

Electronic Supplementary Information

A strategy towards one-step preparation of functional cellulose nanocrystals and nanofibrils with high yield, carboxylation and dispersibility using innocuous citric acid

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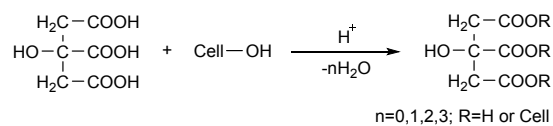
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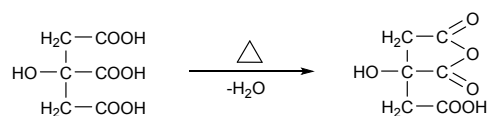
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(a)

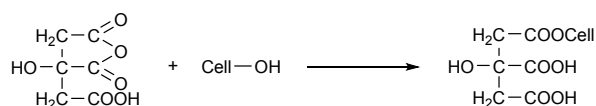


Direct esterification

(b)

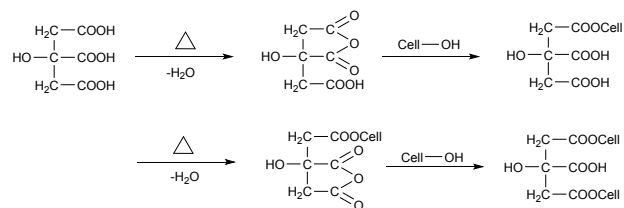


Form cyclic acid anhydride



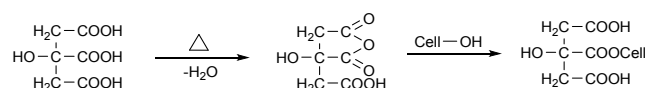
Esterification

(c)

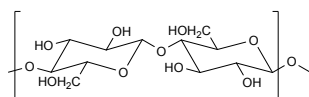


Acid anhydride and esterification via end-carboxylic groups

(d)



Acid anhydride and esterification via middle-carboxylic group



Cell-OH

Figure S1 Four proposed pathways for cellulose carboxylation with citric acid via esterification of one or more acid carboxylic groups.

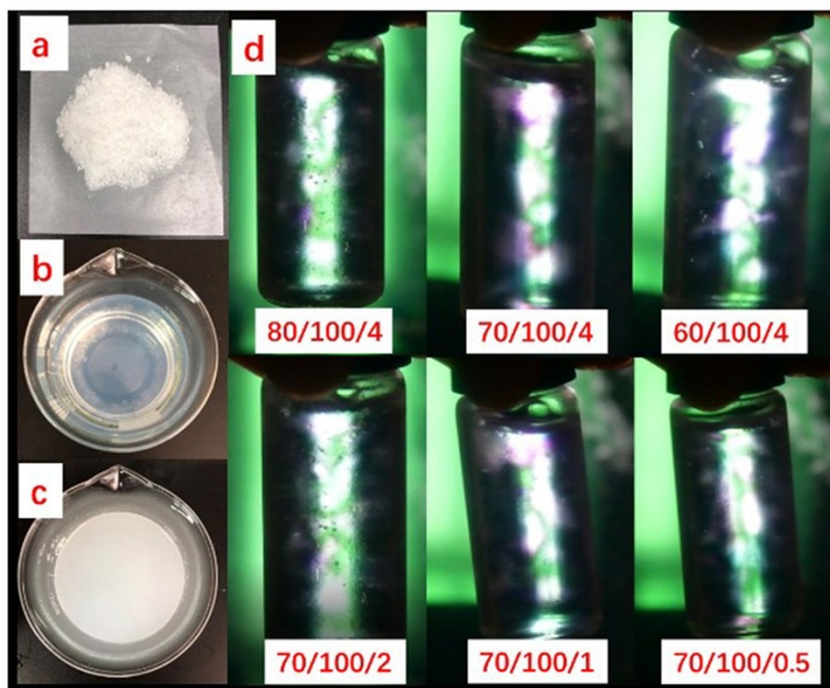


Figure S2 a) Recovered citric acid solid powder; b) Semi-transparent CNCs gel with light-blue color; c) Milky CNFs gel, and d) birefringence of the resultant CNCs under different conditions.

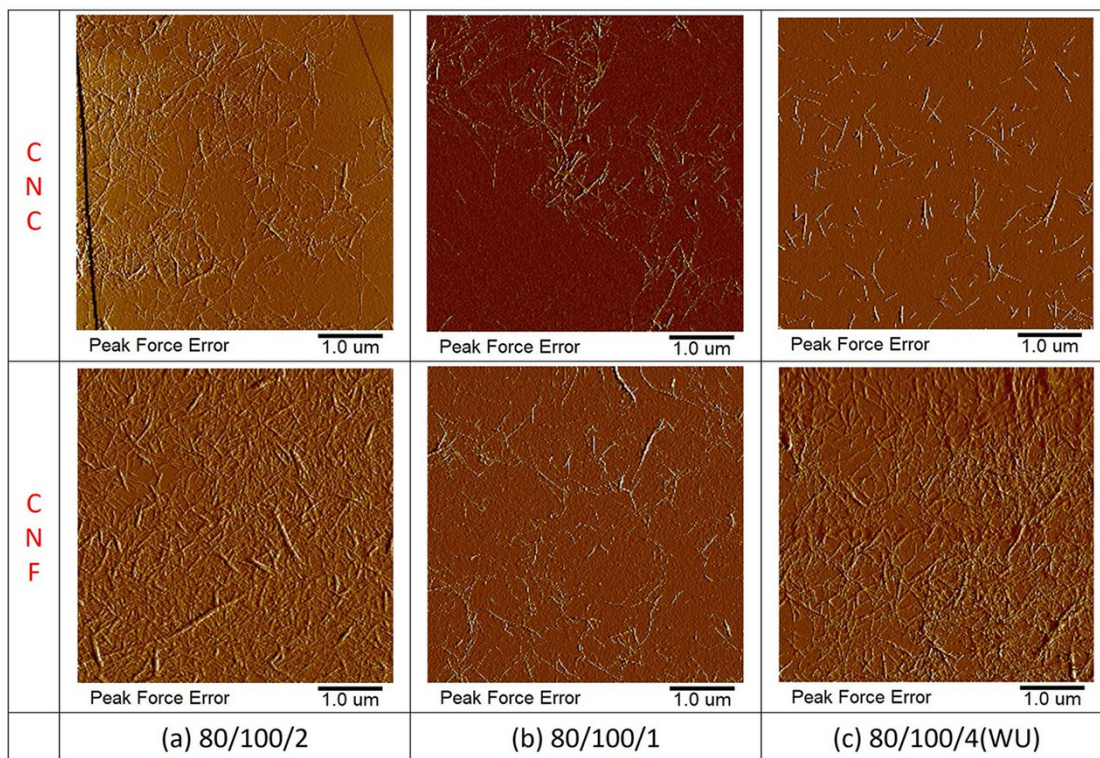


Figure S3 AFM images of CNCs and CNFs produced under different conditions. a) 80/100/2; b) 80/100/1; c) 80/100/4 (WU); the first line is CNCs and the second line is CNFs.

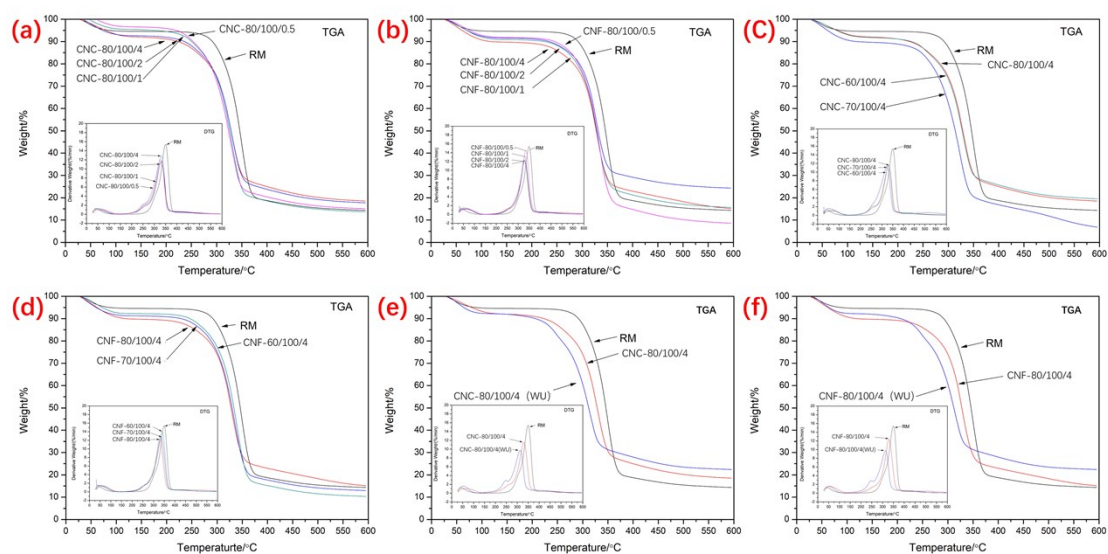


Figure S4 The TGA and DTG images of the CNCs and CNFs under various conditions. RM: Raw bagasse pulp; WU: Without ultra-sonication.

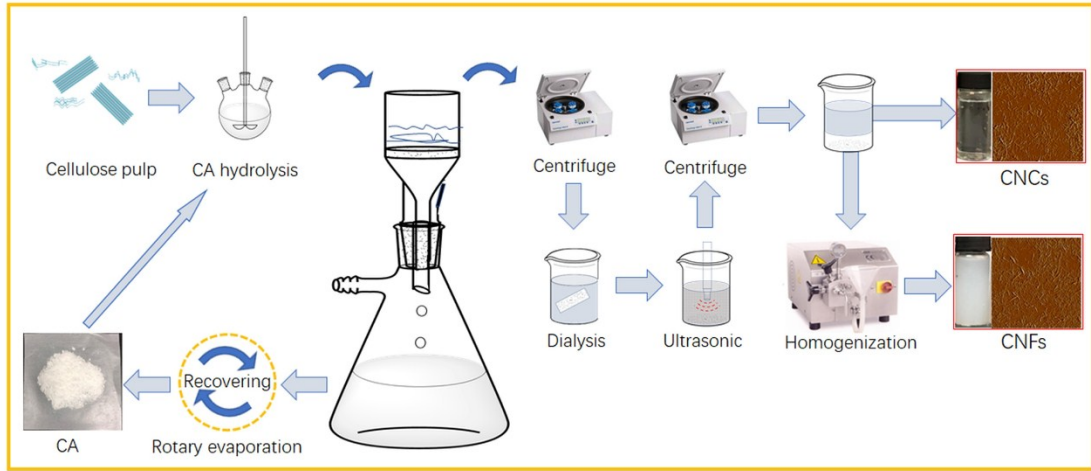


Figure S5 The flow scheme of the whole process for preparing CNCs and CNFs.

Table S1 Mean zeta-potential value of CNC and CNF suspensions with 0.15 wt% concentration at different conditions.

CA concentration /Temperature/Time (%)/(°C)/(h)	Zeta-potential (mV)	
	CNCs	CNFs
80/100/4 (*WU)	-121.1±2	-92.2±1.9
80/100/4	-122.9±1.2	-90.3±0.9
80/100/2	-120.7±2.8	-79.2±2.3
80/100/1	-109.5±1.4	-66.8±3.9
80/100/0.5	-98.4±1.8	-59.1±0.4
70/100/4	-118.2±0.5	-81.1±3.6
70/100/2	-113.7±1.7	-63.1±2.9
70/100/1	-110.1±3	-54.1±0.7
70/100/0.5	-90.9±0.5	-50.4±1.1
60/100/4	-115.1±2.2	-78.1±2.8
60/100/2	-109.5±1.8	-61.6±1.4
60/100/1	-107.9±0.6	-55.0±2.8
60/100/0.5	-89.9±2.1	-48.4±3.4

*WU: Without ultra-sonic

Characterizations of CNCs and CNFs

Determination of the yields of CNCs and CNFs

The amounts of CNCs and CNFs in the suspensions were determined by oven-dry method and the yields were calculated based on the starting material as the equation ^[Equation (1)] showing as below:

$$Y = \frac{C \times V}{M} \times 100\% \quad (1)$$

where Y is the yield of CNCs or CNFs; C is the solid content of the suspensions which was measured by oven dry; V is the volume of suspensions and M is the oven-dry weight of the starting material.

Analysis of carbohydrate content in acid hydrolysate

The content of carbohydrate in the citric acid hydrolysate after acid hydrolysis was analyzed by a Dionex ICS-3000 Ion Chromatography (IC) System with an ion-exchange analytical column and a guard column (2×250 mm, Carbopac PAI, Dionex, USA). The column compartment temperature was controlled at 30°C. The analysis process of each sample was 52 min with the following gradient: 0-2 min: 200 mM NaOH at 0.25 ml/min; 2-36 min: 2 mM NaOH at 0.5 ml/min; 36-52 min: 90% (v/v) 2 mM NaOH and 10% 1 M NaAc at 0.25 ml/min. The sample was injected at 20 min. Before analysis, the filter liquor was diluted between 0.1 ppm to 10 ppm with the pH ranged from 6 to 7 and each liquid sample was filtered through 0.22 μm polyethersulfone (PES) needle filter (Anpel Inc., Shanghai, China).

Morphological characterization of CNCs and CNFs

Flow birefringence is a preliminary and very easy method to visually confirm the presence and dispersion of CNCs in water. The whole setup includes two cross-polarized filters and a lamp.

The morphology of the obtained CNCs and CNFs were determined by Atomic Force Microscopy (AFM, Nanoscope III, Veeco, USA) in tapping mode. The diluted samples were treated for 5 min with 5 seconds interval prior to the sampling by ultra-sonication in order to get well-dispersed suspension. A drop of diluted CNCs/CNFs suspension (0.01 wt% concentration) was injected on the surface of a clean mica film and dried in the oven at 60°C for 1.5 h. The diameter and the length of the CNCs and CNFs were determined from the amplitude images using the Nanoscope Analysis 1.5 program by randomly picking approximately 50 particles for each sample.

Dispersion stability studies

The dispersibility of the obtained CNCs and CNFs was observed by preparing CNC and CNF dispersions with the concentration of their origin, respectively. The dispersibility of all samples was investigated by taking pictures of the obtained suspensions immediately after sampling and regularly after up to 30 days, respectively.

Zeta-potential analysis

The zeta-potential of the CNC and CNF suspensions were determined by a Nanoparticle Analyzer (SZ-100Z, Horiba, Japan) using a green light source with a wavelength of 532 nm. Graphite electrode pool was used and 100 μ l samples

was needed for each test. Before testing, all samples were diluted to 0.15 wt% and further dispersed by ultra-sonication for 5 min. The measurements were carried out in triplicates for each sample and the mean value of zeta-potential was reported in this work.

Characterization of esterification and carboxylation

Fourier transform infrared (FT-IR) spectrophotometer (Tensor 27, Bruker, Germany) was applied to analyze the absorption of CNC and CNF samples as well as the original bleached bagasse pulp from an accumulation of 32 scans in an absorbance range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1} . Before the analysis, all samples were dried in an oven at 60°C for 6 hours. CNC and CNF films were formed after drying, and the dried original bagasse pulp was mixed with KBr (weight ratio of pulp:KBr was 1:100) and ground to slice for the FT-IR analysis.

The carboxylic group contents of the resulting CNCs and CNFs were determined by conductometric titration method using a conductance meter (FiveGo F3, Mettler Toledo, USA). About 0.1 g freeze-dried sample was dispersed in a mixture of 55 ml DI-water and 5 ml 0.01 mol/l NaCl with the help of ultra-sonication for 5 min. Then 0.1 mol/l HCl was added to adjust the pH for 2.5–3.¹ Subsequently, the suspension was titrated using freshly prepared 0.1 mol/l NaOH by adding 50 μl in 30 second intervals. The conductivity decreased clearly in the beginning and then kept stable until an obvious increase was

observed. The content of the carboxylic group was calculated based on the equation [Equation (2)] as below:

$$C_{COOH} = \frac{(C_{NaOH}V_2 - C_{NaOH}V_1)}{M} (mmol/g) \quad (2)$$

Where V_1 and V_2 are the volume of the consumed NaOH when the conductivity turned to be stable and started to increase, respectively; M is the oven-dry weight of the starting CNC or CNF material.

X-ray diffraction (XRD) analysis

X-ray diffraction patterns for all samples were determined with an X-ray Diffractometer (Xpert Powder, Panalytical, Netherlands) equipped with Cu $K\alpha$ radiation which was generated at an operating voltage of 40 kV and a filament current of 40 mA. Scattered radiation was detected in the angle (2θ) ranged from 5° to 60° at a scan rate of $1^\circ/\text{min}$, and further analyzed using an MDI Jade 5.0 software (Materials Data, USA). The crystallinity index (Crl) of each sample was calculated using the empirical equation [Equation (3)] shown as follows:

$$C_r I = \frac{I_{200} - I_{am}}{I_{200}} \quad (3)$$

where I_{200} is the maximum peak intensity at lattice diffraction (200); I_{am} is the minimum intensity between planar reflection (200) and (110).

Thermal stability analysis

Thermal stability property of the produced CNCs and CNFs was determined by Thermogravimetric Analyser (TGA, Q500, TA Instruments, USA). A small amount of the sample (5–10 mg) was analyzed using nitrogen as carrier gas. The thermal

degradation temperature of the samples was increased from room temperature to 600°C at a heating rate of 10°C/min with a flow rate of nitrogen 60 ml/min.

Notes and references

1. T. Saito and A. Isogai, *Biomacromolecules*, 2004, **5**, 1983-1989.