Supplementary information (ESI)

Wet Esterification of Never-dried Cellulose: A Simple Process to Surface-Acetylated Cellulose Nanofibers

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Table S1: Process parameters in the organosolv pulping.[1]

Sample	Temperature / °C	Pressure / bar	H_2SO_4 / %	Duration / min
L-Cell	170	15	0	90

Table S2: Chemical composition of the used pulp samples. Cell refers to the bleached beech dissolving pulp L-Cell to a lignin-rich organosolv pulp, processed according to the conditions in Table S1.

Sample	Glucose / wt%	Xylose /wt%	Mannose / wt%	Lignin / wt%
L-Cell	56.2	16.9	1.3	17.0
Cell	96.1	3.0	-	-

Table S3: Acetyl content before and after surface-acetylation of bleached pulp (Cell) and non-bleached pulp (L-Cell).

Sample	Acetyl content[#] / mmol/g
Cell	-
Cell-Ac	0.10, 0.10*
L-Cell	0.10[$]
L-Cell-Ac	0.21

[#]The degree of acetylation was approximated from NMR spectra in Figure 2C and Figure S2B by relating the methyl group peak of the acetyl moiety to the C1 peak of cellulose. *Determined by titration according to Kim *et al.*[2] [$]Residual, native acetyl groups in hemicellulose.[3]

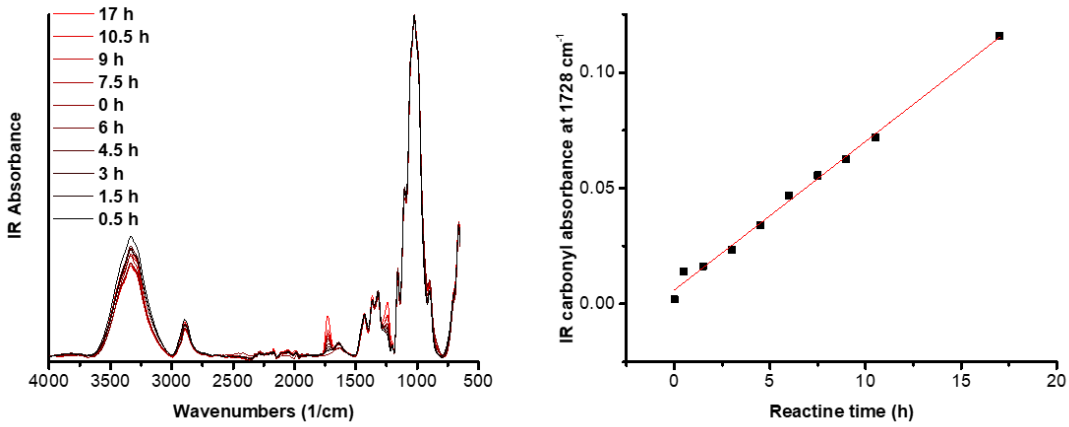

Figure S1: Kinetics of aqueous acetylation of bleached cellulose fibers with *N*-acetyl-imidazole.

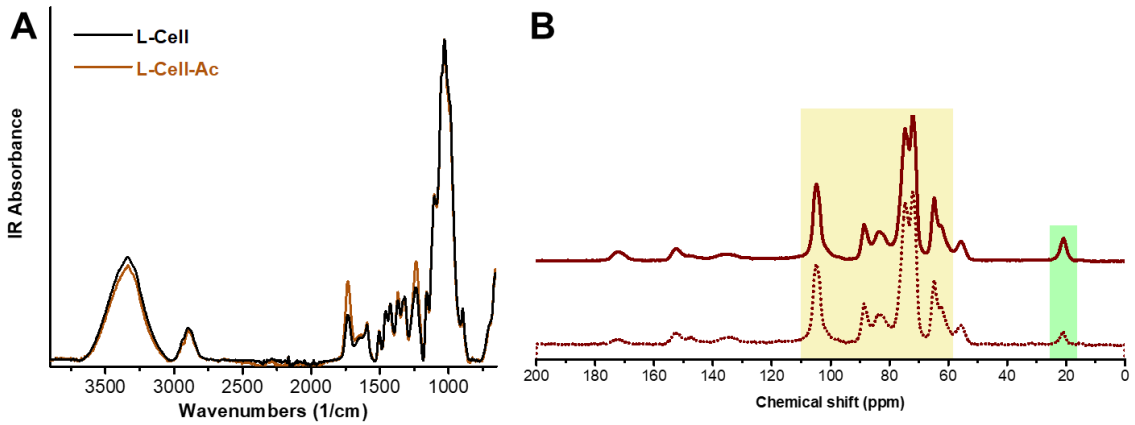

Figure S2: IR spectra of L-Cell and L-Cell Ac (A) showing an intensity-increase of the carbonyl band (acetyl) and solid-state nuclear magnetic resonance spectrum of both samples (B). The highlighted regions (yellow: Carbohydrate carbons, green: Methyl carbon of acetyl group) were used to estimate the degree of acetylation (mmol/g).

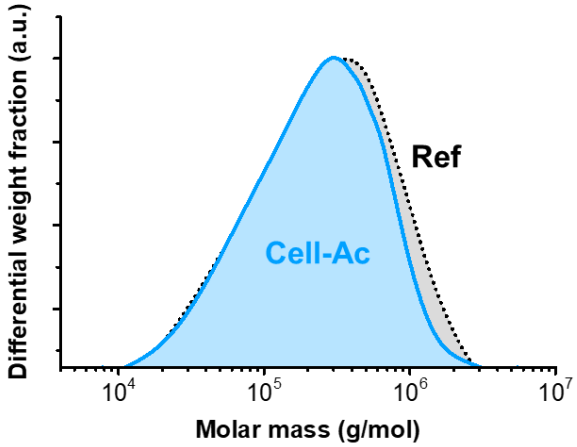

Figure S3: Comparison of molar mass distributions of Cell-Ac and reference sample (Ref).

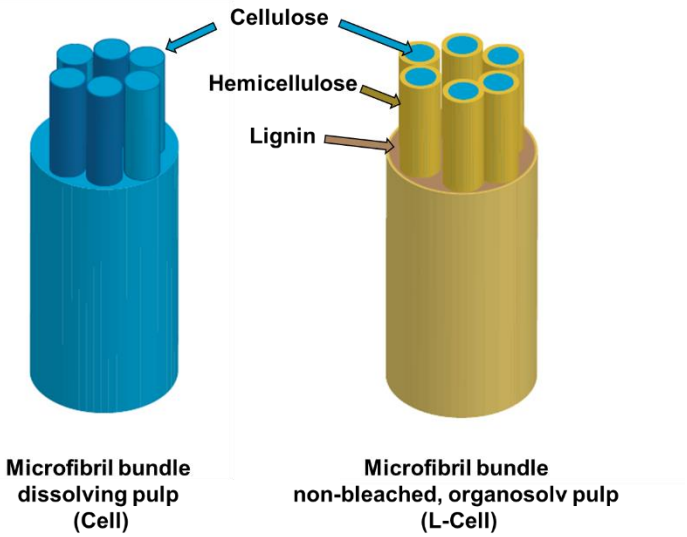

Figure S4: Schematic and simplified structural comparison of a microfibril bundle in dissolving pulp (Cell) and lignin-hemicellulose-rich pulp (L-Cell). Cell consists of high-purity cellulose with only negligible traces of hemicellulose; whereas the cellulose microfibril of L-Cell are embedded into a complex matrix of hemicellulose and lignin.

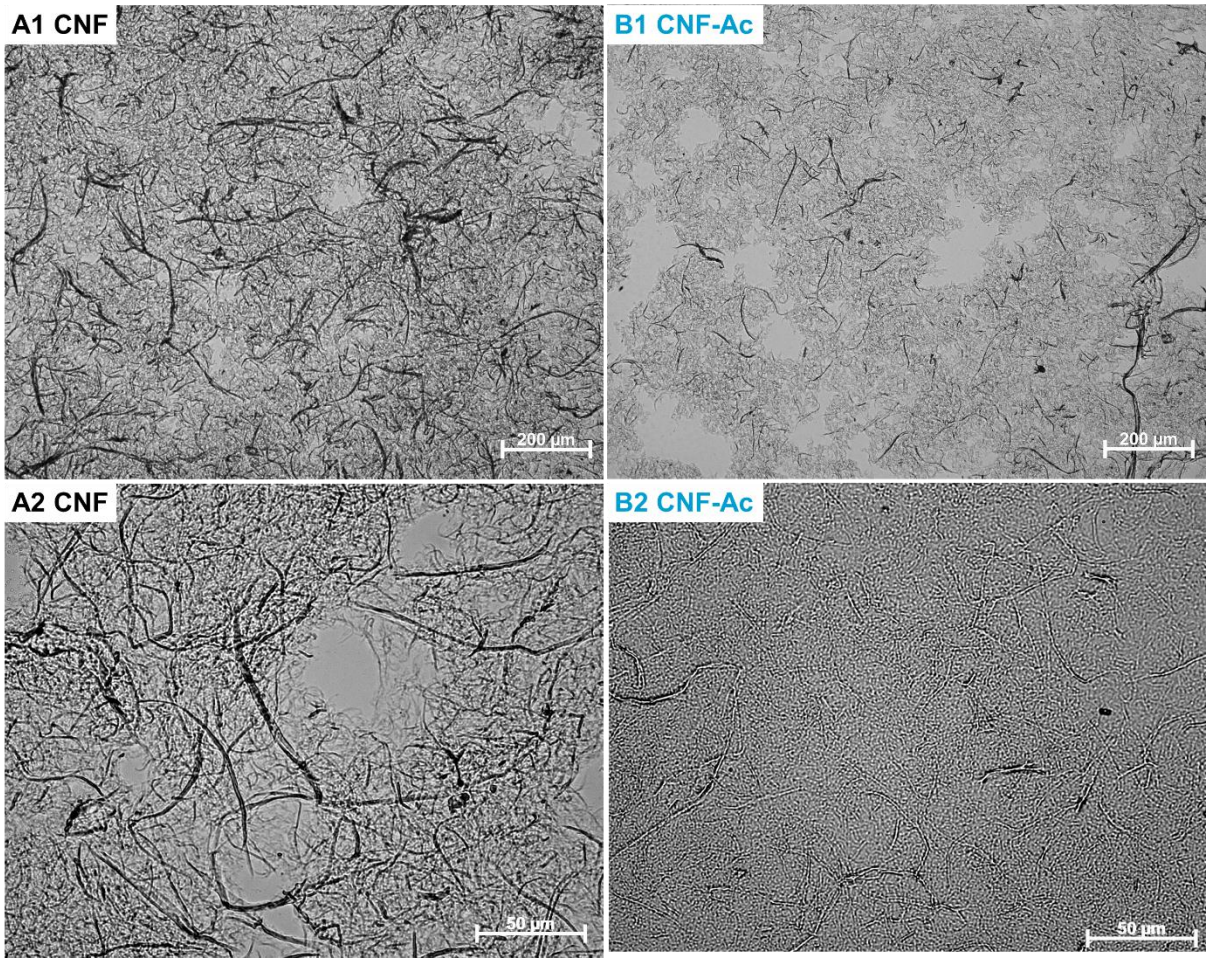

Figure S5: Microscopic image of CNF (A1 and A2) in comparison to wet-acetylated CNF-Ac (B1 and B2)

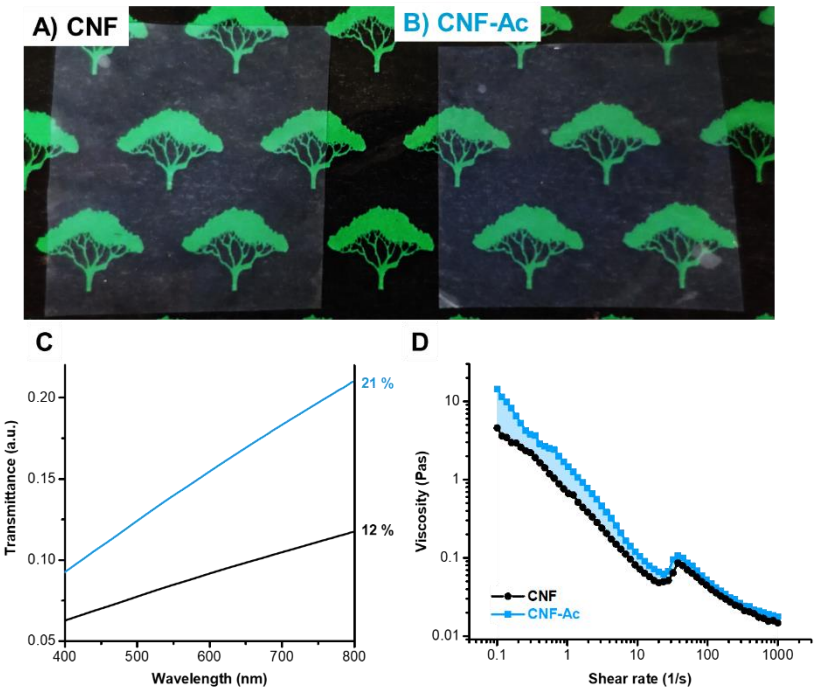

Figure S6: Nanopaper prepared from CNF (A) and CNF-Ac (B) and UV-VIS measurements of the respective films to compare their transparency (C). Comparison of the transparency values at 800 nm and viscosity curves of CNF and CNF-Ac suspensions (D) confirms the higher aspect-ratio of CNF-Ac.

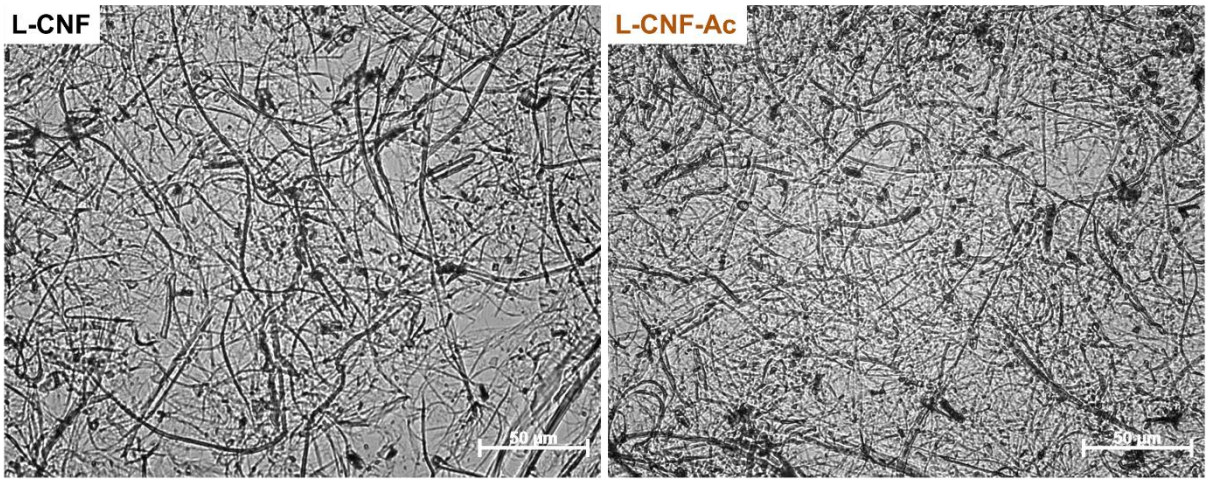

Figure S7: Microscopic image of L-CNF (left) and L-CNF-Ac (right).

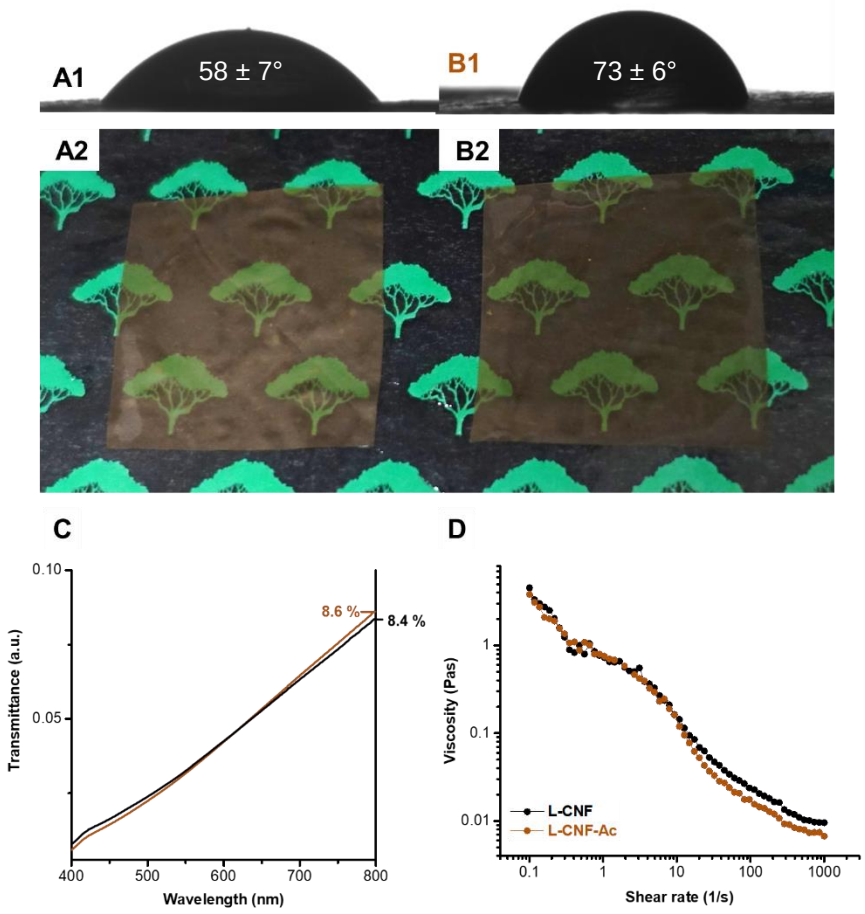

Figure S8: Nanopaper prepared from L-CNF (A2) and L-CNF-Ac (B2), their water contact angles (A1) and (B1) and UV-VIS measurements of the respective films to compare their transparency (C). Rheology of L-CNF and L-CNF-Ac suspensions in water (used in the film fabrication) was very similar (D).

Experimental Part

Never-dried bleached beech sulfite dissolving pulp (Cell) with a solid content of 48 wt% was provided by Lenzing AG (Lenzing, Austria) and used in the production of the lignin-free acetylated pulp (Cell-Ac). Never-dried lignocellulose pulp (L-Cell) was produced by organosolv pulping from milled beech wood according to sample MFLC1 from a previous publication.[1] The treatment parameters and compositions of the used pulps are listed in **Table S1** and **S2**. *N*-Acetylimidazole (98%) and dimethyl sulfoxide (DMSO, ≥99%) were purchased from Sigma-Aldrich Handels GmbH (Vienna, Austria). Both pulps were pretreated in wet state with a coffee blender to increase their surface area.

Wet acetylation (Cell-Ac and L-Cell-Ac)

First, 4.5 g of *N*-acetylimidazole (AI) was dissolved in 18 mL DMSO by warming the solution with hot water (AI solution). High temperature should be avoided in this dissolution step, since it could result in a side reaction of DMSO and AI (*cf*. Swern-oxidation).[*] The acetylation of the respective pulp sample (Cell and L-Cell) was conducted in a kneader IKA HKD-T 0.6 (Staufen im Breisgau, Germany). The respective wet pulp sample (48 wt% solid content, 9.3 g, 57.4 mmol based on anhydroglucose unit) was treated in the kneader and the AI solution (4.5 g in 18 mL DMSO, 41 mmol, 0.71 Eq) was added in portions. The pulp was kneaded for 1 h at 25 °C to obtain a homogeneous mixture and reaction was continued in a closed container overnight. The crude product was washed with water by filtration to remove impurities. The final acetylated and purified pulp (Cell-Ac) was stored in never-dried state at 8°C.

Acetylated Lignocellulose pulp (L-Cell-Ac) was produced accordingly using never-dried L-Cell (41 wt% solid content, 9.3 g).

In both cases, blank samples were prepared using the same procedure without the addition of AI, to consider possible swelling effects during DMSO treatment.

Fibrillation of Cell (CNF) and Cell-Ac (CNF-Ac)

10 g of the specimens (50 wt% solid content, 5 g dry mass) were dispersed in 500 mL DI water in a blender for 2 min and finally treated with an IKA Ultra-Turrax T25 at 15000 RPM for 10 min. Then, the samples were diluted to 0.8 wt% with DI water and homogenized in an APV-1000 (SPX Flow Inc, Charlotte, US) high-pressure homogenizer (2 times at 500 bar and 8 times at 800 bar).

Fibrillation of L-Cell (L-CNF) and L-Cell-Ac (L-CNF-Ac)

7.5 g of the lignin-rich samples (40 wt% solid content, 3 g dry mass) were dispersed in 500 mL DI water to solid content of 0.6 wt% by dispersion with a kitchen blender for 5 min and an IKA Ultra-Turrax at 15000 RPM for 20 min. The samples were then homogenized in an APV-1000 (SPX Flow Inc, Charlotte, US) high-pressure homogenizer (2 times at 200 bar, 2 times at 500 bar and 10 times at 800 bar).

Nanocellulose films

The respective nanocellulose films from CNF, L-CNF, CNF-Ac and L-CNF-Ac were produced by filtration. The respective CNF suspensions were diluted to a solid content of 0.09 wt% in a volume of 50 mL DI water and deposited on a Millipore glass microfiber filter (pore size 1 µm) by vacuum filtration. After removing the water excess, the film was gently immersed into EtOH, acetone and finally detached from the glass microfiber filter. The produced wet films were dried

[*] We studied mixtures of *N*-acetylimidazole in deuterated DMSO after dissolution to ensure that no acetylation of DMSO occurs at our employed conditions (to rule out occurrence of possible oxidative side reactions).

at ambient conditions between two flat polytetrafluoroethylene film (with 3 mm thickness) and finally pressed at 130°C and 1 bar for 5 min.

Contact angle measurement

The measurements were carried out on a Drop Shape Analyzer DSA30 (KRÜSS Optronic, Germany) operated by the KRÜSS ADVANCE 1.5.1.0 software. The volume of every water drop was 1 µL at a dosage speed of 0.16 mL/min. The contact angles were measured at 20 frames per second for 1 s and 5 measurements were performed for each sample.

Molar mass determination

The dried samples (15 mg) were activated by dispersion in water with a kitchen blender and solvent-exchange to EtOH and then DMAC, prior to dissolution in DMAc/LiCl (9 %, w/v). 0.3 mL of the dissolved samples were diluted with 0.9 mL of DMAc and filtered through a 0.45 µm syringe filter. The specimens were analyzed by gel permeation chromatography according to Röhrling et al. 2002.[4]

Infrared spectroscopy (IR)

Attenuated total reflection (ATR) FTIR spectra were obtained using a PerkinElmer (PerkinElmer Inc., MA, USA) Frontier IR single-range spectrometer. The spectrometer was equipped with a ZnSe ATR crystal and a LiTaO3 detector. The spectra were base-line corrected and normalized to one. Four scans per measurement were performed for each sample at a resolution of 4 cm^{-1}.

Nuclear magnetic resonance (NMR) spectroscopy and crystallinity

Solid-state 13C-NMR experiments (cptoss, 5000 Hz) were carried out on a Bruker Avance III HD instrument (Bruker Corporation, NH, USA). The data was processed with the Bruker TopSpin 3.5 software and the crystallinity was determined by relating the integrated crystalline part of the C4 peak (86.3-91.0 ppm) to the amorphous part of the C4 peak (79.3-86.3 ppm) according to the NMR peak separation method.[5]

Determination of the acetyl content

The acetyl content of the samples was approximated from the solid-state NMR spectra. The integral of the carbon peaks of the polysaccharide fraction in the NMR spectra (region of 58 to 110 ppm) was related to the methyl carbon of the acetyl group (integral of 17 to 25 ppm), as shown in the NMR spectra in **Figure S2B**. The molar amount of polysaccharides in 1 g of sample was determined from the pulp compositions in **Table S2** (6.2 mmol/g and 4.8 mmol/g carbohydrate content of Cell and L-Cell, respectively) and used to calculate the acetyl content (mmol/g) of the samples from the NMR integrals.

The resulting acetyl values were further compared to a standard titration method according to Kim *et al.*[2] to validate the method.

Rheology measurement

The viscosity curves of the samples were measured with a Bohlin Instruments (Gloucester, England) CVO 50 rheometer. All measurements were performed at 20°C using a cone-plate measuring system (4°/40 mm) with a gap size of 200 µm. Viscosity was measured at shear rates from 0.1 s^{-1} to 1000 s^{-1}.

References

1 A. Winter, L. Andorfer, S. Herzele, T. Zimmermann, B. Saake, M. Edler, T. Griesser, J. Konnerth and W. Gindl-Altmutter, *J Mater Sci*, 2017, **52**, 60–72.
2 D.-Y. Kim, Y. Nishiyama and S. Kuga, *Cellulose*, 2002, **9**, 361–367.
3 P. M.-A. Pawar, S. Koutaniemi, M. Tenkanen and E. J. Mellerowicz, *Front. Plant Sci.*, , DOI:10.3389/fpls.2013.00118.
4 J. Röhrling, A. Potthast, T. Rosenau, T. Lange, G. Ebner, H. Sixta and P. Kosma, *Biomacromolecules*, 2002, **3**, 959–968.
5 S. Park, J. O. Baker, M. E. Himmel, P. A. Parilla and D. K. Johnson, *Biotechnol Biofuels*, 2010, **3**, 10.