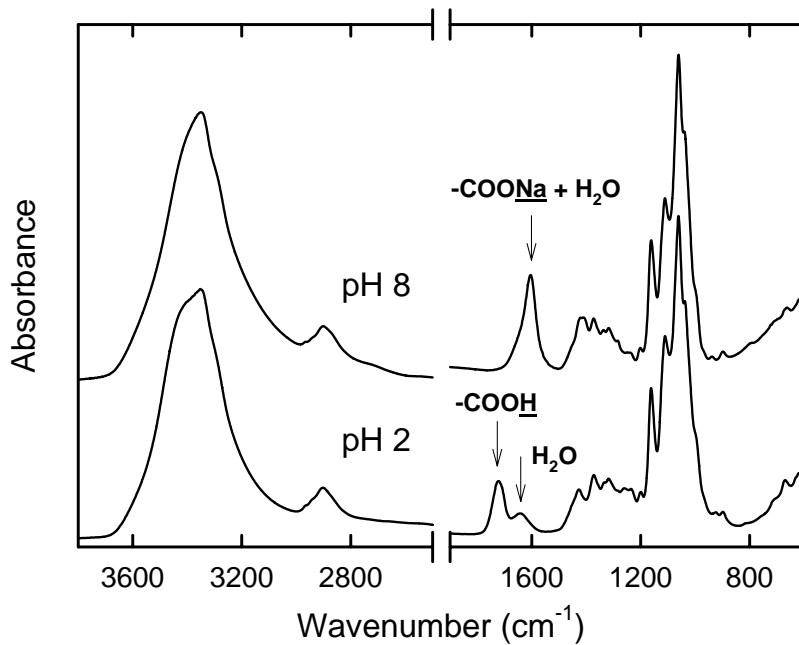


Figure S5. FTIR spectra of cellulose nanofibrils through acid treatment. The spectrum was measured for a film formed from the nanofibril dispersion by casting and drying (pH 8). The film was then soaked in 0.01 M HCl for 6 h and thoroughly rinsed with distilled water (pH 2). Counter ions of the surface carboxyls of nanofibrils changed from sodium (1600 cm^{-1}) to proton (1720 cm^{-1}).⁴

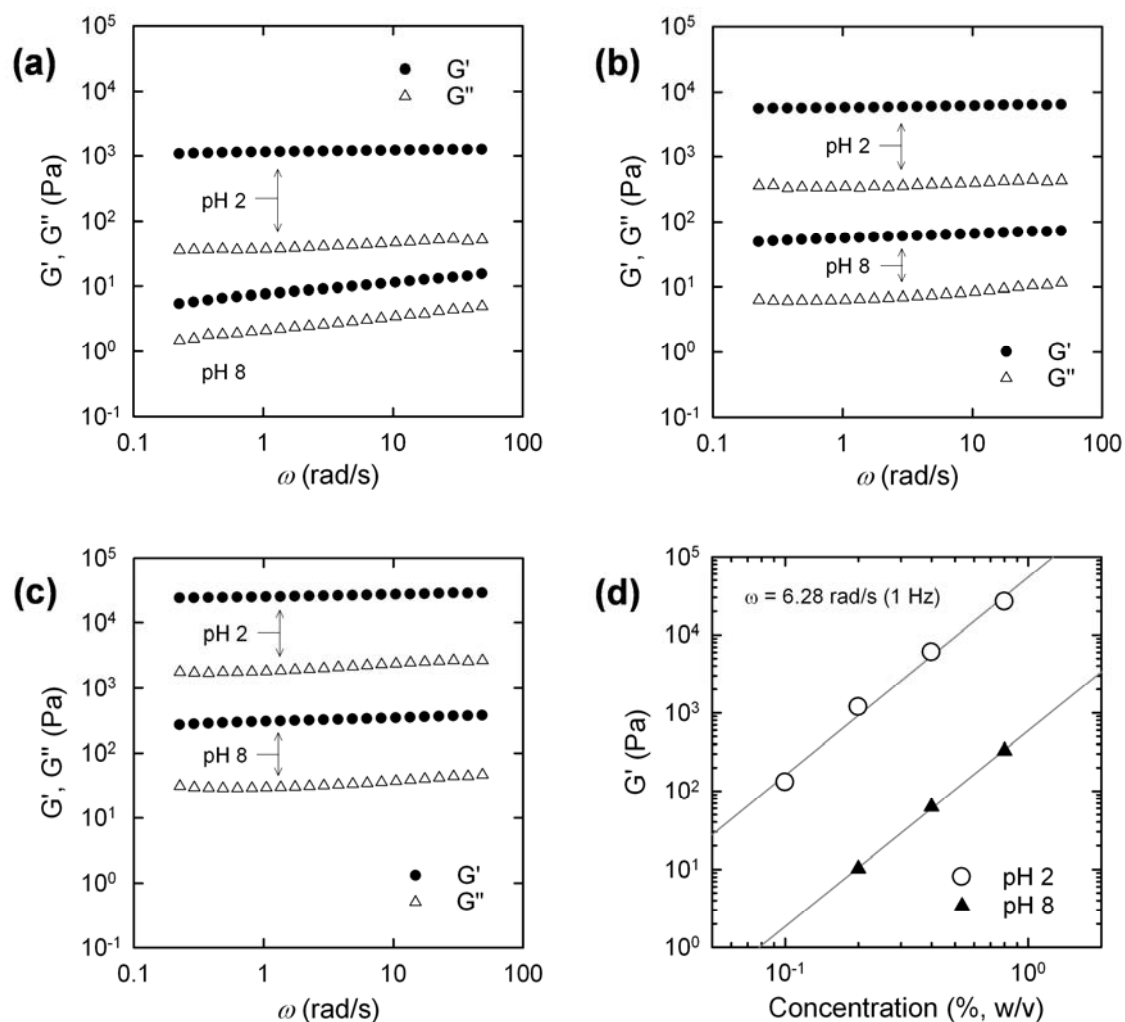


Figure S6. Changes in dynamic viscoelasticity of nanofibril dispersions by the pH decrease. G' and G'' values as a function of frequency: a) 0.2%, b) 0.4%, and c) 0.8% dispersions. d) G' values for the dispersions as a function of concentration at the frequency of 1 Hz ($\omega = 6.28 \text{ rad s}^{-1}$). For all the dispersions, G' values increased by two orders of magnitude with the pH decrease. The slope of G' , or α in the equation of $G' = Ac^\alpha$, is 2.5 at pH 8, which is the same value as that at pH 2.

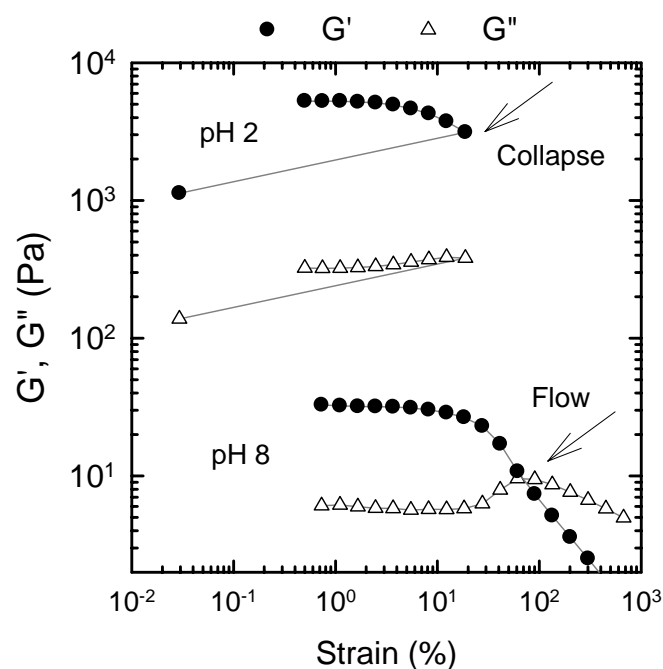


Figure S7. Strain sweep tests of hydrogels. G' and G'' values as a function of strain for the 0.4% nanofibril dispersion (pH 8) or its gel (pH 2). The hydrogel collapsed at ~20% strain without flowing, while the dispersion showed the flow state; G'' went over G' at ~100% strain.

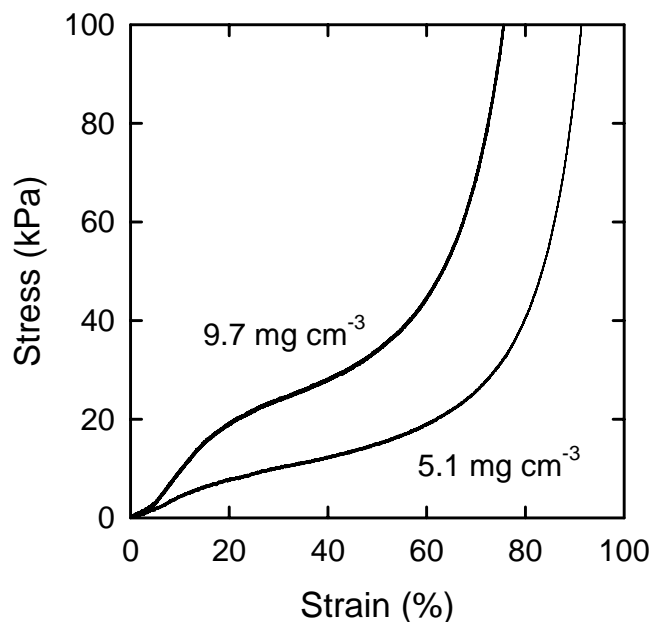


Figure S8. Compression stress-strain curves of aerogels. Densities of the aerogels are presented next to the corresponding curves. The aerogels behaved as linear elastic materials at the low strain region, and had the yielding point. Cellulose aerogels show the strain-hardening behavior;⁵ compression stress drastically increased in higher strain region after the yielding point.

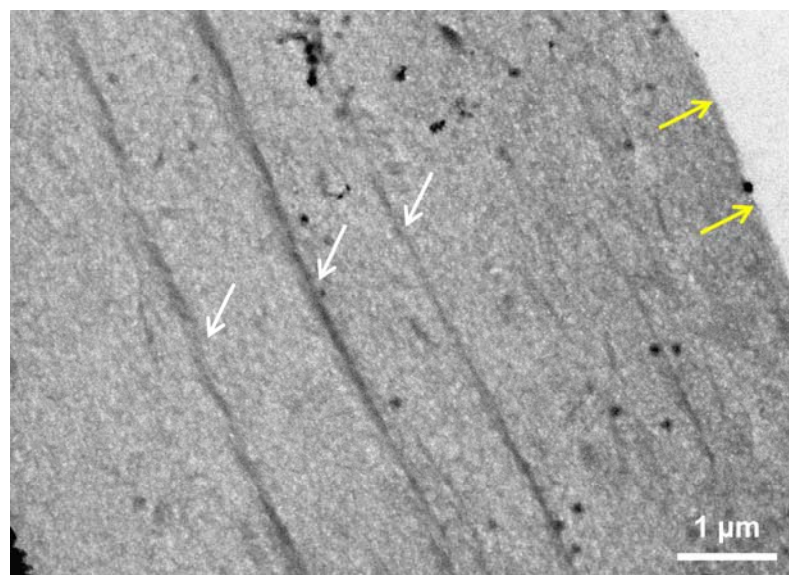


Figure S9. TEM image of a film cross-section at lower magnification. The image shows a layered structure parallel to the film surfaces. The yellow arrows point the film surface, and the white arrows point distinct layers of aligned nanofibrils as shown in Figure 4.

References

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- [2] S. Elazzouzi-Hafraoui *et al.*, *Biomacromolecules* **2008**, *9*, 57.
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- [4] S. Fujisawa *et al.*, *Carbohydr. Polym.* **2010**, *84*, 579.
- [5] H. Sehaqui, M. Salajková, Q. Zhou, L. A. Berglund, *Soft Matter* **2010**, *6*, 1824.