CELLULOSE CHEMISTRY AND TECHNOLOGY

PREPARATION AND CHARACTERIZATION OF CELLULOSE NANOCRYSTALS FROM BAMBOO PULP

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Cellulose nanocrystals (CNCs) can be obtained from bamboo pulp by hydrolysis with sulfuric acid. Firstly, the authors conducted a series of experiments under different conditions, and concluded that the optimal parameters were as follows: sulfuric acid concentration 60%, temperature 45 °C, the time is 90 minutes and the solid-liquid ratio is 1:8. Then, transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR) and thermal gravimetric analysis (TG) were employed to characterize and test the morphology, structure and thermal stability of the CNCs obtained under the optimal conditions. It was found that CNCs mainly exist in two forms, as a rod network and as a porous network, and they have the basic chemical structure of cellulose, while the hydrogen bonds are destroyed. Compared with bamboo pulp, the degree of crystallinity of CNCs is obviously improved, but the thermal stability is weakened.

Keywords: bamboo pulp, cellulose nanocrystal, morphology, thermal stability

INTRODUCTION

Nowadays, it is recognized that most of the synthesized polymer materials cannot be degraded, leading to environment pollution and human health problems in the world. Considering this, it is imminent to find green renewable resources.

Natural cellulose is almost ubiquitous and easy to obtain, it exists in plants, animals, and even in some bacteria. It has been found that plant fibers of gramineae, phragmites and woody plants have a large proportion of natural cellulose. The cellulose is synthesized through photosynthesis and the annual output of cellulose is 1.5×10^{12} tons, which can meet the growing human needs.[1-3] However, natural cellulose has such shortcomings as low strength, poor thermal stability, and high water absorption. Its physical form restricts its use to certain areas of application. If natural cellulose is used to make nanometer materials, it can improve the performance and expand the application of renewable resources to a certain degree.[4] According to Samir (1877), Nageli and Schwendener first confirmed that the crystalline region of cellulose materials interpenetrated into the amorphous region.[5] However, the amorphous regions have structural defects and are prone to lateral split to short single crystals when in contact with acids. Therefore, the degree of polymerization and the particle size of cellulose decrease under acid treatment. Nanometer-sized cellulose is known as cellulose nanocrystals (CNCs). They are widely used for obtaining reinforced nanocomposites, foams and aerogels,[6] optically transparent functional materials and oxygen-barrier layers.[7-8] Some applications of CNCs have been reported, such as for the fabrication of polymethylmethacrylate/CNC composites, of reinforcement components in polyethylene nanocomposites,[9-12] etc.

Several methods have been used to obtain highly purified nanocrystals from cellulosic materials, including the chemical method, mainly carried out by acid hydrolysis and enzyme-assisted hydrolysis,[13-16] mechanical treatments, such as high-pressure homogenizing,[17-18] grinding and ultrasonication,[19-20] as well as a combination of two or several of the aforementioned methods.

Sulfuric acid hydrolysis is a well-known process that is used to prepare cellulose nanofibers, allowing to disintegrate amorphous regions, introduce negative charges to nanoparticle surfaces,[21] and form stable nanocrystal suspensions. Several materials have been used to obtain nanocrystals from cellulosic materials, including *Posidonia oceanica* marine biomass,[22] corn stover,[23] sweet potato residue,[24] kraft pulp,[25] etc. However to the best of our knowledge, CNCs obtained from bamboo pulp by sulfuric acid hydrolysis have not been reported in the literature so far.

In this study, our objective was to prepare CNCs from bamboo pulp by sulfuric acid hydrolysis and to investigate their morphological, crystalline, thermal and physicochemical properties.

EXPERIMENTAL

Materials

Bamboo pulp was provided by MCC Paper Group Co., Ltd. Sulfuric acid, sodium hydroxide, benzene, ethanol, nitric acid, hydrochloric acid, sodium bromate, sodium bromide, sodium thiosulfate, starch, phenolphthalein, potassium iodide, barium chloride, sodium chlorite and glacial acetic acid were purchased from Hangzhou Mick Chemical Co. Ltd., and were analytically pure.

Chemical composition of bamboo pulp

The main chemical composition of the bamboo pulp (moisture content, cellulose, hemicelluloses and lignin) was determined by the method described by the National Institute of Standards, applying the analysis and testing procedure for pulp and paper.[26]

Preparation of CNC suspension

The bamboo pulp (4 g) was treated with sulfuric acid (6, 8, 10, 12, 14, 16 mL of sulfuric acid solution/g pulp) at acid concentrations of 48, 52, 56, 60, 64, 68 wt%, temperature of 30, 35, 40, 45, 50, 55 °C, and reaction time of 30, 60, 90, 120, 150, and 180 minutes, respectively. When reaching a predetermined time, each reaction was terminated by adding 100 mL deionized water, and the suspended substances were washed with deionized water using repeated centrifugation cycles of 10 min at 12000 rpm, i.e. the supernatant liquor was removed from the sediment and replaced by new deionized water and mixed. The last washing was done to use dialysis with deionized water until the wash water reached a constant pH. The centrifugation was stopped when the supernatant liquor became turbid or the supernatant liquor was washed for five times. At last, the samples were sonicated for 20 min in an ice bath to avoid overheating, which might cause desulfation of the sulfate groups on the cellulose.

Yield measurement

The total volume of CNCs was weighed accurately and 20 mL of the suspension liquor was taken using a pipette and was put into a weighing bottle at constant weight. Then, the weighing bottle was put into an oven at 105 °C for drying to constant weight. At last, it was retrieved and placed into a desiccator to cool for 30 minutes and weighed on a balance.

$$\text{Yield}\,(\%) = \frac{(m_1 - m_2)v_1}{m_3 v_2} \times 100\%$$

where m_1 is the total mass of the sample and the weighing bottle after reaching a constant weight (g); m_2 is the mass of constant weight weighing bottle (g) and m_3 is the mass of the raw material (g); v_1 is the total volume of CNCs and v_2 is the pipetted volume of CNCs.

Instruments and characterization methods

Morphology

Structural and morphological characteristics of CNCs were observed with a JEM-1230 TEM provided by JEOL Company, Japan. A dilute suspension (0.1 wt%) was dropped onto a thin carbon film spread on a copper grid. Dried CNCs were examined by TEM at 120kV accelerating voltage.

Structural change of functional groups

The characteristics of functional groups were observed with a Nicolet 5700 spectrometer. Bamboo pulp powder and CNCs were mixed with KBr, and then pressed into transparent sheets using a preforming machine. The FTIR spectra were measured from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1}.

Thermal stability

The thermal behavior of bamboo pulp powder and CNCs was studied by a Pyris Diamond TGA system provided by Perkin-Elmer Company, USA, and the test conditions were the following: nitrogen protection, gas flow rate of 20 mL/min, a heating rate of 20 °C/min from 20 to 500 °C.

RESULTS AND DISCUSSION

Determination of chemical composition

The contents of moisture, cellulose, hemicelluloses and lignin in the bamboo pulp were of 9.86%, 78.29%, 19.16% and 0.07%, respectively. There was a high content of cellulose and little lignin in the bamboo pulp.

Single factor experiment of sulfuric acid hydrolysis of bamboo pulp

Effect of sulfuric acid concentration on the yield of CNCs

The experimental conditions applied were as follows: temperature of 45 °C, reaction time of 90 minutes and solid-liquid ratio of 1:12. The effect of sulfuric acid concentration on the yield of CNCs is shown in Fig. 1. The yield of CNCs increased first and then decreased with an increase in sulfuric acid concentration. When the concentration was less than 60%, the CNC yield was very low, mainly because the extent of hydrolysis was not enough under low acid concentration. The yield underwent exponential growth and reached a maximum of 21.8% when the acid concentration was 60%, and then despite further increase in acid concentration, the yield kept dropping because of a homogeneous hydrolysis reaction, which led to cellulose degradation into glucose. In addition, the carbonation phenomenon appeared at the concentration of 68%. In conclusion, a sulfuric acid concentration of about 60% was the most appropriate.

Effect of temperature on the yield of CNCs

The following experimental conditions were applied: sulfuric acid concentration of 60%, reaction time of 90 minutes and solid-liquid ratio of 1:12. The effect of temperature on the yield of CNCs is presented in Fig. 2. When the temperature was below 45 °C, the yield of CNCs lowered because of the lower temperature and less acid hydrolysis, although a milky white suspension could be obtained. At a temperature of 45 °C, the yield of CNCs reached a maximum of 21.8%. When the temperature was further increased, the yield began decreasing. This behavior is explained by the fact that a higher temperature can lead to a cleavage of the glycosidic bonds of the cellulose molecules, decrease the degree of polymerization, and then promote the release of single crystals. On the other hand, when the temperature is too high, cellulose undergoes further hydrolysis to produce glucose, resulting in reduced yields, its color becomes deeper, and it may be even carbonized.[27-28] Therefore, the preferred reaction temperature was about 45 °C.

Effect of time on the yield of CNCs

The experimental conditions applied were the following: temperature of 45 °C, sulfuric acid concentration of 60% and solid-liquid ratio of 1:12. The effect of reaction time on the yield of CNCs is shown in Fig. 3. As can be seen, CNC yield went up first and then decreased with an increase in the hydrolysis time. The main reason is that the non-crystalline regions of the bamboo fiber gradually hydrolyzed with increasing reaction duration, while the glycosidic bonds within cellulose fractured and single crystals were released under acid conditions.[29] When the reaction duration was up to 120 minutes, the CNC yield reached a maximum of 23.89%. As the reaction time further increased, the cellulose hydrolyzed into glucose, the CNC yield declined rapidly. Therefore, the most favorable hydrolysis time was considered 120 min.

Effect of solid-to-liquid ratio on the yield of CNC

The following experimental conditions were tested: sulfuric acid concentration of 60%, temperature of 45 °C and reaction time of 90 minutes. The effect of solid-to-liquid ratio on the yield of CNCs is shown in Fig. 4. Different solid-liquid ratios were could lead to a milky white suspension, however, a solid-liquid ratio of 1:8 led to a maximum yield of 31.61%. So, it was considered that a solid-to-liquid ratio of 1:8 was an optimal condition.

Optimization of process conditions

According to the results of the single factor experiments, the orthogonal experiment was designed to study the effect of the four main factors (sulfuric acid concentration, temperature, time and solid-liquid ratio) on the yield of CNCs, thereby determining the optimum hydrolysis conditions. The results are shown in Table 1.

As can be seen from Table 1, the influence of sulfuric acid concentration on the cellulose nanocrystal yield is the strongest, followed by those of temperature, time and solid-to-liquid ratio. Also, the optimal conditions for sulfuric acid hydrolysis of bamboo pulp were obtained in accordance with the average values of the respective parameters: 60 wt% sulfuric acid concentration, 45 °C temperature, 90 min reaction time and 1:8 solid-liquid ratio. A confirmation experiment was performed using these specific conditions and the maximum value obtained for the CNC yield was 32.3%. Our results are thus different from those reported in other literature on the process of sulfuric acid hydrolysis, which might be explained by the different materials used.

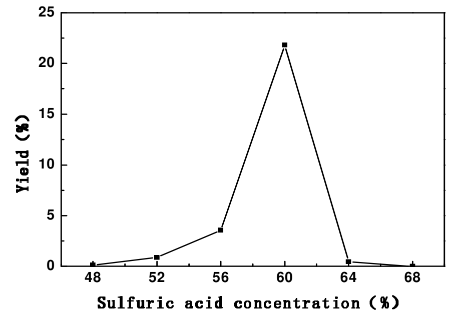


Figure 1: Effect of concentration on the yield of CNCs

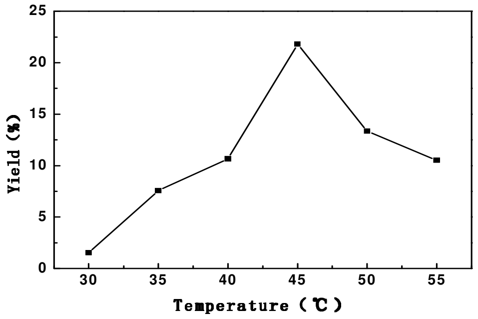


Figure 2: Effect of temperature on the yield of CNCs

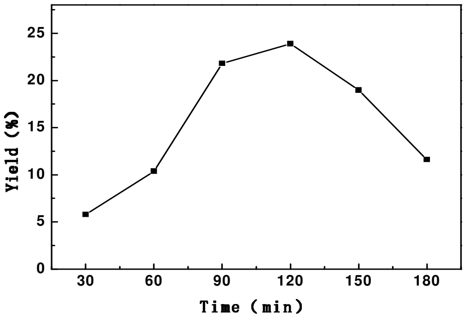


Figure 3: Effect of time on the yield of CNCs

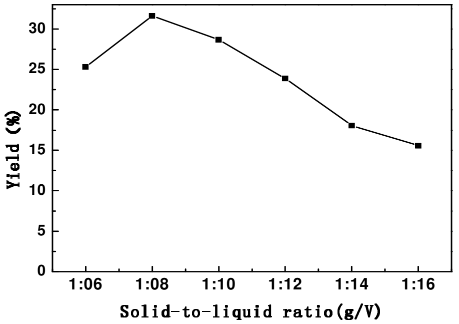


Figure 4: Effect of solid-to-liquid ratio on the yield of CNCs

Table 1
Results of orthogonal experiments

No.	Sulfuric acid concentration (%)	Temperature (°C)	Time (min)	Solid-to-liquid ratio (g/v)	Yield (%)
1	58	40	90	1:6	19.8
2	58	45	120	1:8	24.88
3	58	50	150	1:10	18
4	60	40	120	1:10	14.8
5	60	45	150	1:6	30.75
6	60	50	90	1:8	25.38
7	62	40	150	1:8	13.21
8	62	45	90	1:10	17.1
9	62	50	120	1:6	11.57
K1	20.893	15.937	20.760	20.707	
K2	23.643	24.243	17.083	21.157	
K3	13.96	18.317	20.653	16.633	
R	9.683	8.306	3.677	4.524	

(a)

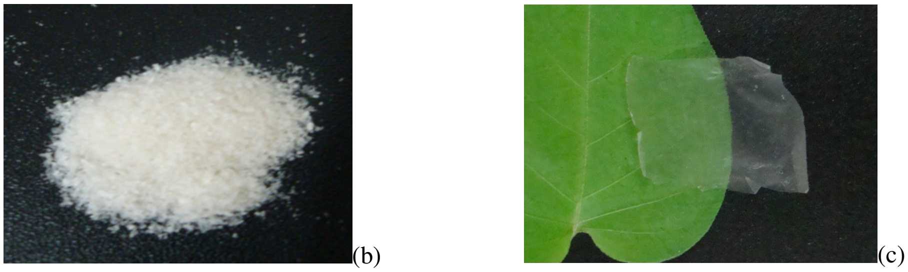
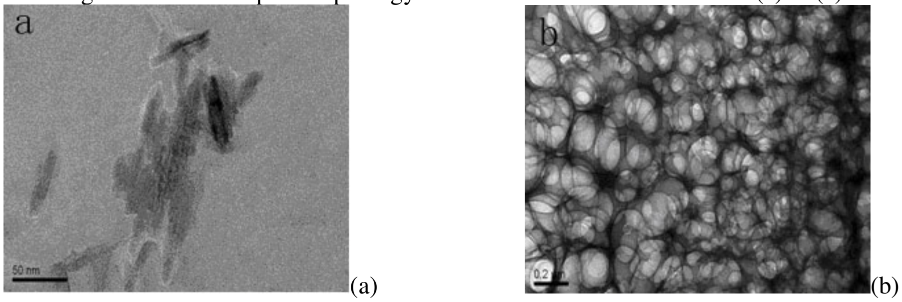

(b) (c)

Figure 5: Macroscopic morphology of different forms of CNCs from (a) to (c)



(a) (b)

Figure 6: TEM images of CNC in the form of (a) rods and (b) porous network

Characterization of CNC performance

Macroscopic morphology

Fig. 5 shows the morphologies of CNCs in different concentrations. Fig. 5(a) represents a CNC suspension obtained directly after centrifugation using a mild acid concentration of 0.5%. Fig. 5(b) shows freeze-dried CNC powder from the suspension. Fig. 5(c) represents cellophane with a smooth and transparent surface, which was obtained by placing and naturally drying the suspension in the air.

Micro-morphology

When the pulp fiber was treated with sulfuric acid at 45 °C, it first swelled and then separated into smaller crystalline cellulose products in the form of rods (Fig. 6(a)) and a porous network (Fig. 6(b)).[30] Neither form could be separated by filtration and centrifugation. As shown in Figure 6(a), the length and diameter of the rod-like CNCs were 100 nm or less, the size was thus much smaller than previously reported in relevant literature. It was mainly due to the strong hydrogen bonding among the CNCs, overcoming the repulsive force of the surface charge and resulting in self-assembled porous networks.[31]

FTIR analysis

As can be remarked in Fig. 7, the FTIR spectra of bamboo pulp and CNCs are similar, which indicates that the CNCs preserved the cellulose structure. However, the absorption intensity and location of the CNC spectra are slightly different, revealing that the structure of CNCs underwent some slight changes during acid treatment. The first strong absorption bands of bamboo pulp and CNCs appeared at wavenumbers of 3405 cm^{-1} and 3357 cm^{-1}, which could be caused by the O-H stretching vibrations of bamboo pulp and CNCs. Comparing the absorption positions, it can be noted that the O-H stretching vibration absorption band of CNCs moved toward a lower frequency, and the absorption intensity was weakened, indicating that part of the intramolecular hydrogen bonding was broken after the acid treatment, while the intermolecular hydrogen bonds were enhanced. The second strong absorption bands were located at 1058 cm^{-1} and 1059 cm^{-1}, respectively, and there were many weak acromions belonging to the ether bond and O-H stretching vibration.[31] The peaks of C-H and CH_2 stretching vibration of bamboo pulp and CNC were at 2898 cm^{-1} and 2900 cm^{-1} respectively. The 1637 cm^{-1} band could be assigned to O-H bending of absorbed water. The peak at 897 cm^{-1} belonged to the characteristic β-D glucosyl group, where the absorption intensity of CNC decreased, indicating that in the process of acid treatment, a part of the β-1,4 glycosidic bonds were fractured. This bond cleavage further showed that cellulose intramolecular hydrogen bond was broken. CNC had a weak sulfur peak at 1202 cm^{-1}, which did not appear in the FTIR spectra of bamboo pulp. This absorption peak was mainly produced by the esterification reaction.[30]

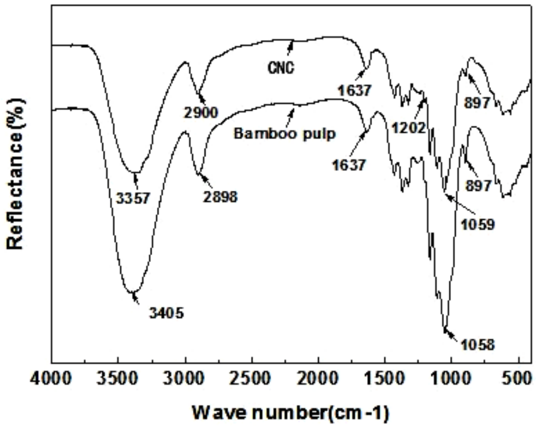
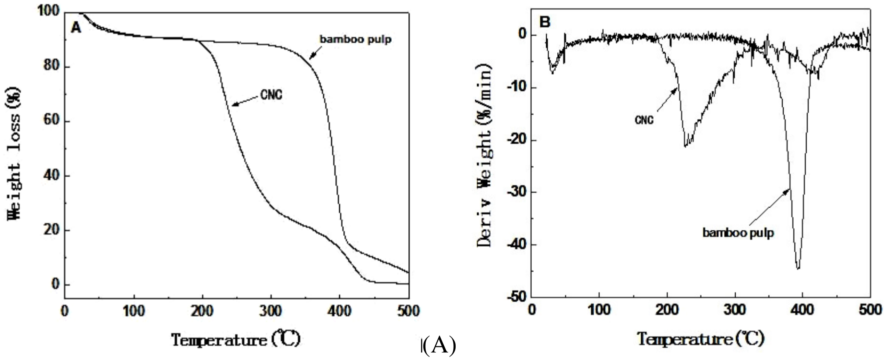


Figure 7: FTIR spectra of bamboo pulp and CNCs



(A) (B)

Figure 8: TG (A) and DTG (B) curves of bamboo pulp and CNCs

Thermal stability

As can be seen from Fig. 8, two samples had an endothermic peak in a low temperature range (<100 °C), which was mainly caused by the evaporation of adsorbed water. However, in a high temperature range, the degradation behavior of CNCs was different from that of bamboo pulp, as shown by the TG and DTG curves. For bamboo pulp, there was only one apparent weightlessness peak between 340 °C and 430 °C, the main decomposition interval.

In this interval, the pulp fibers experienced pyrolysis, generating small molecule gases and condensable volatile macromolecules. During this process, the original weight underwent a considerable loss and about 10% residue of the pulp fibers remained. Above 400 °C, the residue decomposed slowly. On the other hand, CNCs showed more gradual thermal transitions under a lower temperature. CNCs started to decompose upon onset temperature of 180 °C, and the main decomposition interval was from 180 °C to 320 °C, which is lower than that of bamboo pulp. There were two reasons for this.[32-33] First, following the acid treatment, the particle size of cellulose decreased sharply and the degree of polymerization also decreased, while the surface area increased; thus, there were many free end chains and reactive groups in CNCs, which started decomposition at a lower temperature. Second, cellulose chains are broken during the hydrolysis process, as a result, many small molecules and breaking points would appear on the surface of the CNCs. At the same time, cellulose chains present more defects because of irregular and not very compact arrangement, therefore degradation occurs at a lower temperature. For CNCs, there were 25% more residues left than for bamboo pulp after the main decomposition interval. However, these residues were not stable. With an increase in temperature, they further degraded into volatile compounds and a solid coke then formed, this happened during the second decomposition interval from 350 °C to 450 °C.

CONCLUSION

The optimal conditions for sulfuric acid hydrolysis of bamboo pulp carried out in order to obtain CNCs were found to be the following: sulfuric acid concentration of 60%, reaction temperature of 45 °C, reaction time of 90 minutes and solid-liquid ratio of 1:8. Under these conditions, the maximum CNC yield was reached – of 32.3%. Furthermore, the morphology, structure and thermal stability of the CNCs were investigated by TEM, FTIR and TG. TEM analysis indicated that the CNCs prepared by sulfuric acid could take two forms: as rods and a porous network. On the other hand, FTIR analysis demonstrated that the CNCs still maintained the basic chemical structure of cellulose. Finally, the TG analysis revealed that the thermal stability of the CNCs was lower than that of the bamboo pulp, and presented two degradation ranges: at 180~320 °C and 350~450 °C.

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