Electronic Supplementary Information

Simultaneous preparation of cellulose nanocrystals and micron-sized colloidal particles of cellulose by TEMPO-mediated oxidation

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The ESI contains: Experimental section; Details on HOCl consumption upon TEMPO-mediated oxidation of microgranular cellulose (Figure S1); Titration curves of conductometric titration (Figure S2); Optical micrograph of the starting material, i.e., microgranular cellulose (Figure S3); Results of polyelectrolyte adsorption for charge determination (Figure S4); Gel permeation chromatography results for the starting material and the coarse fraction (Figure S5); Representative SEM images and optical micrographs for determining the particle size data presented in Figure 3 of the main article (Figure S6).

Experimental section

TEMPO-mediated oxidation

Microgranulars of cellulose from cotton (10 g) were dispersed in 1153 mL of deionized water. While stirring, 10 mL of a TEMPO solution in aqueous ClO_2 was added to obtain a concentration of 0.6 mmol.L^{-1}. The pH was then adjusted with NaOH to pH 5. Finally, 49 mmol of NaClO was added and the solution was stirred overnight at 25ºC. The reaction occurred around pH 8 and the amount of HOCl in the solution was monitored by active chlorine titration with $Na_2S_2O_3$ and KI.

Separation in 3 phases

After TEMPO oxidation, the solution was centrifuged twice: 20 minutes at 9000 rpm and 1 hour at 3153 rpm. The supernatant was dialyzed in milli-Q water until the conductivity was lower than 5 µS.cm^{-1}: this contained dispersed nanocrystals or the fine phase. The solid recovered after centrifugation was dispersed and dialyzed in milli-Q water until the conductivity of the water - in the beaker - was lower than 5 µS cm^{-1}. After dialysis, the suspension was filtrated and 2 phases were obtained: a coarse phase (TEMPO oxidized microcrystals) and the middle phase (filtrate, dispersed microcrystals).

Characterization

For the conductometric titration, the pH of the dispersed crystals solutions was adjusted to 2 with HCl and the solution was stirred for 30 minutes before dialysis. After dialysis, 0.5 g of material (dry weight) was mixed with 500 mL of degased milli-Q water, 0.5 mL of NaCl at 0.5 mol.L^{-1} and 1 mL of HCl at 0.1 mol.L^{-1}. The titration was conducted with a NaOH solution at 0.1 mol.L^{-1} (751 GPD Titrino, Metrohm). Vitrified samples were prepared using a FEI Vitrobot Mark IV by placing 3 µl of sample solution on 200 mesh copper grids with holey carbon film under 100% humidity, then blotted with filter papers (1–2 s) and immediately plunged in -170°C ethane/propane mixture and cryo-transferred to the microscope. The images were taken in bright field mode using zero loss energy filtering (Omega type) with a slit width of 20 eV. Micrographs were recorded with a Gatan Ultrascan 4000 CCD camera and with Gatan DigitalMicrograph software. The specimen temperature was maintained at -187 °C during the imaging. The optical microscopy images were obtained with a LEICA ICC50 HD (LasEz).

The polyelectrolyte adsorption was conducted with PDADMAC (polydiallyldimethylammonium chloride) purchased from Sigma-Aldrich (M_w > 300 000 g.mol^{-1}). 1 mL of a TEMPO solution at 1.75 g.L-1 was mixed with 40 mL of a $NaHCO_3$ solution (1 mM). Increasing volumes of PDADMAC (0.5 mL, 1 mL and 1.5 mL) were added to the previous mix and made up to 50 ml with milli-Q water. After 20 minutes of stirring, 10 mL of the solution was taken for titration with a PesNa (sodium polyethensulfonate, M_w = 19 100 g.mol^{-1}) solution at 0.002 M.

Scanning electron microscopy was performed using a Zeiss Sigma VP microscope operating at 3 kV. A thin layer of Au/Pd was sputtered onto the samples before imaging.

Determination of molecular weight and degree of polymerization was done using a RI-101 detector (Shodex) coupled with an UltiMate 3000 LC system (Dionex). A 50±5 mg sample was weighed into a tube and activated overnight by adding 4 mL of milli-Q water. The water was then removed and the sample rinsed with 2 mL of acetone before activation in 4 mL of acetone overnight. The last activation was made in DMAc (N-N-dimethylacetamide) overnight. The activated cellulose was finally dissolved in 5 mL of LiCl/DMAc (90 g.L^{-1}) at room temperature under a constant slow speed magnetic stirring. After dissolution, 0.50 mL of sample was diluted with 4.5 mL of pure DMAc and stirred well. This gave a sample concentration of 1.0 mg.mL^{-1} and LiCl concentration 9 g.L^{-1}. 1. The dissolved and diluted samples were filtered into vials using 0.2 µm syringe filters.

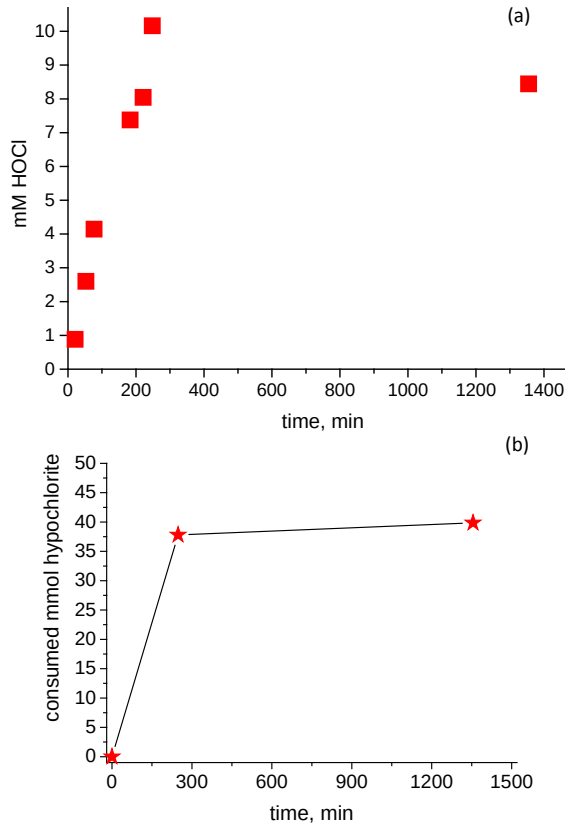

Figure S1. (a) Evolution of the quantity of hypochlorite during the TEMPO-mediated oxidation. (b) Consumption of hypochlorite during the TEMPO-mediated oxidation.
Hypochlorite was added slowly during 248 min and (a) shows the quantity due to both addition and consumption. A significant amount (38 mM) of hypochlorite was consumed simultaneously during addition (b). After 248 min, the reaction was left to proceed without the addition of hypochlorite (only with automatic pH adjustment), and the consumption of HOCl during the following 18 h was 2.1 mmol (b) which is typically similar to self-decomposition reaction of HOCl under these conditions. Therefore, we can assume that the oxidation had proceeded to the maximum extent feasible for microgranular cellulose under the present conditions.

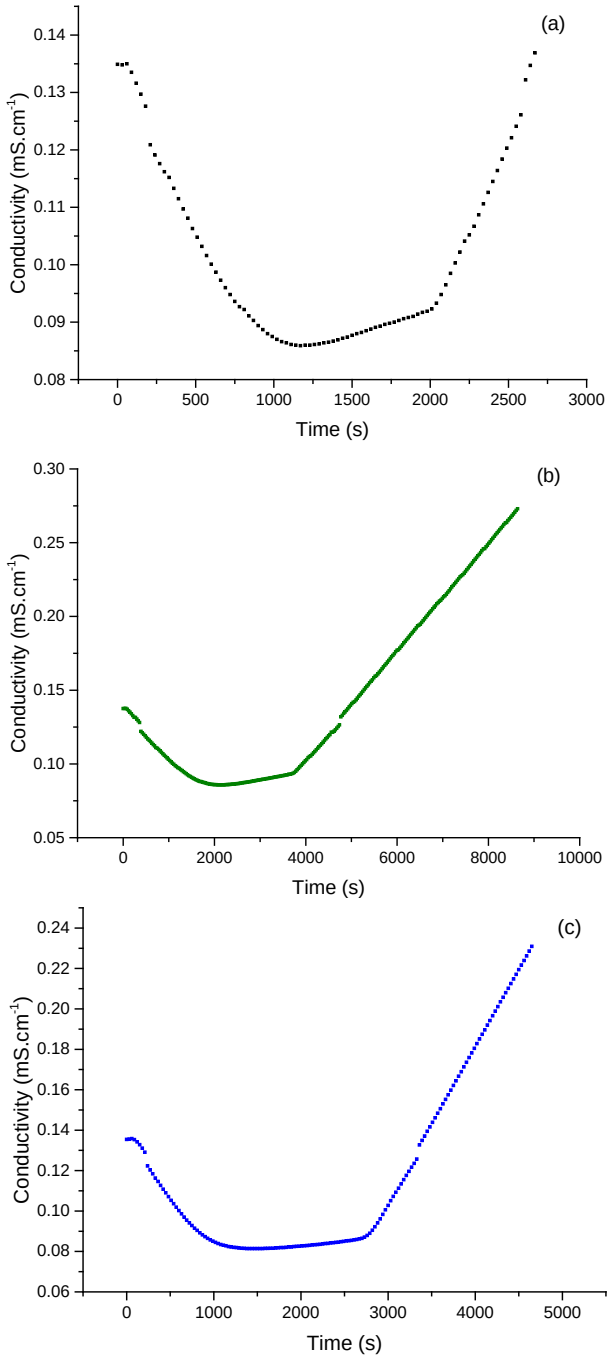

Figure S2. Titration curves from conductometric titration: (a) TEMPO fine fraction, (b) TEMPO medium fraction and (c) TEMPO coarse fraction.

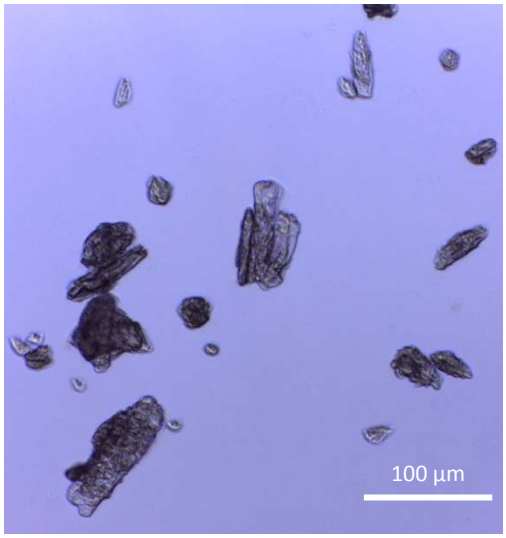

Figure S3. Optical microscopy image of the starting material.

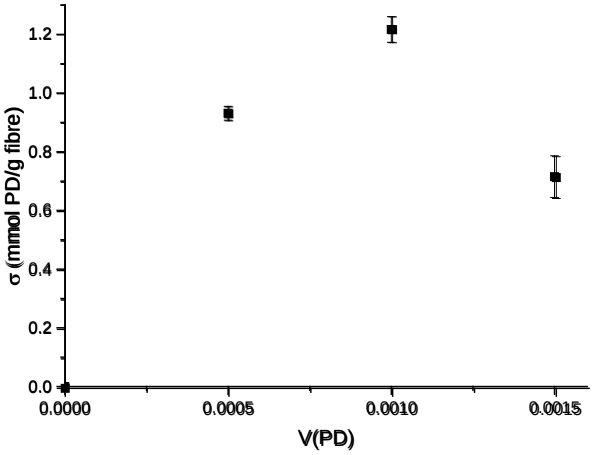

Figure S4. Charge determination of the coarse fraction by adsorption of a cationic polyelectrolyte (PDADMAC). The graph indicates that the plateau value of the adsorption isotherm has been reached already with the lowest quantity of the adsorbate. Averaging the measurement points, the charge of the coarse fraction is around 0.9 mmol of COOH/g of pulp and this correlates well with the result of the conductometric titration (0.81 mmol of COOH/g of pulp). The correlation of these two methods means that the PDAMAC is able to penetrate everywhere in the crystals to neutralize all the charges. This agrees with the Cryo-TEM images which suggest that the microcrystals in the coarse fraction are highly porous.

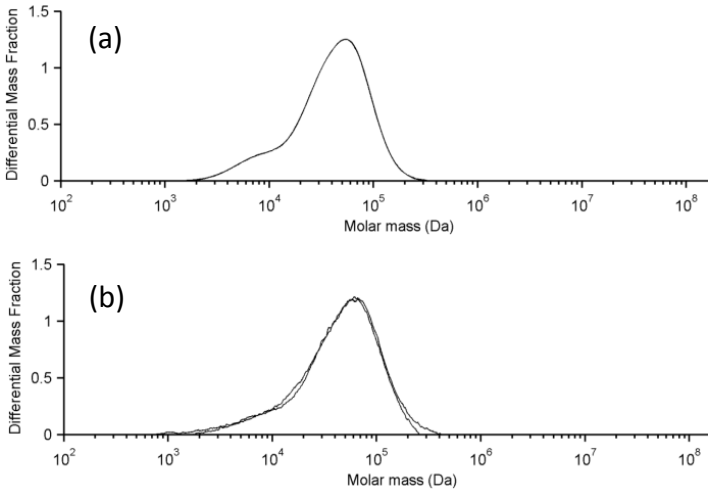

Figure S5. GPC analysis of (a) starting product and (b) coarse fraction. This shows that the oxidation of the cellulose does not affect the molecular weight of the crystals.

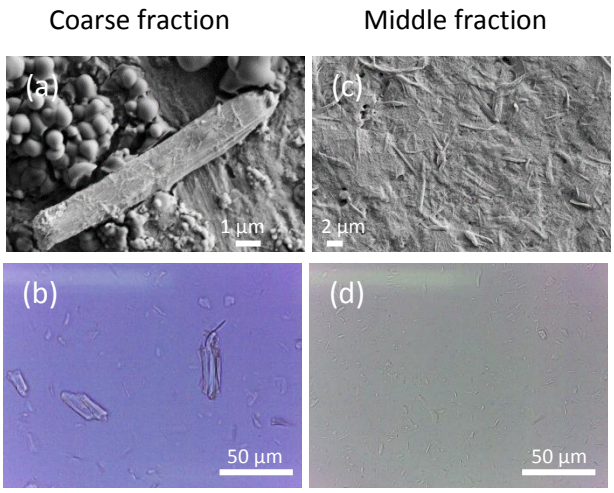

Figure S6. Representative images of coarse fraction (left hand side): (a) SEM images, (b) Optical microscopy; and middle fraction (right hand side): (c) SEM images and (d) Optical microscopy. 10 similar SEM images together with a variety of optical micrographs were applied to calculate the lengths and the widths.