

Electronic Supplementary Information (ESI)

1. Materials and methods

1.1 Materials

Commercial microcrystalline cellulose (Avicel PH101; Sigma Aldrich) was used to prepare the cellulose whiskers. *N*-(9-Fluorenylmethoxycarbonyl)-L-leucine (Fmoc-leucine), *N*-Ethyl-*N'*-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC.HCl), 4-(dimethylamino)pyridine (DMAP), piperidine, and ethanol were purchased from Sigma Aldrich and used as received. Sulfuric acid (95-98%) and anhydrous *N,N*-dimethylformamide were acquired from VWR.

1.2 Cellulose whiskers preparation

Cellulose whiskers (CW) were prepared by sulfuric acid hydrolysis according to the methodology described in Bondeson *et al.*¹ with slight modifications. Briefly, hydrolysis was performed at 45 °C for 130 minutes using a 64 wt % sulfuric acid solution (preheated) under mechanical stirring. The Avicel/sulphuric acid ratio used was 8:100 (w/v). The hydrolysis reaction was stopped by adding a 10-fold excess of deionized water. Thereafter, the suspension was washed with deionized water by using repeated centrifuge cycles (10000 rpm for 10 min at 10 °C) until that the supernatant became turbid. The resulting precipitate was collected and dialyzed (MWCO: 12-14000) against tap water until the solution pH remained constant. The obtained suspension was sonicated in an ice bath (6 min with a 40% output control) and then centrifuged (10,000 rpm for 7 min at 10 °C) to separate aggregates. The obtained suspension was frozen and thereafter lyophilized in order to obtain dried cellulose whiskers.

1.3 Chemical modification

The chemical modification of CW with Fmoc L-leucine was performed in a 100 mL one neck-flask equipped with a stopper and a magnetic stirring bar at room temperature ($\approx 25\text{ }^{\circ}\text{C}$) by using a procedure adapted from Kalaskar *et al.*² and Khan *et al.*³ Initially, 0.250 g (1.543 mmol) of freeze-dried cellulose whiskers were suspended in 50.00 mL of anhydrous DMF. Then, DMAP (0.283 g, 2.316 mmol) was introduced followed by the addition of EDC.HCl (0.478 g, 3.081 mmol) and Fmoc L-leucine (1.089 g, 3.081 mmol). The reaction mixture was left to stir for 24 h at room temperature and thereafter added dropwise to a diluted acid solution (300 mL) to promote the precipitation of the derivative CW. The solid was collected by centrifugation (10000 rpm for 7 min at $10\text{ }^{\circ}\text{C}$) and washed with deionized water ($3\times 150\text{ mL}$) and ethanol ($3\times 100\text{ mL}$). The removal of the protecting Fmoc group was performed by stirring the sample in a 20% (v/v) piperidine solution in DMF for 30 min. Thereafter, the sample was washed with DMF ($4\times 75\text{ mL}$) and left to dry. The resulting modified cellulose whiskers still remained as a suspension in aqueous systems.

1.4 Characterization

FT-IR spectra were recorded on a Nicolet Magna-IRTM 550 Spectrometer by using KBr pellets. Spectra were recorded between 400 and 4000 cm^{-1} at a resolution of 4 cm^{-1} and co-adding 64 scans.

Transmission electron microscopy (TEM) images were acquired on a JEOL 100CX transmission electron microscope using an acceleration voltage of 100 kV. The TEM samples were prepared by placing a drop of a diluted suspension of CW on a carbon coated grid followed by stain with a 2 wt % uranyl acetate solution. Calculation of cellulose whiskers size was performed using the

ImageJ software from Broken Symmetry software. X-ray photoelectron spectroscopy analyses were performed in a Thermo K-alpha XPS spectrometer with a monochromatic aluminum K α source and operating at 12 Kv under a current of 6 mA and pressure of 10⁻⁸ mbar. The spectra were shifted to ensure that the C-C/C-H contribution to the C 1s signal occurred at 285 eV.

Solid-state NMR measurements were carried out on a Bruker Avance-400 spectrometer operating at a frequency of 100.55 MHz for ¹³C using a Bruker triple-resonance MAS probe-head at spinning speeds of 10 kHz. CP/MAS experiments used a 5 μ s (90°) proton pulse, 1.5 ms contact pulse, 4 s recycle delay and 2K scans. The samples were packed in 3.2-mm cylindrical ceramic MAS rotors fitted with Kel-F caps. The analysis of all spectra was performed using NUTS NMR Data Processing software (Acorn NMR, Inc). The quantification of C-4 carbons was performed using the following approximate integration limits: crystalline forms of cellulose and *para*-crystalline domains between 86.0-92.0 ppm and less ordered or non-crystalline domains between 80.0-86.0 ppm. The crystallinity index corresponds to the ratio of the integrated area between 86.0-92.0 ppm and 80.0-92.0 ppm⁴.

References

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