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Extraction and comparison of carboxylated cellulose nanocrystals from bleached sugarcane bagasse pulp using two different oxidation methods

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ABSTRACT

Two kinds of carboxylated cellulose nanocrystals (CCNs) were prepared by using ultrasonic assisted 2,2,6,6-tetramethylpiperidinyl-1-oxy radical (TEMPO) mediated oxidation and one-step ammonium persulfate (APS) oxidation, which were denoted as TEMPO-oxidized CCNs (TO-CCNs) and APS-oxidized CCNs (AO-CCNs), respectively. The effects of oxidant content on the yield, carboxyl content, degree of polymerization (DPv) and morphology of the oxidized celluloses in the two oxidation methods were studied. Furthermore, the chemical structure, crystallinity and thermal stability of TO-CCNs and AO-CCNs were evaluated and compared by Fourier transformed infrared spectra, X-ray diffraction and thermogravimetric analyses. The results showed that with increase of oxidant content in the two methods, the carboxyl groups on the surfaces of TO-CCNs and AO-CCNs were both improved. And a remarkable decline of the DPv of cellulose sample also appeared in the two oxidative treatments. In addition, AO-CCNs exhibited a higher crystallinity and an enhanced thermal stability compared with TO-CCNs.

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1. Introduction

Cellulose, as the most abundant natural polymer on the earth, has attracted intense interest for use as a renewable carbon resource (Jonoobi et al., 2015; Rafieian & Simonsen, 2014). It is a biodegradable and biocompatible material, which could be obtained from plants, bacteria, algae and even animals (Moon, Martini, Nairn, Simonsen, & Youngblood, 2011; Tingaut, Zimmermann, & Sebe, 2012). Within the family of cellulose derivatives, cellulose nanocrystals (CNs) are particularly attractive due to their unique and appealing features: excellent mechanical properties (Young's modulus of 100–140 GPa and tensile strength of 1.7 GPa) (Chen, Yu, Li, Liu, & Li, 2011), high aspect ratios (3–30 nm in diameter and several micrometres in length) (Leung, Lam, Chong, Hrapovic, & Luong, 2013), high surface reactivity, low density (1.45 g/cm^3) (Dufresne, 2013) and self-assembling property (Li et al., 2015a; Li, Wu, Song, Qing, & Wu, 2015b). Therefore, this green material has been used in various applications such as polymer reinforcement, antimicrobial and medical materials, green catalysts, biosensors, drilling fluids and drug delivery (Cirtiu, Dunlop-Briere, & Moores, 2011; Khalil, Bhat, & Yusra, 2012; Wu et al., 2013; Li et al., 2015b; Xiong, Lu, Zhang, Zhou, & Zhang, 2013).

Till now, there are mainly two approaches applied to extract cellulose nanocrystals from cellulosic materials, which are mechanical and chemical methods. More specifically, high-pressure homogenization (Jonoobi et al., 2015), high-intensity ultrasonication (Li, Yue, & Liu, 2012) and steam explosion (Cherian et al., 2010) are all the mechanical methods. Acid hydrolysis, enzymatic hydrolysis and oxidation method (Jonoobi et al., 2015; Penttila et al., 2013) would be the chemical methods. Although the isolation of CNs by mechanical ways is environmental-friendly with less chemicals used, the procedure is normally associated with high energy consumption (Dufresne, 2013). Likewise, even the acid hydrolysis is the most widely used way to extract CNs, the waste acid solution it produced is inevitable. In recent years, oxidation

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methods to prepare CCNs have been reported by several researchers. Saito et al. extracted CCNs from the 2,2,6,6-tetramethylpiperidinyl-1-oxy radical (TEMPO) oxidized wood celluloses combined with moderate mechanical disintegration (Saito, Kimura, Nishiyama, & Isogai, 2007; Saito, Nishiyama, Putaux, Vignon, & Isogai, 2006). Besides, another one-step oxidation method to prepare CCNs was also reported by Leung et al. (2011) in which ammonium persulfate (APS) was used as a strong oxidant to degrade the amorphous regions and the removal of non-cellulosic plant contents by pretreatment was avoided. For the case of the oxidation method, it has relatively less pollution compared with acid hydrolysis and lower energy consumption in comparison to mechanical ways. Furthermore, carboxylated CNs (CCNs) could be also obtained from the oxidized celluloses in oxidation method. And the presence of carboxylate ions on the surface of CCNs could result in strong electrostatic repulsion between CCNs in water, act as a good template to support metal nanoparticles and offer great potential for further functionalization of CCNs (Koga et al., 2010). However, to our limited knowledge, comparison between CCNs prepared by TEMPO mediated oxidation and APS oxidation using one same raw material has not been investigated in literature.

For environmental protection as well as government regulations in some countries, more efficient utilization of agro-industrial residues has become increasingly significant (Shaikh, Pandare, Nair, & Varma, 2009). Sugarcane bagasses is a by-product resulting from the sugar and alcohol industries (Abdel-Halim, 2014). Although some reports about the preparation of CNs from sugarcane bagasses via acid hydrolysis (Slavutsky & Bertuzzi, 2014), enzymatic hydrolysis (de Campos et al., 2013) and high pressure homogenization methods (Li et al., 2012) have been reported. The study on isolation of CCNs by oxidation method is less studied. Herein, we chose bleached sugarcane bagasses pulp as raw material in this paper.

Two kinds of CCNs were isolated from bleached sugarcane bagasse pulp by ultrasonic assisted TEMPO-mediated oxidation and one-step APS oxidation methods in this work. The study aimed mainly to explore the effects of sodium hypochlorite (NaClO) and APS content on the yield, carboxyl content, degree of polymerization (DPv) and morphology of the oxidized cellulose in the two methods. In addition, CCNs obtained from the two different methods were also studied by Fourier transformed infrared spectra (FTIR), X-ray diffraction (XRD) and thermogravimetric analyses (TGA) so as to compare the chemical structure, thermal stability and crystallinity of CCNs in the two methods.

2. Experimental

2.1. Materials

Bleached sugarcane bagasse pulp was obtained from Jiangmen sugarcane chemical factory (group) Co., Ltd. It was cut into small pieces by a crusher. And the chemical composition of bleached sugarcane bagasse pulp was analyzed (TAPPI, 1993, 2000, 2002, 2009; Yokoyama, Kadla, & Chang, 2002) and the data are shown in Table 1. TEMPO, APS, sodium bromide, sodium hypochlorite solution (15%), HCl, and NaOH were supplied by Sigma–Aldrich and used without further purification. Milli-Q water was used in all experiments.

Table 1
Chemical composition of bleached sugarcane bagasse pulp.

Component	Content (wt%)[a]
Moisture	4.68 ± 0.47
Ashes	0.17 ± 0.02
Extractives	2.54 ± 0.32
Insoluble lignin	0.42 ± 0.05
Holocellulose	94.05 ± 0.40
Hemicellulose	16.31 ± 0.42
Alpha-cellulose	72.25 ± 0.53

[a] Mean ± Standard error.

2.2. Methods

2.2.1. Preparation of CCNs by ultrasonic assisted TEMPO-mediated oxidation

The preparation of CCNs by ultrasonic assisted TEMPO-mediated oxidation was performed and illustrated in Fig. 1a and b according to the procedure described by (Saito & Isogai, 2004). The sugarcane cellulose fibers (1 g) were suspended in water (100 mL) containing TEMPO (0.016 g, 0.1 mmol) and sodium bromide (0.1 g, 1 mmol). The NaClO solution (2 mmol, 5.0 mmol, 7.0 mmol, 9.0 mmol and 11.0 mmol), which served as an oxidant, was added drop wise to the cellulose suspension, and the mixture was stirred at room temperature and kept at pH 10 for 5 h. The oxidation was stopped by adding 10 mL of ethanol, and oxidized fibers were filtered and completely washed with deionized water until the solution conductivity was below 20 μS/cm. Oxidized cellulose fibers suspension with a solid content of 0.4% was sonicated for 30 min using an ultrasonic homogenizer and an output power of 450 W (6 mm probe tip diameter) until the suspension became transparent. The suspension was centrifuged at 5000 rpm for 30 min, and the recovered supernatant became the CCNs aqueous suspension. All the resulting suspensions were lyophilized to yield white cellulosic product. The yield of oxidized fibers was calculated as a percentage of the weight of the final dried oxidized sugarcane bagasse fibers divided by the initial weight of bleached sugarcane bagasses. CCNs prepared by ultrasonic assisted TEMPO-mediated oxidation were called as TEMPO-oxidized CCNs (TO-CCNs) in this paper.

2.2.2. Preparation of CCNs by one-step APS oxidation

Using APS as oxidant, CCNs were prepared by the literature method (Leung et al., 2011). In brief, bleached sugarcane bagasses pulp (2 g) was hydrolyzed in 1 M, 1.5 M, or 2 M APS (200 mL) at 60 °C for 16 h. The white suspension was washed with H_2O, centrifuged three times at 9000 rpm for 10 min, and lyophilized to yield a white-colored product, and the yield of CCNs was calculated as a percentage of the weight of the final products divided by the initial weight of bleached sugarcane bagasses pulp. CCNs isolated by APS oxidation method were called as APS-oxidized CCNs (AO-CCNs) in this paper. Oxidation mechanism of bleached sugarcane bagasse pulp using APS oxidation is shown in Fig. 1c and would be discussed in Section 4.

3. Characterization

3.1. Carboxyl content

The carboxyl content of the oxidized cellulose was determined by the electric conductivity titration method. Dried oxidized celluloses (0.1 g) were added to 70 mL 0.01 M HCl, and then the mixture was sufficiently sonicated for about 10 min. After ultrasonication, the suspensions were titrated with 0.01 M NaOH. The titration curves showed the presence of strong acid corresponding with the excess of HCl and weak acid corresponding to the carboxyl content (da Silva Perez, Montanari, & Vignon, 2003). The carboxyl content (mmol/g) is given by the following equation:

$$C(\text{mmol/g}) = \frac{c(V_2 - V_1)}{m}(\text{mmol/g cellulose}) \quad (1)$$

with C, the carboxyl content (mmol/g); V_2 and V_1, the equivalent volumes of added NaOH solution (mL); c, the exact concentration of NaOH solution (mol/L); m, the weight of dried product (g).

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