PREPARATION OF ULTRASONIC-ASSISTED HIGH CARBOXYLATE CONTENT CELLULOSE NANOCRYSTALS BY TEMPO OXIDATION

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Cotton linter pulp was oxidized in the TEMPO-NaBr-NaClO system with ultrasonic treatment, and cellulose nanocrystals having high carboxylate content were produced directly. Results showed that the C6 primary hydroxyl group of cellulose fiber was converted to the carboxylate group, whose amount could be up to 1.66 mmol/g. During the oxidizing reaction, some of the amorphous region in the cellulose fiber was modified and gradually hydrolyzed, but the crystalline region still remained. It was also shown by TEM (Transmission electron microscopy) that the widths of cellulose nanocrystals were approximately 5-10 nm, and the lengths were approximately 100-400 nm. The high carboxylate content cellulose nanocrystals could be produced in one step by this method, yielding a stable and well dispersed aqueous suspension.

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INTRODUCTION

Cellulose nanocrystals have attracted great attention in recent years because of their great potential in a broad range of applications (Hubbe et al. 2008). Cellulose nanocrystals are the elementary assemblies of glucopyranose polymeric chain fibrils, being 3 to 20 nm in width, and having lengths from 100 nm to several micrometers. But their overall size, shape, and specific dimensions depend heavily on the preparation conditions of the cellulose nanocrystals and the cellulosic source materials (Beck et al. 2005). Generally, cellulose nanocrystals are produced by acid hydrolysis of the amorphous region of cellulose followed by the conversion of the remaining crystalline region by mechanical or other means to nanocrystals (Habibi et al. 2010).

Cellulose is a natural polymer composed of β-D-glucopyranose units that are linked together by (1→4)-glycosidic bonds. A cellulose molecular chain, depending on the source of the cellulose, consists of 300 to 15000 D-glucose units. The unit has three hydroxyl groups on C2, C3, and C6, respectively, and the hydroxyl group of C6 is much more reactive than that of C2 and C3. TEMPO (2,2,6,6-tetramethyl-piperidine-N-oxyl) is a stable nitroxide radical, which can catalytically oxidize primary and secondary alcohols under aqueous condition with high selectivity and efficiency (Wight and Davis 2000; Sheldon et al. 2002). Recently, TEMPO-mediated oxidation was applied to cellulose fibers under various conditions (Tahiri and Vignon 2000; Saito et al 2009). It was also reported that cotton linters were hydrolysed by hydrochloric acid, then the hydrolyzate

was oxidized by the TEMPO-mediated oxidation, finally yielding carboxylated cellulose nanocrystals (Montanari et al. 2005).

Ultrasonic technology has been widely applied in chemical processes. For example, ultrasonic treatment has been used for degradation of polymers, the synthesis of inorganic or organic compounds, and the catalytic acceleration of reactions (Kawasaki et al. 2007; Toukoniitty et al. 2005). Ultrasonication in the solution can give rise to cavitations and micro-bubbles (Suslick et al. 1986). Micro-bubbles collapse in very short times, releasing high energy, which is converted to heat and high pressure in the local area.

In this paper, TEMPO oxidation and ultrasonic treatment were employed to prepare cellulose nanocrystals having high carboxylate content from cotton linter pulp.

EXPERIMENTAL

Materials

Cotton linter pulp (from Anhui Xuelong Pulp Mill, China) was used as the cellulose source fiber. The 2,2,6,6-tetramethyl-pipelidine-1-oxyl (TEMPO, Changzhou JiaNa Chemical Co. Ltd, China), sodium bromide (Sinopharm Chemical Reagent Co. Ltd, China), 8.6% sodium hypochlorite solution (Shanghai Jiuyi Chemical Co. Ltd, China, as weight/volume), and other chemicals were used without further purification. An ultrasonic cleaner (KQ-300DE, Kunshan Ultrasound Instrument Co. Ltd, China) was used as an ultrasonic generator with frequency of 40kHz and 300 Watts; its volume was 10 L.

TEMPO Oxidation with and without Ultrasonic Treatment

TEMPO oxidation with ultrasonic treatment

Cotton linter pulp (3 g) was dispersed in distillated water (500 mL) with TEMPO (0.048 g, 0.3 mmol) and sodium bromide (0.48 g, 4.8 mmol). Then, 30 mL of sodium hypochlorite solution was added, and the pH was adjusted to 10 by 0.5 M hydrochloric acid. The mixtures was then poured into a four-neck flask, and dipped into the trough of an ultrasonic cleaner. The reaction was initiated by setting the power of the ultrasonic cleaner at 100%. Circulating cooling water was used to maintain the reaction at $25^{o}C$ temperature. The pH was maintained at 10 by adding 0.5 M sodium hydroxide solution. After the oxidation, the pH of the solution was adjusted to 7 by adding 0.5M hydrochloric acid and separated by centrifugation at 12,000 rpm. The precipitate was dispersed in distilled water and centrifuged three times to remove superfluous acid, inorganic salt, and TEMPO, respectively. The oxidized fibers were freeze-dried.

TEMPO oxidation with post-treatment

The cotton linter pulp (3 g) was oxidized by TEMPO (0.048 g, 0.3 mmol), sodium bromide (0.48 g, 4.8 mmol), and 30 mL of sodium hypochlorite solution in 500 mL water, and kept at 25 ^{o}C temperature for 24 hrs without ultrasonication. After oxidation, the oxidized cellulose fibers were filtered and washed three times. The oxidized fibers were freeze-dried.

As the post treatment, the 0.1 g of the oxidized fibers were dispersed into 100 mL water either with a homogenizer at 10,000 rpm or with ultrasonic treatment for 1 hr.

Scanning Electron Microscopy (SEM) of Fibers and Oxidized Fibers

The untreated cotton linter and the oxidized cellulose fibers were observed with an ESEM (Quanta 200 environmental scanning electron microscopy FEI, Netherlands). The operated voltage was 20 kV, and the current changed with the vacuum of the observed circumstance.

Determination of Carboxyl Content of Oxidized Cellulose Fibers

The carboxyl content of the oxidized cellulose fibers was determined by the electrical conductivity titration method (Shi et al. 2009). A sample (3 g) was soaked twice in 100 mL of 0.1M hydrochloric acid, then washed with de-ionized water until the electrical conductance didn't change. After washing, the sample was dispersed in 450 mL 0.001M sodium chloride solution, and titrated by 0.1M sodium hydroxide under a blanket of nitrogen in the presence of magnetic stirring. The pH was determined by pH meter (PHS-25 Shanghai Precision & Scientific Instrument Co. LTD., China). The total content of the oxidized cellulose fibers was calculated according to Eq (1),

$$\text{The carboxylate content (mmol/g)} = \frac{\text{Vright(L) - V left (L)}}{\text{Weight of the sample (g)}} \times \text{the concentration of NaOH} \times 1000 \tag{1}$$

where V_{right} and V_{left} are the consumed volume of NaOH solution at the right and left isoelectric point, respectively.

The content of sodium hypochlorite was determined by the iodometric method (Shi et al. 2009). 5 mL of the processed solution was added to a 250 mL conical beaker, then reacted with 100 mL of 100 g/L potassium iodide solution and 20 mL of 20% (w/v) acetic acid, and titrated by 0.1 M sodium thiosulfate solution, respectively. The content of sodium hypochlorite was calculated according to following formula (2) (Fig. 2),

$$\text{The content of available chlorine(g/L)} = \frac{V(mL) \times c \ (mol/L) \times 0.0355(g/mmol)}{5mL} \times 1000 \tag{2}$$

where V is the consumed volume of sodium thiosulfate solution and c is the molar concentration of sodium thiosulfate solution.

Crystallinity Determination by X-Ray Diffraction (XRD)

Each sample was filled into the sample holder. The sample holder was loaded onto the X-ray diffractor (DX-2000 Dandong Fangyuan Instrument Co. LTD., China) to analyze from 10° to 40° 2θ with data acquisition taken at $0.04°\cdot s^{-1}$ by the reflection method. The operated voltage was 35kV and the current was 25mA. The crystallinity was calculated according to the following formula (Table 2):

$$\text{Relative crystallinity} = (\,I_{crystalline} - I_{amorphous}\,) \times 100\% \,/\, I_{crystalline} \qquad (3)$$

where $I_{crystalline}$ was identified with the intensity at 22.5^o, and $I_{amorphous}$ was the intensity at 18.6.

Transmission Electron Microscopy (TEM) of Cellulose Nanocrystals

Cellulose nanocrystals were examined by transmission electron microscopy (JEM-1011 JEOL, Japan). The suspension was sampled by using a capillary pipet and dropped onto the copper grid. After being dried for 3 min at ambient condition, filter paper was used to remove the excess liquid on the copper grid. Afterwards, the dye liquor of phosphotungstic acid was dropped and dyed for 2 min. The dried sample was prepared for observed. The operated voltage was at 100 kV.

RESULTS AND DISCUSSION

TEMPO Oxidation of Cotton Linter Pulp with and without Ultrasonic System

The cotton linter pulps were oxidized by TEMPO with and without ultrasonic treatment. The SEM images of fibers are shown in Fig. 1. Frames (a) through (d) show how the fiber morphology changed during oxidation. The surfaces of linter fibers without any treatment were smooth and long fibers, as shown in SEM image (a). After 1hr of oxidation, the fiber surface appeared to have lots of fine pits and plaques, but the length of the fiber did not change. After 2 hrs of oxidation, deep pits were observed, and some fine particles were found to be stripped off the surface gradually. Even though the length of fiber remained stable, the widths of fiber decreased slightly. When the reaction time increased to 3h, the long fibers started to break into fragments, and some nano-size fibers could be found, which began to be liberated from the surface of fragments.

(a)

(b)

(c)

(d)

(e)

(f)
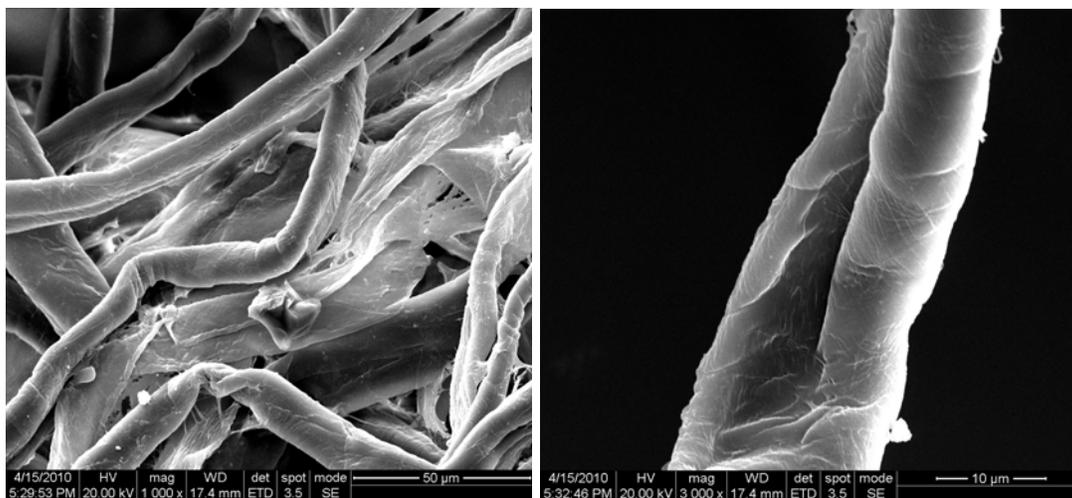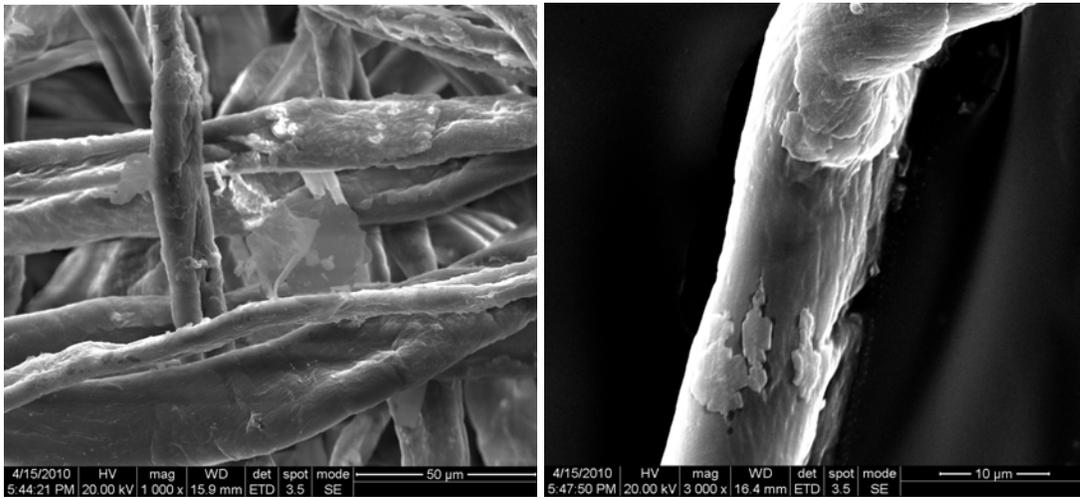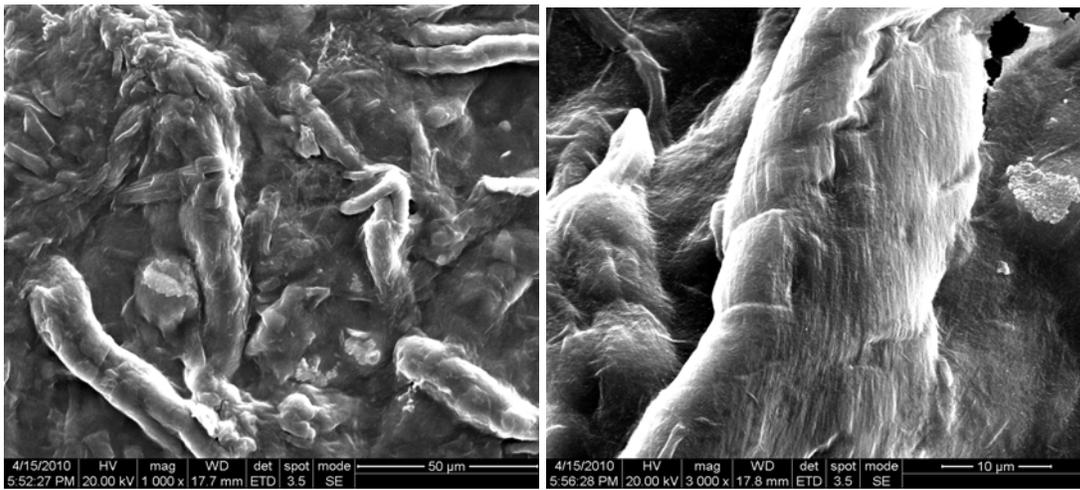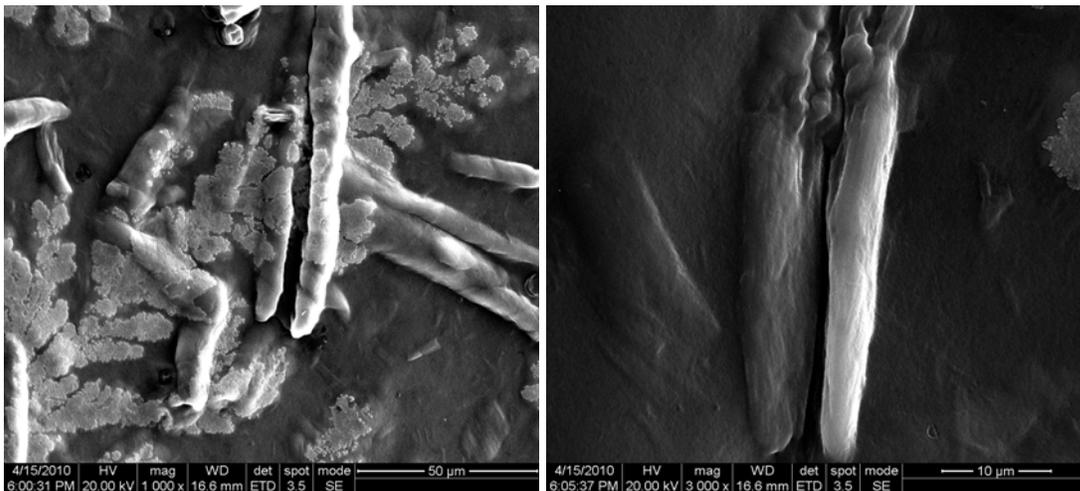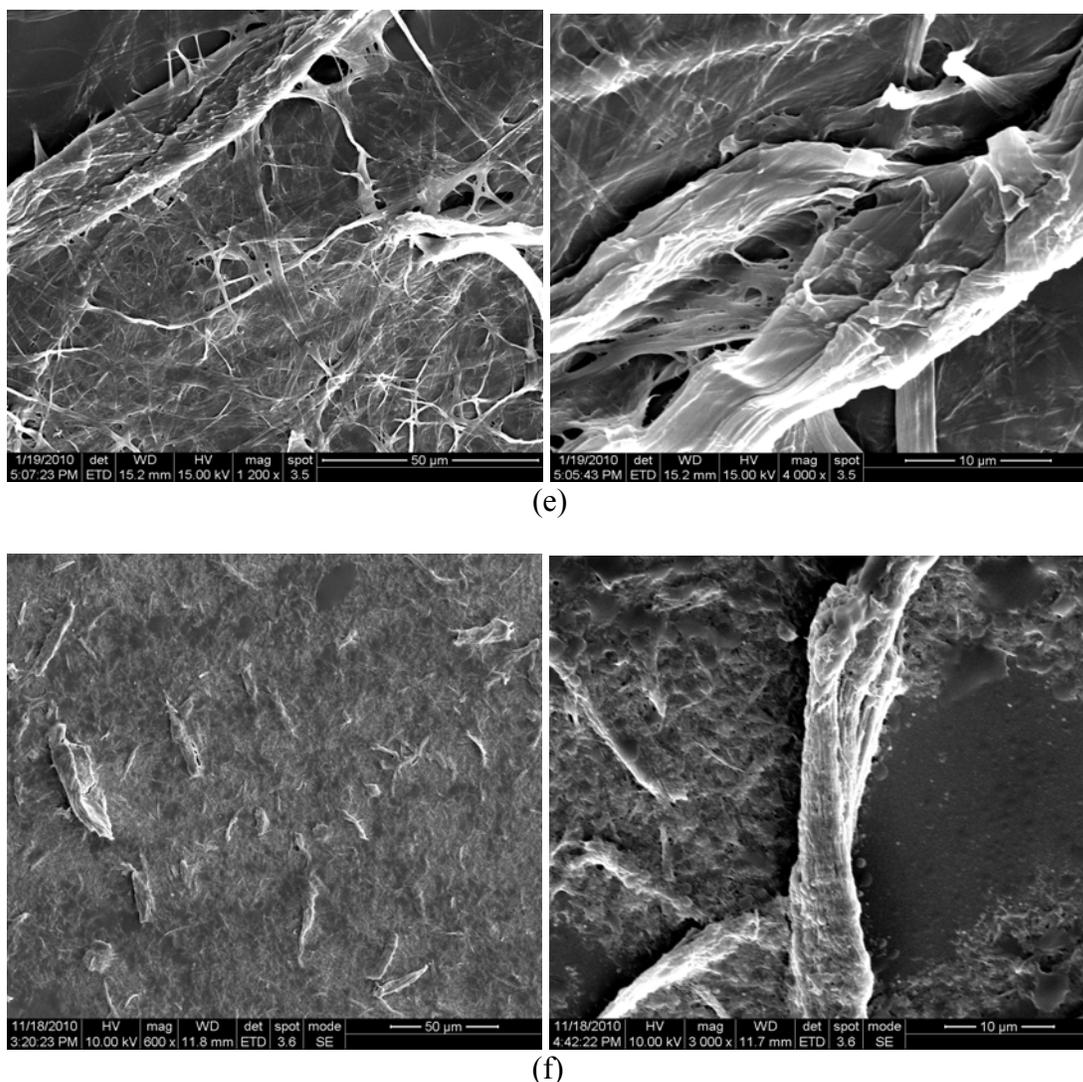
Fig. 1. SEM Images of cellulose fibrils with different reaction time under the conditions of the TEMPO oxidation with ultrasound system (a) 0h, (b) 2h, (c) 3h, (d) 4h, after which the oxidized cellulose fibrils were treated by the homogenizer (e) or ultrasonic treatment (f) for 1h after the TEMPO oxidation without ultrasound system.

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 amorphous regions of fibers (Montanari et al. 2005). As the carboxyl content was increased to a certain amount, cellulose began to disperse in aqueous solution. But the crystalline region remained intact and therefore was liberated as cellulose fibers. When fibers were oxidized for 4 hrs, only a few fragments could be observed, since the most of them had been liberated as nano-size crystals. It was difficult to find fragments of fibers after 5 hrs TEMPO oxidation with the ultrasonic treatment.

In Fig. 1(e), the fiber was TEMPO oxidized without ultrasonic treatment for 24 hrs and then was treated by homogenizer at 10,000 rpm for 1 hr. In Fig. 1(f), the fiber was TEMPO oxidized without ultrasonic treatment for 24 hrs, then treated with ultrasonic energy for 1hr after TEMPO oxidation. It was clearly shown that the oxidized fibers with

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homogenizer treatment were able to maintain their length as fibers, and they were easily dispersed to achieve narrower width. The ultrasonic treatment with oxidized fiber was able to separate the fiber into fines and fragments. But it could not disperse the fiber completely in the aqueous suspension.

The carboxyl groups of oxidized fibers were determined by the electrical conductance titration method, and results are shown in Fig. 2. The carboxyl content and NaClO consumption are shown vs. reaction duration. After 2 hrs of oxidation, the carboxyl content increased from 0 mmol/g to 1.1 mmol/g, and 1 g cellulose consumed 7 mmol of NaClO. The carboxyl content increased up to 1.66 mmol/g after 12 hrs of oxide-tion. From 2 hrs to 13.5 hrs, each gram of cellulose consumed only 4.6 mmol NaClO, and the production of 1 mole of carboxylate groups corresponded to about 7 mole of NaClO consumption. Fig. 2(b) shows that the carboxyl content was lower when TEMPO oxidation was carried out without ultrasonic system. The carboxyl content increased from 0 mmol/g to nearly 1 mmol/g after 3 hrs oxidation, but the carboxyl content increased only 0.1 mmol/g from 8 hrs to 24 hrs oxidation. The carboxyl content of TEMPO oxidized fiber without ultrasonic system reached only 1.1 mmol/g after 24 hrs.
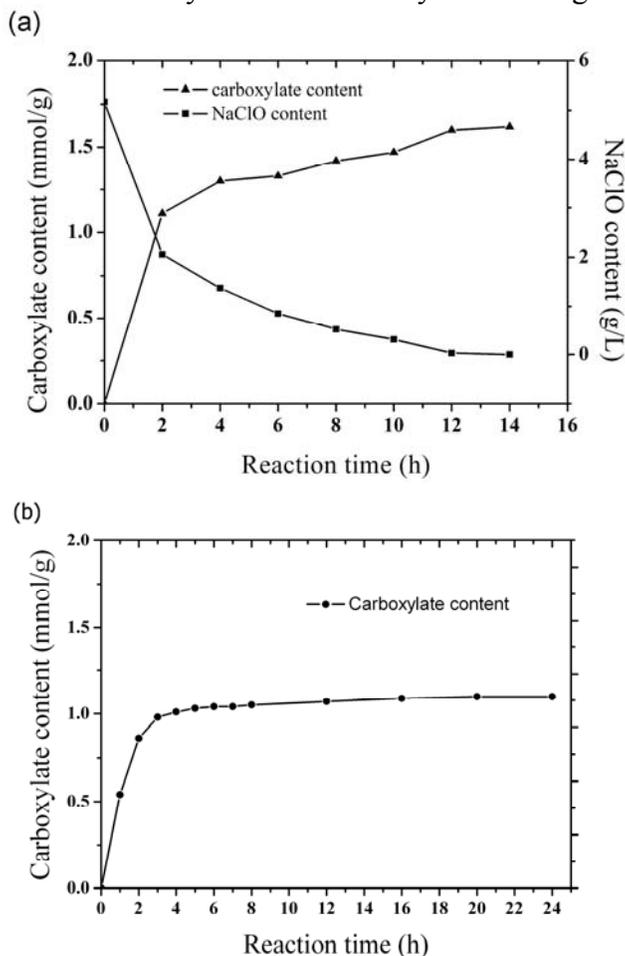
Fig. 2. (a) Contents of carboxylate and sodium hypochlorite in the mixtures vs. reaction time. (Reaction was carried out by TEMPO-NaBr-NaClO oxidation under the condition of ultrasonic cleaner, working frequency 40kHz). (b) The relationship of the carboxylate content and the reaction time when cotton linter was oxidized by the TEMPO oxidation without ultrasound system.

Noting that the cotton linter fiber had very high crystallinity, most of the TEMPO oxidation can be expected to have taken place on the surface of fibers. The ultrasound could help to destroy the surface of oxidized fiber to increase the interfacial area accessible to the reagents and cellulose fibers. Based on Fig. 1(b)-(d), the C6 primary hydroxyl groups of the cellulose surface was easily oxidized, and the long cellulose fibers were slightly oxidized at the early reaction stage and then rapidly broken down into the small particles. Consequently, specific surface areas of these particles were larger than before, which raised the reaction probability of the C6 primary hydroxyl groups with TEMPO oxidation. As a result, the ultrasonic system could help to promote oxidation of fibers during the TEMPO treatment.

Change of Crystallinity of Cellulose during TEMPO Oxidation

As shown in Fig. 3 and Table 1, the crystallinity of cotton linter fibers was different before and after TEMPO oxidation with ultrasonic treatment. During the oxidation process, the crystallinity of cotton linter showed an increasing trend. The micro-jet generated by ultrasonic cavitation damaged the surface of cellulose, and fibrillation was generated; hence the surface area was increased, leading to an acceleration in the oxidization reaction. At the same time, the process of degradation also would be accelerated, especially in the amorphous regions of cellulose fibers; on the other hand, the amorphous cellulose also was hydrolyzed and the crystalline material remained (Filson et al. 2009). Consequently, it was concluded that the crystallinity of the cellulose slightly increased during the reaction.
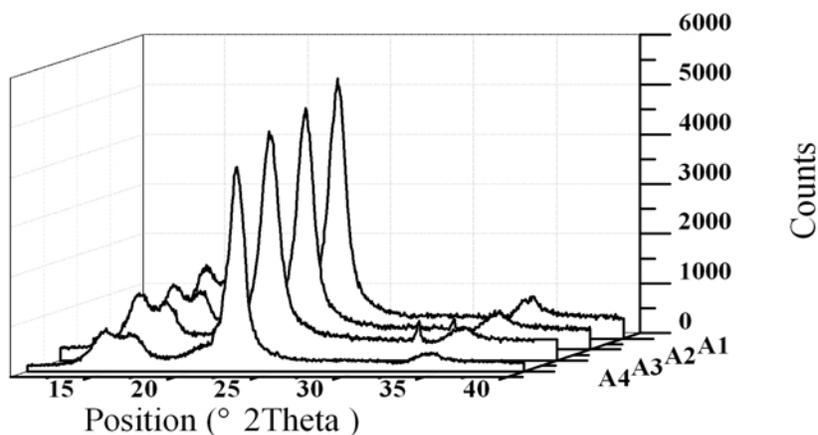
Fig. 3. X-ray diffraction patterns of the original cotton linter (A1), and oxidized cellulose by the TEMPO oxidation with ultrasonic system for 2h (A2), 8h (A3), and 13.5h (A4), respectively

Table 1. Crystallinity of Cellulose Fibers

Sample	A1	A2	A3	A4
Crystallinity, %	83.66	83.78	84.03	84.12

Transmission Electron Microscope(TEM) Images of Cellulose Nanocrystals

TEM images of the cellulose nanocrystals are shown in Fig. 4. The appearance of the cellulose nanocrystals is shown in the case of dilute samples (diluted to 0.1%) prepared after 13.5 hrs of TEMPO oxidation with the ultrasonic system.
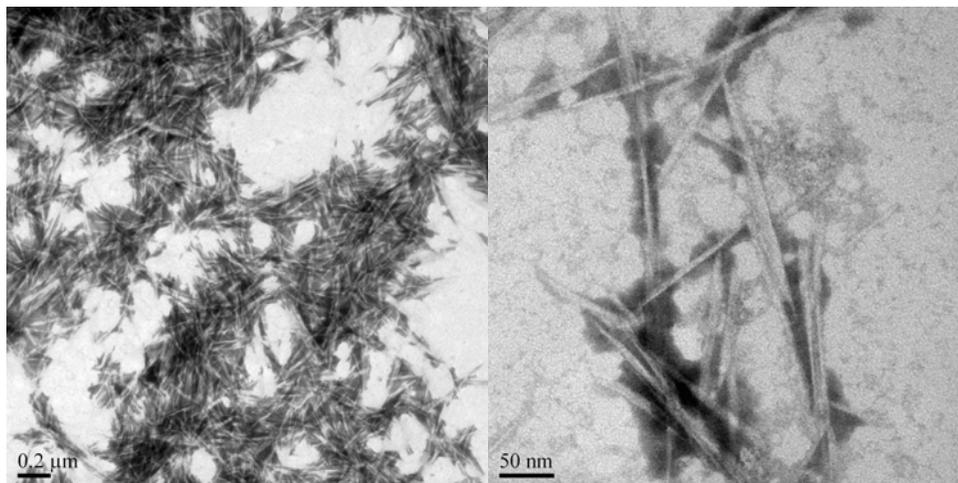
Fig. 4. TEM images of the cellulose nanocrystals

Fig. 5. Appearance images of cellulose nanocrystal suspensions after oxidation (A) and dilution to 0.1%; (B), the oxidized fibers (the water-ratio of that was 0.1%); after treatment by the homogenizer (C) and ultrasound (D)

As shown in Fig. 5 (A) and (B). the bottle A contained the solution obtained directly after reaction, since the cellulose nanocrystals were too concentrated and they trended to aggregate because of their ultra high surface area; bottle B contained solution that was diluted to 0.1% from the original solution (bottle A) and whose carboxyl content was 1.66 mmol/g. It was well-dispersed, transparent, and light blue in color. Bottle C contained cotton linter fiber that had been oxidized by the TEMPO without ultrasonic system for 24 hrs, then treated with a homogenizer at 10,000 rpm for 1hr. 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, so many of the oxidized fibers ended up deposited on the bottom of bottle C. After the oxidized fibers were treated by ultrasound for 1 hr, a few big fragments still remained, so that the bottle D was non-transparent. (Fig. 5 D). From the images in Fig. 4, the cellulose nanocrystals were the 5 to 10 nm in width and 200 to 400 nm in length. With ultrasonic assistance, the oxidized cellulose nanocrystals could plenty of hydrophilic carboxylic groups and its content could approach 1.66 mmol/g. The H-bonds will be formed between the carboxylic groups and surrounding H_2O molecules, which provide more stability for the cellulose nanocrystals and allow them to be well-dispersed in the aqueous solution. Another reason was that cellulose nanocrystal carried a substantial amount of negatively charged carboxylic groups, which could help them to remain in suspension as colloids.

CONCLUSIONS

1. High carboxylic acid content nanocrystals were produced by direct ultrasonic-assisted TEMPO oxidation of cotton linter pulp.
2. A high carboxyl acid content, 1.66 mml/g, of nanocrystals was achieved.
3. The width and length of the cellulose nanocrystals were 5 to 10 nm and 200 to 400 nm, respectively.
4. The nanocrystals produced were stable in water.

ACKNOWLEDGMENTS

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