Electronic Supplementary Material (ESI) for Green Chemistry.

Electronic Supplementary Information

Highly Thermal-stable and Functional Cellulose Nanocrystals and Nanofibrils Produced Using Fully Recyclable Organic Acids

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Table S1. Yields of Fibrous cellulosic solid residue (FCSR) and CNC and recovery of reducing sugars from organic acid treatments of a bleached kraft Eucalyptus pulp under various conditions. All yield or recovery data are reported based on original BEP fiber mass.

Acid [1]	**Concentration (%)**	**Temperature (°C)**	**Time (min)**	**FCSR yield (%)**	**CNC yield (%)**	**Reducing sugar recovery (%)**	**Xylose recovery (%)**	**Glucose recovery (%)**
O	30	80	240	97.2±0.4	ND	1.5		
	50	90	60	98.3±0.7	ND	1.2		
			90	97.9±0.2	ND	1.6		
			120	95.5±0.2	ND	2.2		
			150	92.1±0.4	1.4±0.2	3.2		
			180	92.7±0.5	2.3±0.0	4.8		
		100	30	93.2±0.1	4.5±0.1	7.2	9.62	0.65
			45	91.4±0.2	8.3±0.0	7.2		
			60	91.5±0.4	8.1±0.1	9.2	11.6	1.2
			90	88.5±0.5	11.0±0.1	10.3	11.6	2.1
			120	85.8±0.1	12.4±0.2	11	11.4	2.6
			150	82.6±0.1	13.9±0.0	12.3	12.9	3.4
			180	78.5±0.2	13.5±0.3	12.7	13.7	4.5
			240	75.1±0.1	15.8±0.2	13.9	14.7	5.0
		120	45	86.7±0.3	12±0.0	8.5		
	60	100	45	89.1±0.3	9.0±0.2	10.3		
			90	87.3±0.5	11.0±0.3	12.5		
		110	45	83±0.2	13.7±0.0	10.8		
		120	45	76.7±0.5	11.2±0.0	13.7		
	70	100	45	80.8±0.7	11.4±0.2	14.9		
			60	73.5±0.3	24.7±0.2	16.3		
		110	45	71±0.2	17.3±0.0	14.1		
		120	15	73.5±0.3	12±0.0	13.4		
M	50	100	45	95.9±0.3	1.1±0.0	ND		
	60	100	45	95.3±2.3	3.9±0.0	ND		
		110	45	85.6±0.7	8.8±0.0	ND		
	70	100	45	83.9±0.4	12.0±0.0	ND		
			180	80.1±0.2	12.7±0.1	ND		
	80	100	45	92.6±0.9	8.7±0.0	ND		
		120	45	85.2±0.5	10.3±0.0	ND		
T	50	100	45	86.6±0.2	6.4±0.0	ND		

[1] O, M, and T stand for oxalic, maleic, and *p*-toluenesulfonic acids, respectively.

Table S2. Comparisons of onset thermal degradation temperature and temperature at 5% weight loss among different CNC samples and original BEP.

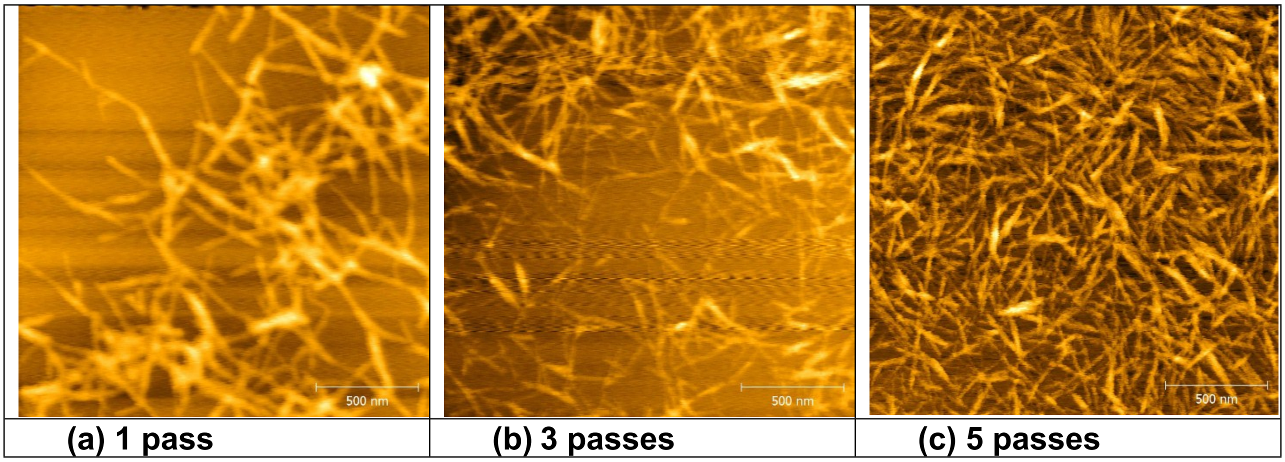
Hydrolysis conditions	**CNC**			**CNF**
	Onset degradation T_{onset} (°C)	**Weight loss at T_{onset} (%)**	**T_{95} at 5% weight loss (°C)**	**Onset degradation T_{onset} (°C)**
(O70, 100, 60)	322	4.99	323	296
(M60,100, 45)	301	5.40	297	
(T50, 100, 45)	299	5.20	297	
(B50, 100, 45)	307	5.25	304	
BEP	274	2.75	290	
(P67, 100, 45)	268	3.84	277	292
(S64, 45, 45)	218	5.05	217	
(H14, 100,45)	284	4.65	287	295

Table S3. Identifications of FT-IR absorption peaks

Peak wavenumber (cm^{-1})	**Identification**
3319	OH hydroxyl group stretching
2885	C-H vibration
1737	**C=O ester carbonyl group**
1640	H_2O (moisture) in cellulose
1018, 1157	C-O stretching
896	β-glycosidic linkages

Table S4. Fitting constants for predicting solubility using Eq. (S1)

Acid	s_0	$\boldsymbol{B}$	r^2
Oxalic acid	6.03×10^6	3,928	0.999
Maleic acid	3.14×10^5	2,461	0.984
Toluenesufonic acid	6.03×10^4	1,737	0.986



(a) 1 pass **(b) 3 passes** **(c) 5 passes**

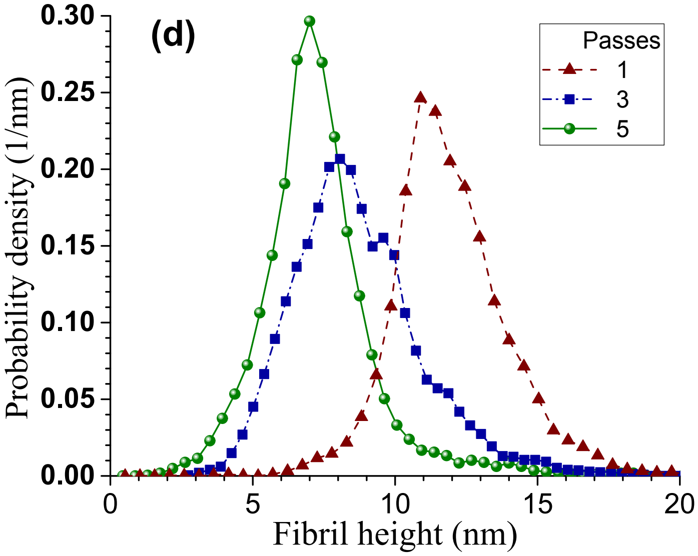


Fig. S1. Effect of the degree of mechanical fibrillation measured by the number of passes through the 87 μm chamber of the microfluidizer on CNF morphology. The FCSR was produced from hydrolysis of BEP under (A70, 100, 30). (a), (b) and (c) are AFM images of the CNFs. (d) is the AFM measured CNF height (equivalent to diameter) distribution.

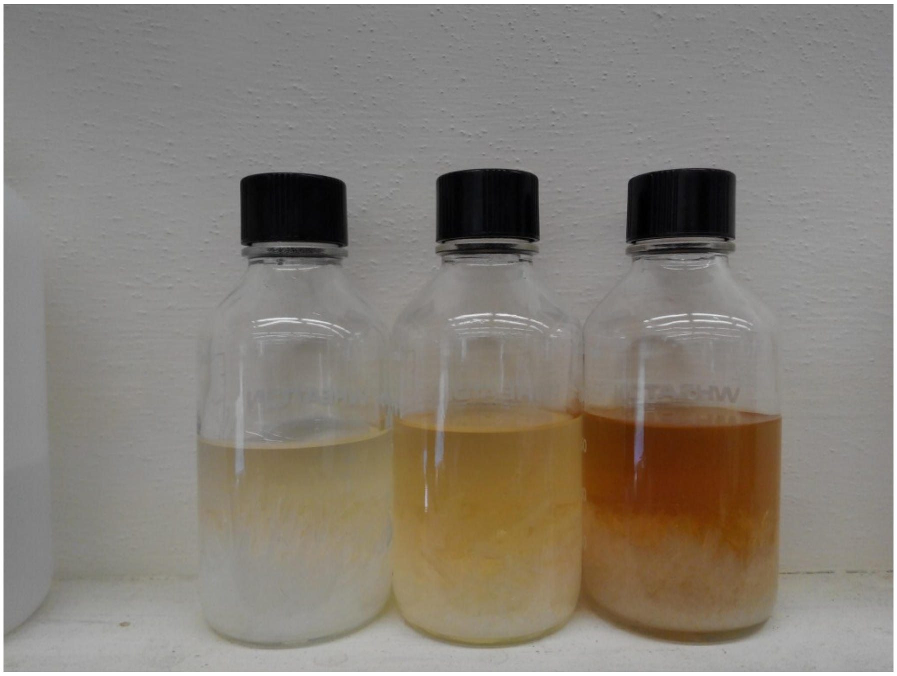


Fig. S2. Crystallization of oxalic acid at ambient temperature in hydrolysates (diluted 3 times at 80°C) after reacting with BEP fibers at different acids concentrations. From left to right: (O50, 100, 45); (O60, 100, 45); and (O70, 100, 45).

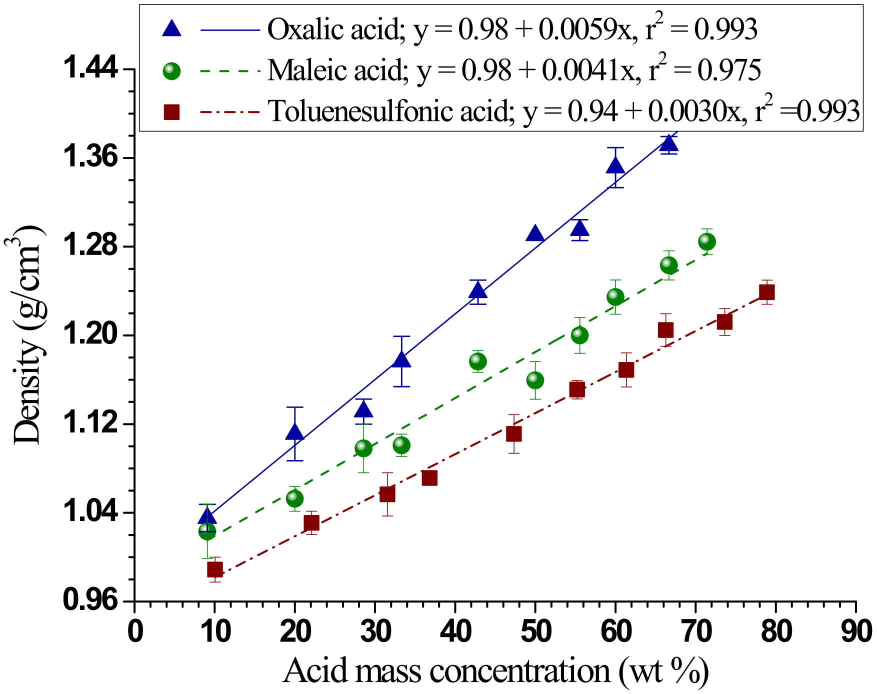


Fig. S3 Densities of concentrated organic acid aqueous solutions at different concentrations at 100 °C.

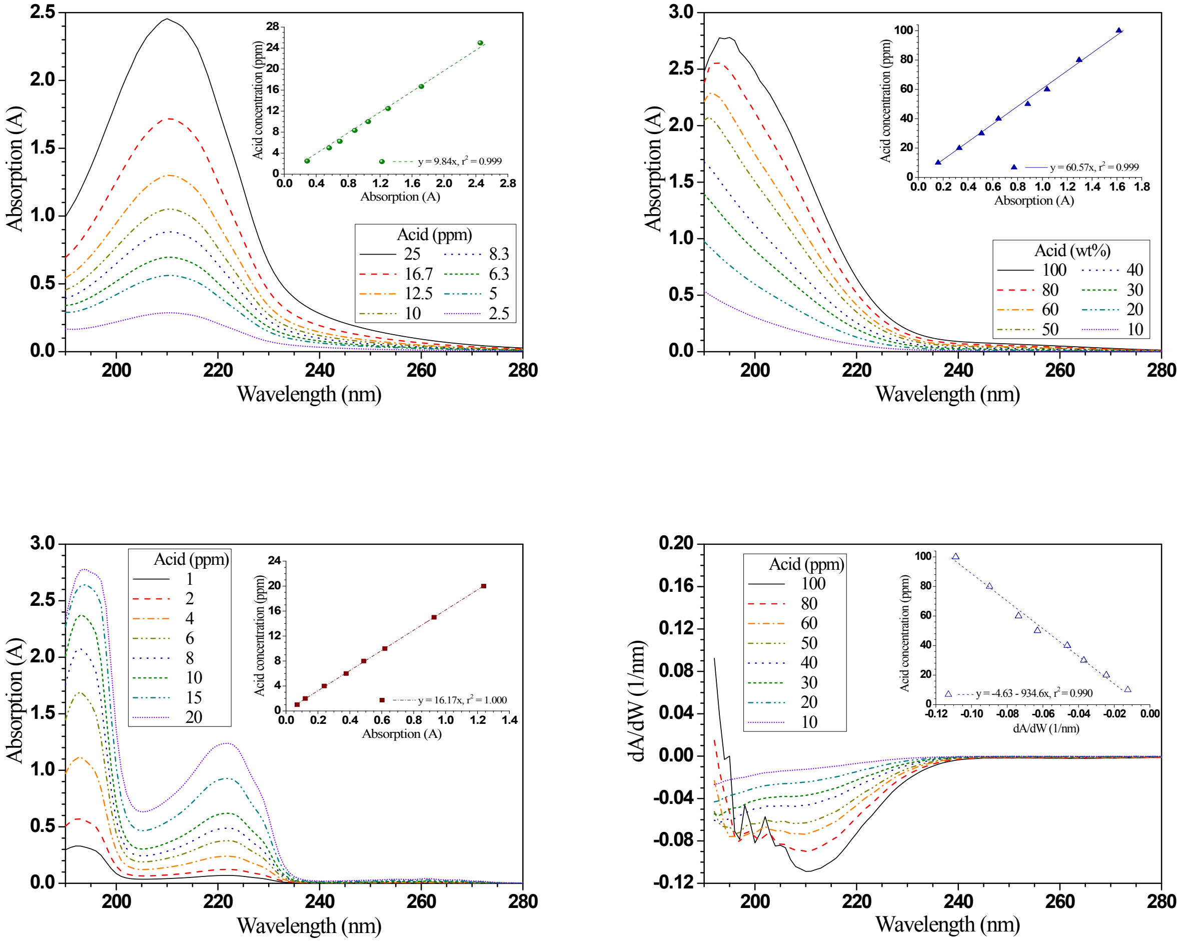


Fig. S4. Absorption spectra and wavelength derivative spectra of three organic acids at various concentrations in aqueous solutions. (a) Maleic acid; (b) p-Toluenesulfonic acid; (c) Oxalic acid; (d) Oxalic acid wavelength derivative spectra. Inserts show acid concentration calibration lines.

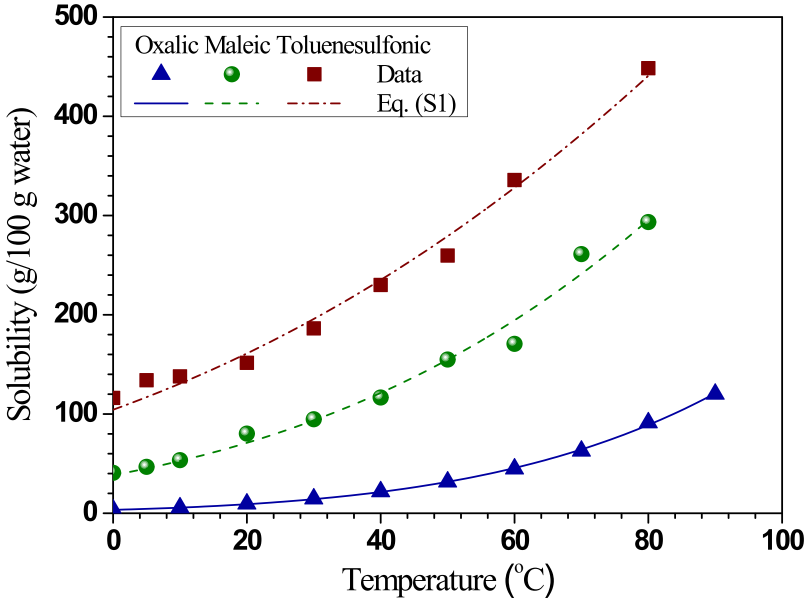


Fig. S5 Solubilities of three organic acids at different temperatures

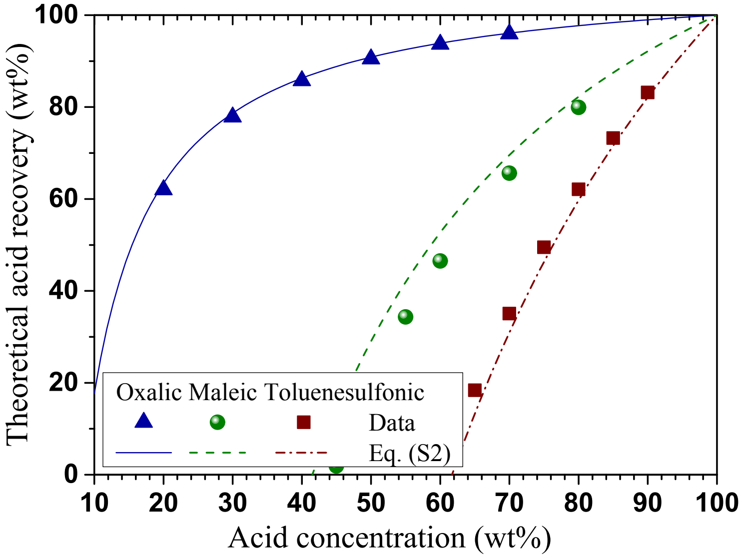


Fig. S6 Acid recoveries at different acid concentrations estimated based on UV absorption measured acid concentrations and solubility limit.

Determination of the solubilities of solid organic acids

The solubilities of solid organic acids in water at different temperatures can provide two pieces of important information: (1) the upper-limit of acid concentrations to be used for acid hydrolysis; (2) the potential of recovery of these acids as solids through crystallization and precipitation at a lower temperature. UV absorption spectrophotometric methods were employed for rapidly determining the soluble acid concentration in a solution. Maleic and toluenesulfonic acids have absorption peaks at 210 and 222 nm (Fig. S4a-b), respectively. The absorptions at these two wavelengths were used to determine the amounts of soluble maleic and toluenesulfonic acids, respectively, through calibration as shown. The absorption spectra of oxalic acids do not have absorption peaks (Fig. S4c), however, the absorption intensity at wavelength 210 nm can also be used for quantification through calibration. Furthermore, we can use the absorption derivative vs wavelength at 210 nm for quantification through calibration (Fig. S4d). Excellent linear relationships between soluble acid concentrations and absorption intensities (or derivatives of absorption for oxalic acid) were obtained. Therefore, accurate acid concentrations in solutions can be quickly determined through UV absorption measurements.

The solubilities of oxalic, maleic, and toluenesulfonic acids at different temperatures were determined from UV absorption measurements in saturated solutions at different temperatures. The solubilities of the three acids increased exponentially with temperature as shown in Fig. S5. The measured solubility data were fitted to an exponential function as shown by Eq. (1). The maximum acid concentration (or loading) that can be used for acid hydrolysis at a given temperature can be determined from the exponential expression.

$$s_T = s_0 \times \exp\left(-\frac{B}{T}\right) \tag{S1}$$

Where s_0 and B are fitting constants and listed in Table S4 for the three acids studied while T is in degree Kelvin.

Determination of acid recovery from aqueous acid solutions

From the solubility data, the amount of recoverable acid in an aqueous solution through crystallization at a reduced temperature T compared with the hydrolysis temperature can be estimated. The amount of acid that can be recovered through crystallization and precipitation is simply the amount of acid in a solution minus the maximal amount of soluble acid at the crystallization T determined by the solubility limit s_T. Mathematically, the theoretical acid recovery can be determined using the following expression,

$$R\,(\%) = \frac{100C - (100 - C)s_T}{C} = 100 - \frac{100 - C}{C}s_T = 100 - s_0\frac{100 - C}{C}exp(-\frac{B}{T}) \quad \text{(S2)}$$

Where C is the soluble acid concentration in wt% of the acid solution, s_T is the solubility of the acid in g/100 g water at T (in K) from Eq. (S1). As an example, acid crystallization was assumed to be conducted at T = 20ºC = 293 K (room temperature), then the acid recoveries for the three acids at different concentrations can be obtained according to Eq. (S2). As shown in Fig. S6 approximately 95% of the oxalic acid in a solution of concentration 70 wt% can be recovered. Approximately 80% of the maleic and toluenesulfonic acid can be recovered from solution of concentration at 80 and 90 wt%, respectively. The data points in Fig. S6 were calculated using the measured acid solubilities at 20°C (293K) shown in Fig. S5. It should be pointed out that the recovery calculated from Eq. (S2) is lower than actual recovery due to water absorption in crystallization to form acid-hydrate.