Facile One-step Fabrication of Functional Cellulose Nanocrystals with High Efficiency under Microwave-ultrasound Synergy

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Abstract. The use of cellulosic biomass for the manufacture of functional cellulose nanocrystals (FCNs) in a mild and green process is limited due to the multiple hydrogen bonds between cellulose. Based on the mechanochemical mechanism, an efficient and green approach to cleave hydrogen bonds and fabricate FCNs was realized via microwave-ultrasound synergy. In the one-step process, impact force, crash force, friction, chemical action, and thermodynamic interaction combined to create synergistic effects, accelerating the cleavage of hydrogen bonds and formation of FCNs synchronously. One-step purification of FCNs was implemented after reaction for the recovery of byproducts, which was critical to cost reduction and waste liquor treatment. FCNs with high crystallinity of 80\%, high charge density, and good dispersion stability were obtained. Thus, a facile versatile green avenue for the large-scale production of FCNs was achieved in the study, and is expected to carry significant benefits in terms of economy and sustainability.

1. Introduction

Cellulose nanocrystals (CNs) have been attracted a great interest for their high strength, low density, biodegradability, and fascinating electrical and optical properties [1]. Moreover, CNs are easy to be modified into active groups such as amide, sulfydryl, carboxyl etc. due to the presence of hydroxyl groups on the surface of CNs. Consequently, various functional cellulose nanocomposites with outstanding properties can be developed by appropriate modification of CNs, which would greatly expand their diverse applications [2]. CNs can be obtained by removing the amorphous regions of cellulose and leaving the crystalline parts integrally through acid hydrolysis, enzymatic hydrolysis, or mechanical treatments [3, 4]. Unfortunately, the use of highly corrosive mineral acids, tedious extraction methods, multiple post-processing steps or low yields impedes the large-scale production and real-world applications of CNs. Up to now, the economic and sustainable manufacture of CNs in a facile and mild process is still distant.

It is worth noting that carboxylated CNs have been isolated through ammonium persulfate (APS), a low-cost oxidant with low toxicity and high water solubility instead of conventional acid hydrolysis [5, 6]. The carboxyl groups on the surface of CNs can provide active sites for conjugating with pertinent molecules to regulate hydrophilicity or hydrophobicity, and thus opening new horizons for various applications of CNs [7, 8]. However, the method is time-consuming and low-efficiency, which
requires a reaction time of 16 h, and the byproducts produced during the course are not treated effectively. It is important to cleave the strong hydrogen bonds within cellulose fiber to improve hydrolysis efficiency and reduce energy consumption in CNs isolation. Attempts to overcome these limitations cover the utilization of nonclassical energy sources, including microwave, sonication or mechanochemical techniques.

Microwave irradiation has unique characteristics of rapid heating, high reaction selectivity, short reaction time, less energy loss, and accelerated reaction rate [9, 10]. Microwave has been applied in cellulose derivatives preparation, microwave irradiation disrupted the hydrogen bonds and supramolecular structure within cellulose fiber, causing the improved accessibility of cellulose [11, 12]. Additionally, ultrasonic cavitation can produce intense local heating and high pressure in a flash, which can drive high energy chemical reactions and accelerate the mass transfer in inter-and intra-fiber pores [13]. The energy provided by ultrasonic cavitation is approximately 10-100 kJ mol-1, which is within the hydrogen bond energy scale, and thus the strong hydrogen bonds within cellulose chains can be disrupted [14]. Therefore, microwave-ultrasound synergy would be an efficient approach to enhance efficiency and productivity for CNs manufacturing, but to our knowledge, the synergetic effect between microwave and sonication for the green fabrication of CNs by cleaving strong hydrogen bonds in cellulose has not yet been investigated.

The present study presented a facile and green approach to prepare functional cellulose nanocrystals (FCNs) with high crystallinity and dispersibility based on the cleavage of hydrogen bonds under the synergistic effect of microwave and sonication. In the one-step procedure, the hydrolysis and functionalization of cellulose took place simultaneously, so as to avoid lengthy reactions and realize high efficiency. Moreover, the produced byproducts were recovered to minimize waste that would carry significant benefits in terms of sustainability and low costs for the large-scale production of FCNs.

2. Experimental

2.1. Materials
Dissolving pulp (DP) as cellulose raw material was supplied by Nanping Paper Co., Ltd. (Nanping, Fujian, China). Ammonium persulfate ((NH4)2S2O8) was purchased from Sinopharm Chemical Reagent Co., Ltd. All used chemicals were of analytical grade without any further purification.

2.2. Manufacture of FCNs
3 g DP was added into 90 mL of 2 mol L-1 APS solution and then performed in a microwave-ultrasound instrument at 60 °C for 60-180 min under a microwave power of 600 W and ultrasonic power of 700 W. 50 mL NH4OH was added to the reaction mixture to terminate the reaction and neutralize the byproduct H2SO4. The resultant FCNs suspension was centrifuged five times with distilled water at 11000 rpm for 8 min to remove the byproduct (NH4)2SO4 until attained neutrality. The resulting supernatant was evaporated to dryness to recycle (NH4)2SO4 to improve economic viability for large-scale production of FCNs. The one-pot tandem reaction procedure for the fabrication of FCNs is illustrated in Fig. 1.

As a control, APS hydrolysis of cellulose was implemented at 60 °C in a water bath. The APS concentration and subsequent processing after reaction were the same as mentioned above.
2.3. Optimization of Fabrication Conditions
Response surface methodology was employed for the optimization of fabrication conditions of FCNs. The three independent variables were reaction time (60, 120 and 180 min), APS concentration (1.5, 2 and 2.5 mol L⁻¹) and reaction temperature (60, 70 and 80 °C). The response was the yield of FCNs, and the detailed experimental design was shown in Table 1.

| Trial No. | X₁ (min) | X₂ (mol L⁻¹) | X₃ (°C) | Yield of FCNs, Y (%) |
|-----------|----------|--------------|---------|---------------------|
| 1         | 1(180)   | 1(2.5)       | 0(70)   | 36.95               | 37.24 |
| 2         | 0(120)   | 0(2)         | 0(70)   | 43.50               | 43.28 |
| 3         | 1(180)   | 0(2)         | -1(60)  | 45.24               | 45.85 |
| 4         | 0(120)   | 0(2)         | 0(70)   | 43.40               | 43.28 |
| 5         | 0(120)   | 0(2)         | 0(70)   | 42.06               | 43.28 |
| 6         | 0(120)   | 0(2)         | 0(70)   | 42.06               | 43.28 |
| 7         | 1(180)   | 0(2)         | 1(80)   | 34.91               | 34.48 |
| 8         | 1(180)   | -1(1.5)      | 0(70)   | 36.18               | 35.70 |
| 9         | 0(120)   | -1(1.5)      | -1(60)  | 27.63               | 27.50 |
| 10        | -1(60)   | 0(2)         | 1(80)   | 34.50               | 33.89 |
| 11        | 0(120)   | 1(2.5)       | -1(60)  | 37.80               | 36.90 |
| 12        | 0(120)   | -1(1.5)      | 1(80)   | 25.65               | 26.56 |
| 13        | -1(60)   | 0(2)         | -1(60)  | 32.20               | 30.63 |
| 14        | 0(120)   | 1(2.5)       | 1(80)   | 29.60               | 29.73 |
| 15        | -1(60)   | 1(2.5)       | 0(70)   | 33.60               | 34.08 |
| 16        | -1(60)   | -1(1.5)      | 0(70)   | 23.34               | 23.05 |
| 17        | 0(120)   | 0(2)         | 0(70)   | 43.59               | 43.28 |

Table 1. Box-Behnken experimental design and the response to the yield of FCNs.
2.4. Characterization

The morphology of DP was observed by field emission scanning electron microscopy (FESEM). The morphology and dimension of FCNs were analyzed by transmission electron microscope (TEM) and atomic force microscope (AFM).

The dispersion stability and particle size distribution of FCNs suspensions were determined through a Zetasizer (Malvern Instruments Ltd., UK) which provides multi-angle particle size analysis and low-angle zeta potential analysis. The particle size and zeta potential values were the average of three runs of measurements.

The chemical structure of cellulose samples was analyzed by FT-IR, NMR and XPS. FT-IR spectra were collected with a Nicolet 380 FT-IR spectrometer (Thermo Electron Instruments Co., Ltd., USA) in the frequency range of 4000-400 cm⁻¹ with a resolution of 4 cm⁻¹. Solid-state 13C NMR spectra were acquired on a Bruker Avance III 500 spectrometer (Bruker Biospin AG, Fallanden, Switzerland) at a resonant frequency of 125.73 MHz, a magic angle spinning (MAS) rate of 5 kHz and a contact time of 2 ms. X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250 (Thermo Scientific Instruments Co., Ltd., USA) XPS spectrometer with a monochromatic Al Ka X-ray source (1486.6 eV) and operated at a voltage of 15 kV and current of 10 mA. Survey spectra for each sample ranging from 0 to 1300 eV were obtained at 100 eV pass energy and 1 eV/step resolution for elemental compositions survey. High-resolution spectra of C1s and O1s were acquired at 30 eV pass energy and 0.05 eV/step resolution to analyze the binding energy and elemental concentration quantitatively. Gaussian peak profiles were used for spectral deconvolution of C1s and O1s spectra.

The carboxylic acid contents of FCNs was determined by conductometric titrations. Briefly, 0.25 g FCNs were suspended in 50 mL 0.01 M HCl and sonicated 20 min to disperse uniformly. The FCNs suspension was then titrated against 0.01 M NaOH and the degree of oxidation (DO) was calculated using the following equation:

\[
DO = \left( \frac{162(V_2 - V_1)C}{W - 36(V_2 - V_1)} \right)
\]

where \((V_2-V_1)\) is the consumed volume of NaOH (L), \(C\) is the NaOH concentration (M), \(W\) is the weight of FCNs (g), 162 is the molecular weight of an anhydroglucose unit (AGU), and 36 is the molecular weight difference between an AGU and sodium gluconate [15].

The crystalline structure of FCNs was investigated by X-ray diffraction (XRD) analysis on an X-ray diffractometer (Philips-FEI, Netherlands) with Cu Kα radiation. Diffractograms were collected in the range of 2θ=6°-90° at a scanning rate of 0.1° s⁻¹. The crystallinity (CrI) was calculated according to Eq. (2):

\[
CrI = \left( \frac{I_{200} - I_{am}}{I_{200}} \right) \times 100\%
\]

where \(I_{200}\) is the overall intensity of the peak at 2θ about 22°, representing both crystalline and amorphous regions of cellulose, and \(I_{am}\) is the intensity of the baseline at 2θ about 18°, representing the amorphous regions of cellulose [16].

The thermal property of FCNs was explored by thermogravimetric analysis (TGA) with a thermal gravimetric analyzer (NETZSCH STA 449 F3 Jupiter®, Germany). The cellulose samples were heated from 25 °C to 600 °C at a heating rate of 10 °C min⁻¹ under a nitrogen flow of 30 mL min⁻¹.

3. Results and Discussion

3.1. Optimization of Fabrication Conditions

The yield of FCNs and the three independent variables are related by the following equation:

\[
Y' = 43.28 + 3.90X_1 + 3.14X_2 - 2.03X_3 - 2.37X_1X_2 - 3.66X_1X_3 - 1.55X_2X_3 - 2.36X_1^2 - 8.40X_2^2 - 4.71X_3^2
\]

where \(Y\) is the yield of FCNs, \(X_1\), \(X_2\) and \(X_3\) are the coded variables for reaction time, APS concentration and reaction temperature, respectively.
The analysis of variance for response surface model is shown in Table 2. The F-value of the model is 111.30 and the P-value of the model is less than 0.0001, indicating that the model is highly significant. The determination coefficient (R²) of the model is 0.9931, with no significant lack of fit (P > 0.05), illustrating that the regression model represents the true relationship between the response and the independent variables [17]. Therefore, it can be proved from the above analysis that the regression model is suited to optimize the fabrication conditions of FCNs.

Table 2. Analysis of variance for response surface quadratic model.

| Source          | Sum of squares | Degrees of freedom | Mean square | F-value | P-value |
|-----------------|----------------|--------------------|-------------|---------|---------|
| Model           | 772.53         | 9                  | 85.84       | 111.30  | <0.0001 |
| Residual        | 5.40           | 7                  | 0.77        |         |         |
| Lack of fit     | 3.41           | 3                  | 1.14        | 2.30    | 0.2196  |
| Pure error      | 1.98           | 4                  | 0.50        |         |         |

The effects of independent variables on the yield of FCNs are shown in Fig. 2. The yield of FCNs increases with reaction temperature increasing from 60 °C to 70 °C (Fig. 2a). Higher temperature is contributed to the diffusion of APS into the disordered accessible regions of cellulose and enhances the reaction activity of cellulose, and thus strengthening the hydrolysis efficiency. Furthermore, the mass transfer is intensified with the disruption of strong hydrogen bonds induced by amorphous regions hydrolysis under the synergetic effects of microwave and sonication. Nevertheless, FCNs yield declines gradually with the further increase in temperature because of the excessive hydrolysis of cellulose. In addition, the elliptical contour plot indicates the significant interactive effect of reaction time and reaction temperature [18].

The microwave-ultrasound synergy plays an important role in the hydrolysis of cellulose. The yield of FCNs increases with the increase of reaction time at constant APS concentration, especially within the range of 60-120 min, and a maximum yield of 46.30% is determined (Fig. 2b). In the microwave and sonication process, mechanochemical effect formed which cleaved the strong hydrogen bonds between cellulose chains and caused the depolymerization of ultrastructure of cellulose [19]. Under the APS oxidation, the hydrolysis efficiency of amorphous regions was improved, accelerating the formation of FCNs. The yield decreases slightly at longer reaction time may be attributed to the destruction of crystalline regions. The elliptical contour plot also illustrates the significant interaction between APS concentration and reaction time.

Fig. 2c shows the effect of reaction temperature and APS concentration on the yield of FCNs. Sulfate radicals and hydrogen peroxide produced by APS facilitates the hydrolysis of amorphous regions, and with the increasing of APS concentration, the hydrolysis degree enhances, which results in the increase of FCNs yield [20]. The yield of FCNs declines at higher APS concentration due to the hydrolysis of crystalline regions. The circular contour plot implies the relative mild interactive effect of reaction temperature and APS concentration. Additionally, the optimum fabrication conditions of FCNs are reaction time 204 min, APS concentration 2 mol L⁻¹, and reaction temperature 62 °C. Under these conditions, a yield of 46.41% was obtained, which is not significantly different from the predicted value of 46.93% by response surface model. However, the yield of FCNs via water bath reaction increased slowly to 21% with the extension of reaction time to 16 h. The result suggests that, the processing under microwave-ultrasound synergy significantly diminished the reaction time and improved the reaction efficiency. This is attributed to the unique characters of microwave irradiation and ultrasound arising from non-thermal or thermal effects and cavitation effect. Microwave irradiation caused the rotation of polar -CH2OH groups, meanwhile, ultrasonic cavitation cleaved the strong hydrogen bonds within cellulose network, accelerating the diffusion of APS into cellulose to oxidize -CH2OH groups, and thus lengthy process could be avoided [21].
3.2. Morphology and Size Distribution

FESEM image shows that DP fiber presents a curled and flat shape with diameter of 12 μm and length of hundreds of micrometers, and these micro-sized fibrils entangle together closely through hydrogen bonding to form a net structure (Fig. 3a). After the hydrolysis reaction, the size of DP fiber decreases to nanoscale dimensions. As seen from TEM (Fig. 3b) and AFM images (Fig. 3c), short rod-like FCNs are observed, and the determined diameter is 10-15 nm, length is 100-200 nm. These rod-like nanoparticles intertwine to form a network structure that can offer reinforcing capability in composite materials. However, an average diameter of 7 nm for FCNs suspensions calculated through Zetasizer (Fig. 3d) is smaller than that of determined from AFM image. This is mainly due to image widening that causes an overestimation of the particle size [22]. Additionally, no significant agglomeration of FCNs suspension can be observed owing to the electrostatic repulsion between cellulose nanocrystals arose from the negatively charged carboxyl groups. The determined zeta potential of -46.3 mV for FCNs suspension demonstrates the better hydrophilicity since the absolute value of zeta potential greater than 40 mV will give stability of a colloid dispersion [23]. The results suggest that FCNs suspensions have good dispersion stability which is crucial for their intended applications as reinforcing agent or nanofiller.
3.3. Chemical Structure

Fig. 4a shows the FT-IR spectra of FCNs and DP. The absorption peaks at 1635, 1428, 1110, 1056 and 894 cm\(^{-1}\) are associated with cellulose I\(\beta\) [24]. In comparison, FCNs exhibit similar FT-IR spectrum to DP, indicating that no significant changes occurred in the conformation of the cellulose structure. For FCNs, the bands at 1059 cm\(^{-1}\) arose from C-O stretching vibration of pyranose and 1113 cm\(^{-1}\) arose from glucose ring skeletal vibration are enhanced, implying the increase in crystalline cellulose contents. The peak intensity at 3350 cm\(^{-1}\) for FCNs is enhanced due to the removal of amorphous regions and exposure of more hydroxyl groups. The appeared peak at 1733 cm\(^{-1}\) corresponds to the stretching of carbonyl groups, confirming the existence of carboxylic acid groups [25].

The structure changes of FCNs and DP were also investigated by Solid-state 13C NMR analysis (Fig. 4b). The spectra of FCNs and DP show typical signals of cellulose I, i.e. C1 (104.6 ppm), C2, C3, C5 (71.2 ppm, 74.6 ppm), C4 (88.5 ppm) and C6 (64.9 ppm) arise from carbons of glucopyranose rings in crystalline regions, whereas C4 (83.5 ppm) and C6 (62.6 ppm) belong to carbons of glucopyranose rings in disordered regions [26, 27]. The appearance of a signal at 173 ppm for FCNs attests the existence of -COOH, indicating that the oxidation and hydrolysis of cellulose occurred simultaneously.

According to the conductometric titration curve (Fig. 5), the calculated DO is 0.127 and the COOH content is 0.87 mmol g\(^{-1}\). The estimated charge density is 1.48 e nm\(^{-2}\) by assuming a density of 1.6 g cm\(^{-3}\) and diameter of 7 nm for FCNs, and all the glucose units on the surface of FCNs are completely carboxylated [28, 29]. By contrast, the DO and COOH content of FCNs via water bath reaction are 0.08 and 0.5 mmol g\(^{-1}\), respectively. The results indicate that the hydrolysis efficiency and oxidation degree of cellulose are enhanced significantly under the synergistic effects of microwave and sonication. The energy of 10-100 kJ mol\(^{-1}\) created by ultrasonic cavitation is enough to disrupt the hydrogen bonding within cellulose network and enhance the reaction activity of cellulose [14]. The mass and heat transfer of cellulose in the reaction process is strengthened under microwave irradiation. Therefore, microwave-ultrasound synergy plays a crucial role in the fabrication of FCNs, which facilitates the disintegration of cellulose into cellulose nanocrystals. The highly charged FCNs with plenty of versatile carboxyl groups are easier to further modification or crosslinking to heighten their process ability and flexibility in composites.
The formation of carboxylic acid groups on the surface of FCNs was further confirmed by XPS analysis (Fig. 6). The spectra of FCNs and DP display two peaks at around 286 and 532 eV, corresponding to C1s and O1s (Fig. 6a). For DP, the calculated surface elemental composition is O 39.39%, C 60.61%, and the oxygen to carbon (O/C) ratio is 0.65. By contrast, the composition of O increases to 46.54% whereas C decreases to 53.46% in FCNs, and the O/C ratio increases to 0.87 accordingly. The increase in the concentration of oxygen causes a significant increase of O/C, which can be attributed to the oxidation of -CH2OH to -COOH on FCNs. The high-resolution scans of C1s and O1s levels with their respective deconvolutions are shown in Fig. 6b and Fig. 6c, respectively. The deconvolution of C1s levels gives three peaks C1 (285 eV), C2 (286 eV) and C3 (288 eV), resulting from C1 (a carbon atom bounds only to other carbon atoms and/or hydrogen atom), C2 (a carbon atom bounds to a single noncarbonyl oxygen), and C3 (a carbon atom bounds to one carbonyl oxygen or to two noncarbonyl oxygen atoms), respectively [8]. The deconvolution of O1s levels produces two peaks O1 (533.3 eV) and O2 (532.5 eV), arising from O1 (an oxygen atom linked to a carbon atom by a single bond) and O2 (an oxygen atom linked by a double bond to a carbon atom of a carboxylic group) [30]. Compared with DP, the intensity of C2 peak of FCNs decreases from 40.8% to 25% whereas the intensity of C3 peak increases from 8.23% to 21.31%, which can be attributed to the elimination of hydroxyl groups. The intensity of O2 peak of FCNs increases from 26.95% of DP to 35.22%, which is mainly due to the formation of -COOH.
3.4. Crystal Structure

The XRD patterns of FCNs and DP are shown in Fig. 7. All samples exhibit three diffraction peaks at 2θ=15.3°, 16.2°, 22.5°, corresponding to (1-10), (110) and (200) diffraction planes of cellulose Iβ lattice respectively, suggesting that the crystalline type of FCNs was not altered in the manufacture processing [31]. The peak shape of FCNs and DP is similar, implying that the inner crystal structure of cellulose was not damaged under microwave and sonication. However, the peak intensity of (200) crystallographic plane is enhanced for FCNs which means a higher perfection of the crystal lattice. FNCs have a higher crystallinity of 80% than 62% for DP owing to the hydrolysis of amorphous regions. The high crystalline of F CNs is expected to be important in strengthening the mechanical properties of composite materials since higher crystallinity is associated with higher tensile strength [32].
3.5. Thermostability

TGA and DTG curves of FCNs and DP are shown in Fig. 8. The thermal degradation procedure of FCNs and DP is a one-step decomposition, and mainly divided into three stages: evaporation of absorbed water before 110 °C, degradation of cellulose in the range of 250-400 °C, and carbonation of residual products >400 °C. Compared with DP, the onset degradation temperature of FCNs declines from 300 °C to 285 °C (Fig. 8a), and the maximum degradation temperature declines from 332 °C to 325 °C (Fig. 8b), implying that the thermal stability of FCNs reduces slightly. This is probably due to the active surface groups, small particle size, and high specific surface area of FCNs. Fortunately, FCNs remain stable at 280 °C, which is essential for FCNs applications in thermoplastics because the processing temperature is usually above 200 °C. By contrast, the cellulose nanocrystals acquired by sulfuric acid hydrolysis degrade below 195 °C due to the existence of sulfate groups and have a lower thermostability than that of FCNs.

4. Conclusions

A one-pot green procedure for the cleavage of strong hydrogen bonds of cellulosic biomass was developed for the manufacture of FCNs with high crystallinity and improved dispersion and thermal stability. The mechanochemical effect created by microwave-ultrasound synergy accelerated the disruption of hydrogen bonding within cellulose network and reduced the mass and heat transfer resistance, contributing to the enhancement of productivity. The optimum reaction time was 204 min for hydrolysis at 62 °C with APS concentration of 2 mol L⁻¹ under response surface methodology. Compared to common modified methods of cellulose nanocrystals, the presented way used no organic solvents, decreased separation steps, avoided lengthy reactions, implemented byproducts recovery, and
thus enhanced sustainability and economy. Therefore, the study may pave the way for the green and low-cost fabrication of FCNs. The resultant FCNs with high charge density could be functionalized for a plethora of diversified applications.

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