

# THE ROLE OF FORMIC ACID PRETREATMENT IN IMPROVING THE CARBOXYL CONTENT OF TEMPO-OXIDIZED CELLULOSE

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Received March 25, 2013

In this report, the application of formic acid pretreatment in oxidizing once-dried celluloses for the production of nanocellulose has been explored for the first time. Fully bleached softwood kraft pulp was pretreated with formic acid solution of various concentrations, and then it was oxidized with 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) system. Water-insoluble fractions of carboxyl cellulose (COC) were obtained and their carboxyl contents were between 0.981-1.769 mmol/g cellulose. The oxidized pulp, which had been pretreated with 5% (v/v) formic acid solution, had approximately 10% more carboxyls than the pulp without pretreatment. Moreover, this pretreatment process can be used accompanying other methods (such as NaClO<sub>2</sub> post-treatment, borax buffer and/or ultrasonic treatment) to improve carboxyl content of TEMPO-oxidized cellulose. Additionally, the oxidized fibers were converted into nanofibrils (3-7 nm in width and 300-400 nm in length) by homogenizing with a homogenizer.

**Keywords:** TEMPO, formic acid, pretreatment, native cellulose, carboxyl groups

## INTRODUCTION

Cellulose nanofibers or nanofibrillated cellulose (NFC), obtained by mechanical disintegration of cellulose fiber along their principal axis, are high aspect ratio fibers with diameters ranging from 3 to 100 nm, depending on their origin. Cellulose nanofibers or NFC have gained much attention for their potential uses as coatings, coating layers, and films. The most relevant and important properties that these materials exhibit are nontoxicity, biodegradability, large surface area and high strength, as well as film-forming capacity.<sup>1,2</sup> TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) mediated oxidation of the native cellulose has been found suitable for the production of nanocellulose.<sup>3-6</sup> When TEMPO/NaBr (sodium bromide)/NaClO (sodium hypochlorite) oxidation is applied to native celluloses in water at pH 10 and room temperature, the C6 primary hydroxyls exposed on the crystalline fibril surfaces are selectively oxidized to carboxyls.<sup>4,5,7-9</sup> These oxidized celluloses are fully disintegrated to individual nanofibrils, that is, TEMPO-oxidized cellulose nanofibrils (TOCNs), by mild mechanical

treatment in water.

During the alkaline TEMPO-catalyzed oxidation of native cellulose with the TEMPO/NaBr/NaClO system at pH 9-11, only the primary hydroxyl groups on the surface of cellulose crystals can be oxidized.<sup>5, 10</sup> Neither the crystalline type of cellulose, nor the width of the crystalline region is changed in the oxidation process. In addition, the oxidation process could increase the carboxyl content of cellulose, and as a consequence, would increase the hydrophilicity of cellulose.<sup>2,11</sup>

According to the research carried out so far,<sup>3,5,6,12</sup> the carboxyl groups introduced on the surface of the cellulose are very important to the preparation of cellulose nanofibrils. The created carboxyl groups on the surface of the cellulose render the nanofibrils very hydrophilic and easily separable due to the charge repulsion.<sup>3,12</sup> Several methods have been proposed to improve the carboxyl content of oxidized celluloses. Oxidation of celluloses using NaOCl/NaBr mediated by 2,2,6,6-tetramethyl-4-acetamidopiperidin-1-oxyl (4-acetamido-TEMPO) selectively converts the C6

primary hydroxyl alcohol groups into a C6 aldehyde intermediate to the C6 carboxyl group,<sup>13-16</sup> therefore, it can increase the carboxyl content of oxidized celluloses. In addition, the borax buffer with high ability of penetration could enhance the depth and width of oxidation. If a steady stream of sodium hypochlorite was added continuously with the increase of soaking time, a higher carboxyl group content would be obtained with borax buffer.<sup>2</sup> It was found that under acoustic cavitation, the efficiency of the TEMPO-mediation oxidation of native cellulose was significantly improved for a given reaction time.<sup>12,15</sup> Studies made by Mishra *et al.* indicate that the oxidation efficiency can be significantly improved by 15% to 30% increase in carboxyl content,<sup>3,12,17</sup> when the oxidation is conducted in the presence of ultrasonic cavitation.<sup>18</sup>

Organic acid pretreatment involves mainly a two-step degradation of hemicelluloses and disruptions of lignin followed by solvation of the fragments. Organic acid solvent dissociates partial hydrogen ions (H<sup>+</sup>) to accelerate delignification and hydrolysis of hemicelluloses, and it also dissolves the lignin fragments. Organic acid pretreatment increases the accessible surface area, solubilization of hemicelluloses, solubilization of lignin, and alteration of lignin structure.<sup>19,20</sup> As a cheap and readily available organic solvent, formic acid shows potential as a chemical agent for biomass fractionation.<sup>21,22</sup> The formic acid process is an effective alternative method for fractionating lignocellulosic materials to produce cellulosic pulp/other products.<sup>23-25</sup>

The formic acid is a carbonyl compound; hydrogen bonds are easily formed between the formic acid and cellulose molecules. Formic acid with 0.224 nm of intramolecular bond length can break through the limit to enter the inner space of cellulose crystalline region. Once the formic acid penetrates into the crystal lattice, the crystalline lattice of cellulose strongly swells. The hydrogen bonds between the chains of cellulose molecules are broken down, and the new hydrogen bonds between formic acid and cellulose molecules are formed. Eventually, the rigid framework of the crystalline lattice of cellulose is crushed.<sup>26</sup> Laura Kupiainen found that the crystallinity decreased in both pulp (wheat straw pulp) and MC (microcrystalline cellulose) during formic acid hydrolysis.<sup>27</sup>

According to the aforementioned advantages of formic acid treatment, it may have a positive effect

on the TEMPO-mediated oxidation of cellulose. The oxidation can be promoted, since formic acid treatment can destroy the crystal structure and increase the accessible surface area of cellulose. However, there is no report on the preparation of TEMPO-oxidized nanofibrils by formic acid pretreatment by now.

The objective of this study is to investigate the effect of formic acid pretreatment on TEMPO-mediated oxidation of cellulose. The carboxyl content and degree of polymerization calculated by viscosity measurement (DP<sub>v</sub>) of cellulose were determined, and the cellulose samples were characterized with Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM).

## EXPERIMENTAL

### Materials

A commercial softwood bleached kraft pulp (SBKP) was used as a source of native cellulose whose carboxyl content was 0.0478 mmol/g. Sodium hypochlorite (NaClO) solution ( $\geq 5.2\%$  active chlorine) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and assayed for its molar concentration before use. TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl radical, 97 wt%) was also purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All other chemicals were analytically pure (Sinopharm Chemical Reagent Co., Ltd., China) and used without further purification. All solutions were prepared with de-ionized water.

### Methods

#### *Pretreatment of bleached softwood kraft pulp (SBKP)*

The commercial SBKP was pre-soaked overnight in de-ionized water, and then condensed. About 25 g o.d. once-dried cellulose was added to 500 mL formic acid solution (2-18% (v/v)) and kept for about 24 h at room temperature. After fully washing with de-ionized water, the cellulose was condensed and stored at 4 °C to prevent any microbial attack).

#### *Preparation of TEMPO-oxidized cellulose fibers*

TEMPO-mediated oxidation was applied to 1% (w/v) cellulose fiber/water slurry at pH 10-10.2 and room temperature, with NaClO, TEMPO and NaBr, using a previously reported method.<sup>4</sup> In brief, the aforementioned pretreated cellulose fibers (about 5 g o.d.) were suspended in water (500 mL) containing TEMPO (0.1 g) and sodium bromide (1.0 g). Subsequently, a desired amount of the NaClO solution containing 4.8% available chlorine, corresponding to 0-7.6 mmol/g cellulose, was added slowly to the cellulose slurry under continuous stirring. The pH of the mixture was

maintained at 10-10.2 at room temperature, monitored with a pH stat by adjusting with dilute HCl and NaOH solution. The reaction was stopped after 6 h by adding ethanol (ca. 5 mL). The TEMPO-oxidized fiber suspension was filtered and washed thoroughly with de-ionized water on a filter cloth set in a Büchner funnel. The water-insoluble fractions thus obtained were then collected and kept at 4 °C to prevent from any microbial attack for further treatment and analysis. Similar TEMPO-mediated oxidations were performed in the absence of formic acid pretreatment.

#### **Mechanical fibrillation of TEMPO-oxidized celluloses**

The oxidized cellulose was suspended in water (150 mL) to provide a solid content of 0.1 wt%. The slurry was mechanically homogenized for 0.5-3 h at 15000 rpm with an IKA T25 digital ULTRA-TURRAX® (IKA® Works, Guangzhou). These oxidized celluloses were disintegrated into individual cellulose nanofibrils, *i.e.*, TEMPO-oxidized cellulose nanofibrils (TOCNs). The suspension was left for 24 h at 4 °C, and then the supernatant was subjected to TEM analyses.

#### **Determination of carboxyl content of oxidized cellulose fibers**

The carboxyl contents of the untreated and oxidized cellulose fibers were determined using the method according to TAPPI (TAPPI T237 cm-98, 2006). Pulp was extracted (de-ashed) with 0.1N hydrochloric acid for 120 min, fully washed and filtered. The pulp pad was quantitatively transferred to a tared 250-mL Erlenmeyer flask and weighed to the nearest 0.1 g. Then it was allowed to react with NaHCO<sub>3</sub>-NaCl solution for 60 min, and the mixture was filtered. The filtrate was titrated with 0.010 N hydrochloric acid to methyl red end point. The carboxyl content in milliequivalents (meq) per 100 g of oven-dry pulp was calculated:

Carboxyl, meq/100g

$$= [B - [A + (A \times C/50)]] \times N \times (200/W),$$

where: A = volume of 0.010N HCl consumed in titration of 25 mL of the pulp filtrate, mL

B = volume of 0.010N HCl consumed in titration of 25 mL of NaHCO<sub>3</sub>-NaCl solution, mL

C = weight of water in the pulp pad minus oven dry weight of test specimen, g

N = normality of HCl used in titration

W = weight of oven-dry test specimen, g

50 = volume of sodium bicarbonate-sodium chloride solution added to the test specimen, mL

200 = derived as 2 × 100, where 2 is a factor to account for 25 mL aliquot taken for titration, and 100 is to express the result on 100 g of pulp

#### **Weight recovery ratio**

The water-insoluble fractions of oxidized cellulose obtained were collected and a specimen was weighed out

for moisture determination. Then, the weight of the water-insoluble fractions was determined. The weight recovery ratio was calculated according to the following formula:

Weight recovery ratio = (W2 / W1) × 100%, where

W1 = initial weight specimen before oxidation, g

W2 = weight of water-insoluble fractions, g

#### **Viscosity-average DP (DP<sub>v</sub>) measurement**

Intrinsic viscosities of the water-insoluble fraction were obtained by a capillary viscometer using 0.5M cupriethylene diamine (CED) as a solvent. These values were converted to DP<sub>v</sub> values by the reported method.<sup>4,28</sup>

#### **Scanning Electron Microscopy (SEM) of fibers**

The due test specimen was dispersed in distilled water and filtered on a filtering funnel to get a cellulose pad. The cellulose pad was dried under vacuum at 50 °C. The dried cellulose pads were observed with a Scanning Electron Microscopy (HITACHI SU1510, Japan). It operated at 5 kV.

#### **Transmission Electron Microscopy (TEM) of cellulose nanofibrils**

A drop of 0.1 wt% TOCNs dispersion was dropped onto a carbon-coated copper grid. The copper grid was left to stand for drying. The sample grid was observed with a JEOL JEM-2100(HR) microscope operated at an accelerating voltage of 200 kV.

## **RESULTS AND DISCUSSION**

### **Effect of formic acid (HCOOH) pretreatment on the carboxyl content, weight recovery and DP<sub>v</sub> of the pulp**

The original cellulose and HCOOH (5%, v/v) pretreated cellulose were TEMPO-oxidized with 4.5 and 7.6 mmol NaClO/g pulp, respectively. The amount of NaClO used in TEMPO-oxidation was in the range of 1.0-10.0 mmol/g pulp, as reported by most researchers. An overview of the results is presented in Table 1. It is apparent that the carboxyl content and DP<sub>v</sub> of pretreated cellulose are higher than those of their counterparts without pretreatment, and the residual weight of oxidized cellulose decreased when cellulose was pretreated with formic acid. The increase of DP<sub>v</sub> and decrease of residual weight of the oxidized cellulose may be explained by the degradation of hemicelluloses and disruptions of lignin followed by solvation of the fragments.<sup>19,20,26</sup> The difference in carboxyl content could be attributed to crystallinity. Crystallinity affected microstructures, chemical process, and the oxidation efficiency; fibers with lower crystallinity showed higher reactivity.<sup>29</sup> The rigid framework of

the crystalline lattice of cellulose is crushed when it is pretreated with formic acid and the pretreatment increases the accessible surface area of cellulose, which has been confirmed with Fourier transform infrared spectroscopy (FTIR) spectra by Sun *et al.*<sup>26</sup> Therefore, more hydroxyl groups were oxidized and converted into carboxyl groups.

### Effect of formic acid concentration on carboxyl contents of oxidized cellulose

It is well known that the pulp yield, residual lignin and hemicelluloses were decreased, when formic acid concentration increased.<sup>23,24,30</sup> Our experiments were done at 2, 5, 9, 15, 18% (HCOOH, v/v), while keeping the other conditions constant, to find out the effect of formic acid concentration on the carboxyl contents of oxidized cellulose. The dosage of NaClO was 4.5 mmol/g pulp. The carboxyl content of the oxidized cellulose is plotted as a function of HCOOH concentration, as shown in Fig. 1. The carboxyl content increased with the increase in formic acid concentration up to 5% (v/v) and then decreased. The variation of carboxyl content could be related to the balance of dissolution of amorphous cellulose constituents and

disruption of crystal regions during the course of pretreatment. When the concentration of formic acid was lower, the primary process was the dissolution of the amorphous cellulose constituents. In this case, the accessible area was reduced, leading to lower carboxyl content. Then, in the case of a bit higher concentration, the disruption of the crystal regions increased the accessible surface area of cellulose. Therefore, more hydroxyl groups were oxidized and converted into carboxyl groups. However, as the concentration of formic acid became higher and higher, the disruption of crystal regions was severe, so that more and more fines and fibers departed from the cellulose bundles. In addition, most detached fines and fibers dissolved in the solution and this resulted in the decrease of the carboxyl content, which can be demonstrated by the SEM images. The carboxyl content increased again when the HCOOH dosage exceeded 9%. The reason may be that relatively higher ratios of crystal regions in cellulose were disrupted during the pretreatment.

Table 1  
Carboxyl content, weight recovery and DP<sub>v</sub> of the pulp

Parameter	Amount of NaClO/(mmol·g <sup>-1</sup> ) fiber	Carboxyl content/(mmol·g <sup>-1</sup> ) fiber	Weight recovery/%	DP <sub>v</sub>
Original cellulose	4.5	1.100	94.27	149
HCOOH (5%, v/v)	7.6	1.588	84.94	132
pretreated cellulose	4.5	1.295	93.06	169
	7.6	1.769	79.73	134

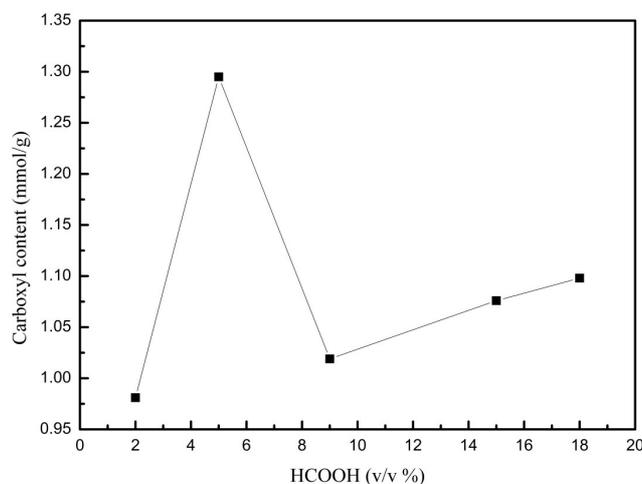


Figure 1: Effect of formic acid concentration on carboxyl contents of oxidized cellulose (the amount of NaClO was 4.5 mmol/g pulp)

### Effect of NaClO consumption on carboxyl contents of oxidized cellulose

It could be seen from Table 2 that a linear relationship existed between the consumption of NaClO and the carboxyl content of oxidized cellulose. Table 2 also shows that the yield decreased with increasing consumption of NaClO in all cases. A reason could be the depolymerization of cellulose and dissolution of the oxidized moieties with the increase of the amount of NaClO. Another possible reason could be the dissolution of the amorphous, non-cellulosic constituents (hemicellulose, pectins, and lignins) during the TEMPO-mediated oxidation. The DP<sub>v</sub> of the TEMPO oxidized pulps decreased with the increase in the NaClO dosage; however, there was no significant difference in the DP<sub>v</sub> of the oxidized pulps in the case of 4.5 mmol/g and 5.8 mmol/g. The depolymerization of polysaccharides having glucuronic acid may occur to some extent by  $\beta$ -elimination during the TEMPO-mediated oxidation under alkaline conditions, e.g. pH 10.0 here. However, besides the above mentioned reasons, the depolymerization of the cellulose has also been attributed to the sodium hypochlorite oxidation of polysaccharides, leading to 2,3-scission of glucose units resulting in the formation of aldehyde and dicarboxylic structures.<sup>12</sup>

### SEM analysis

The SEM images of the fibers are shown in Fig. 2. Frames (a) through (d) show how the fiber morphology changed during formic acid treatment. The fiber surfaces without any treatment were nearly smooth, as shown in SEM image (a). After 5% (v/v) formic acid pretreatment, the fiber surface appeared to have lots of fines, which began to be

liberated from the surface of fragments. It may be attributed to the degradation of hemicelluloses and disruptions of lignin followed by solvations of the fragments<sup>19</sup> and the dissolution of cellulose fragments (fines and amorphous cellulose). As can be seen from images (b), (c) and (d), the fines decreased, while the concentration of formic acid increased. In fact, more and more fines are actually liberated from the surface of cellulose as the formic acid concentration increases. But, hemicellulose, lignin and cellulose fragments are much more likely to dissolve when using a higher concentration of formic acid solution. Therefore, it seems like fines are reduced. In Figure 2 (e), the fibers were oxidized with TEMPO. It can be seen that the long fibers break into fragments. The TEMPO system selectively oxidizes C6 primary hydroxyl groups to carboxyl groups, and it is reasonable that it reacts with C6 groups of cellulose on the surface and in the amorphous regions of fibers.<sup>7</sup> As the carboxyl content was increased to a certain amount, cellulose began to disperse in aqueous solution. However, the crystalline region remained intact and, therefore, was liberated as cellulose fibers.<sup>31</sup>

### TEM analysis

Oxidized fibers were converted into nanofibrils by homogenizing a 0.1 wt% fiber suspension for 0.5-3 h at 15000 rpm with an IKA T25 homogenizer. Almost all the fibers were converted into nanofibrils during homogenization. Fig. 3. shows TEM-images of nanofibrils prepared from 5% (v/v) formic acid pretreated cellulose after 4.5 mmol NaClO/g cellulose treatment. It can be seen from the picture that the nanofibrils had a good individualization with widths of 3-7 nm and lengths of 300-400 nm.

Table 2  
Effect of NaClO consumption on the carboxyl content, weight recovery and DP<sub>v</sub> of the pulp

5% (v/v) HCOOH pretreated sample	Amount of NaClO/(mmol·g <sup>-1</sup> ) fiber	Carboxyl content/(mmol·g <sup>-1</sup> ) fiber	Weight recovery/%	DP <sub>v</sub>
1	4.5	1.295	93.06	169
2	5.8	1.340	88.80	163
3	7.6	1.769	79.73	134

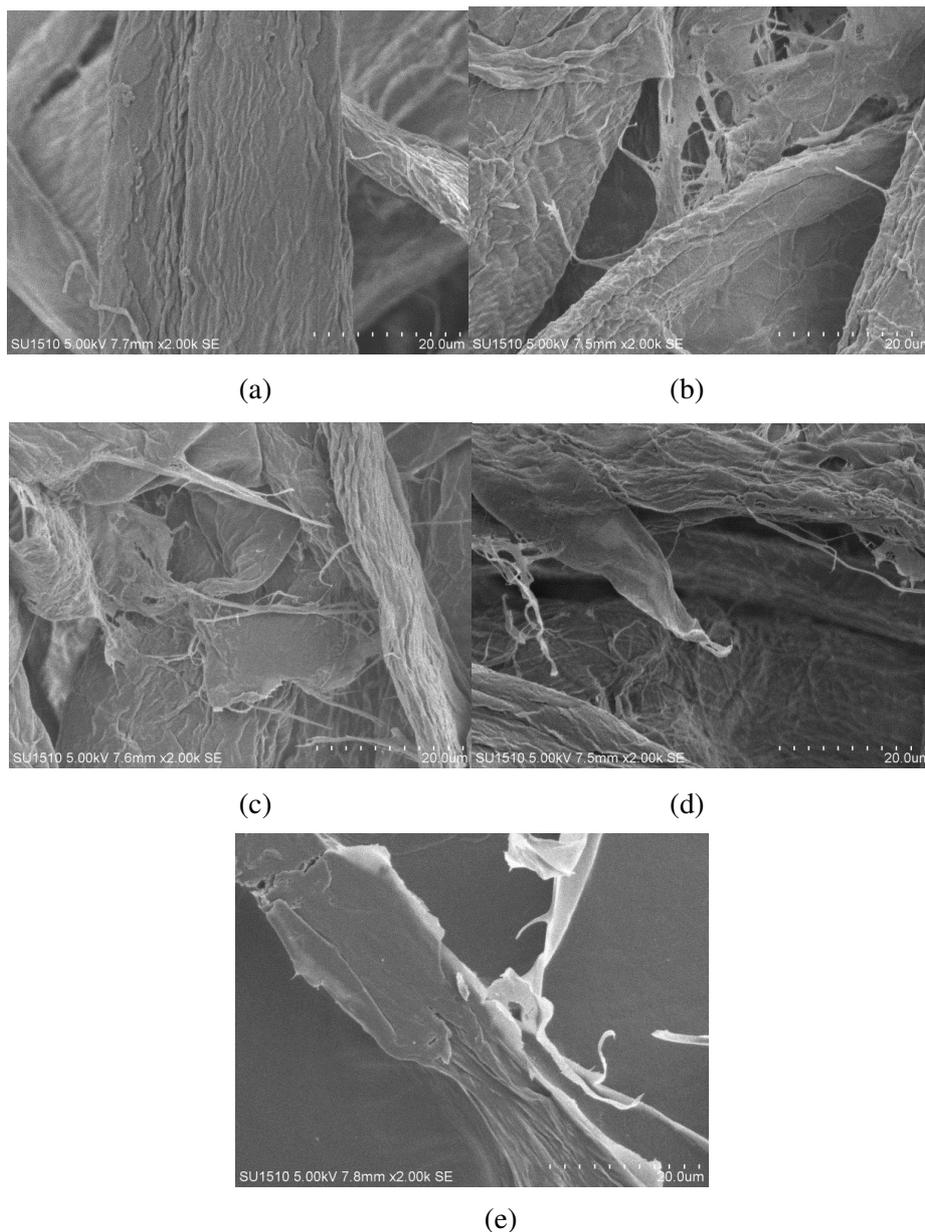


Figure 2: SEM images of cellulose fibers with different conditions of treatment; (a) original cellulose; (b) pretreated with 5% (v/v) HCOOH solution; (c) pretreated with 9% (v/v) HCOOH solution; (d) pretreated with 18% (v/v) HCOOH solution; (e) oxidized cellulose fibers

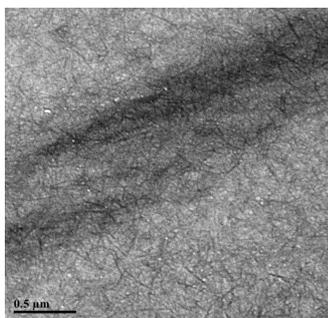


Figure 3: TEM image of oxidized cellulose



Figure 4: Appearance of cellulose nanofibril suspensions; (A) 0.1 wt%; (B) 0.2 wt%

As shown in Fig. 4, the two beakers contained the solution of TEMPO-oxidized cellulose that was treated with a homogenizer at 15000 rpm for 3 h, whose carboxyl content was 1.295 mmol/g. Beaker A contained 0.1 wt% solution and beaker B – 0.2 wt%. The solution in beaker A was well-dispersed and transparent. The solution concentration in beaker B is thicker than in beaker A, and it was shown that the oxidized fibers could not be completely dispersed in water. Although a substantial mass of cellulose fibrils was liberated from the cellulose fibers, there were still plenty of cellulose fibers that had been only partially destroyed or slightly changed in morphology and a few big fragments still remained, so that beaker B was not so transparent as beaker A.<sup>31</sup>

## CONCLUSION

TEMPO-mediated oxidation, combined with a formic acid pretreatment, was used to effectively produce cellulose nanofibrils. The formic acid pretreatment can facilitate the oxidation of native cellulose for the production of nanocellulose and it gave an approximately 10% increase in carboxyl content. The concentration of formic acid solution in the pretreatment has a significant effect on the carboxyl content of oxidized cellulose. In this study, the optimal concentration of formic acid was 5% (v/v) and the highest carboxyl content of oxidized cellulose was 1.769 mmol/g. The oxidized fibers were converted into nanofibrils (3-7 nm in width and 300-400 nm in length) by homogenizing with a homogenizer.

**ACKNOWLEDGMENTS:** The authors are thankful to the National Natural Science Foundation of China (No. 31270633) and the Priority Academic Program Development of Jiangsu Higher Education Institutions for their financial support.

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