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Properties of nanocellulose isolated from corncob residue using sulfuric acid, formic acid, oxidative and mechanical methods

Chao Liu[a,b,1], Bin Li[a,1], Haishun Du[c], Dong Lv[a], Yuedong Zhang[a], Guang Yu[a], Xindong Mu[a,*], Hui Peng[a,*]

[a] CAS Key Laboratory of Bio-based Material, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China
[b] University of Chinese Academy of Sciences, Beijing 100049, China
[c] Tianjin Key Laboratory of Pulp and Paper, College of Papermaking Science and Technology, Tianjin University of Science and Technology, Tianjin 300457, China

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ABSTRACT

In this work, nanocellulose was extracted from bleached corncob residue (CCR), an underutilized lignocellulose waste from furfural industry, using four different methods (i.e. sulfuric acid hydrolysis, formic acid (FA) hydrolysis, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation, and pulp refining, respectively). The self-assembled structure, morphology, dimension, crystallinity, chemical structure and thermal stability of prepared nanocellulose were investigated. FA hydrolysis produced longer cellulose nanocrystals (CNCs) than the one obtained by sulfuric acid hydrolysis, and resulted in high crystallinity and thermal stability due to its preferential degradation of amorphous cellulose and lignin. The cellulose nanofibrils (CNFs) with fine and individualized structure could be isolated by TEMPO-mediated oxidation. In comparison with other nanocellulose products, the intensive pulp refining led to the CNFs with the longest length and the thickest diameter. This comparative study can help to provide an insight into the utilization of CCR as a potential source for nanocellulose production.

1. Introduction

The production of novel nanomaterials from renewable and abundant biomass, such as nanocellulose obtained from native cellulose, is drawing growing attention in the last decade since it offers unique physiochemical properties with little effect on environment. Nanocellulose isolated from plant cell wall can be divided into two main categories: cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs) which are different in morphology (Abdul Khalil et al., 2014). Due to the promising properties as new bio-based nanomaterials such as optical transparency, low thermal expansion, biodegradability and environment-friendly nature (Mariano, El Kissi, & Dufresne, 2014; Moon, Martini, Nairn, Simonsen, & Youngblood, 2011), these nano-sized cellulose fibrils are becoming attractive building blocks for design of new biomaterials. Nanocellulose have been utilized to fabricate diverse functional materials, including transparent films (Zhu, Fang, Preston, Li, & Hu, 2014), reinforcements for polymer composites (Miao & Hamad, 2013), aerogel (Chen et al., 2014), templates (Kelly, Giese, Shopsowitz, Hamad, & MacLachlan, 2014), separation membranes (Metreveli et al., 2014), drug-delivery (Lin & Dufresne, 2014), conductive paper (Tang, He, Mosseler, & Ni, 2014) and many others (Chen et al., 2015). However, controlled properties, reliable and commercial production of nanocellulose is still challenging.

Fundamental properties of nanocellulose, such as morphology, crystallinity, dimension and surface chemistry vary highly depending on the raw material source and extraction process. These key properties are of critical importance for the end use of isolated nanocellulose. A variety of biomass have been utilized for the extraction of nanocellulose (Deepa et al., 2015). Except wood fiber which is the main source for nanocellulose production, the abundant and sustainable agricultural wastes can be potential feedstock for the production of nanocellulose (Chaker, Mutjé, Vilar, & Boufi,

Abbreviations: CCR, corncob residue; FA, formic acid; CNCs, cellulose nanocrystals; CNFs, cellulose nanofibrils; SCNC, cellulose nanocrystals prepared by sulfuric acid hydrolysis; FCNC, cellulose nanocrystals isolated by formic acid hydrolysis; TCNF, cellulose nanofibrils prepared by TEMPO-mediated oxidation; PCNF, cellulose nanofibrils fabricated by FPI refining.

* Corresponding authors.
E-mail addresses: liuchao@qibebt.ac.cn (C. Liu), libin@qibebt.ac.cn (B. Li), haishundu@163.com (H. Du), lvdong@qibebt.ac.cn (D. Lv), zhangyd@qibebt.ac.cn (Y. Zhang), yuguang@qibebt.ac.cn (G. Yu), muxd@qibebt.ac.cn (X. Mu), penghui@qibebt.ac.cn (H. Peng).
URL: http://mailto:penghui@qibebt.ac.cn (H. Peng).
[1] These authors contributed equally to this work.

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2014). The global corn production for 2014 were more than nine hundred million metric tons according to the report from United States Department of Agriculture and approximately forty–fifty million metric tons of corncobs could be collected (Qu, Xu, Lu, Zhang, & Li, 2015). Considerable amount of corncob are used as feedstock for furfural production (Gu, Zhang, & Bao, 2014) and about 300–700 kt of furfural is produced worldwide annually, the majority coming from China (Cai, Zhang, Kumar, & Wyman, 2014). About 12–15 t of corncob residue (CCR) is obtained after 1 t of furfural is produced (Bu, Xing, Yu, Gao, & Jiang, 2012). It was estimated that three million tons of furfural residues are produced per year in China (Zhu et al., 2016). However, the CCR is usually burned to recover heat and causes environmental problems (Bu et al., 2012). Therefore, transforming CCR into valuable products is worthy of concern. Since the hemicellulose in corn cob has been hydrolyzed, the CCR is porous and could be one of the most easily available lignocellulosic materials that can be used as potential raw material for nanocellulose production.

Numerous methods have been reported for nanocellulose production. CNCs are rod-like crystalline particles of 10–30 nm in width and several hundred nanometers in length, and usually produced by strong acid hydrolysis (Habibi, 2014). Sulfuric acid hydrolysis is a typical method used to isolate CNCs with good dispersibility in water. Other acids such as hydrochloric acid, nitric acid or some acids mixture were also used in CNCs fabrication (Jiang & Hsieh, 2013). Recently, formic acid (FA) was used to replace the mineral acids to manufacture CNCs, because FA can be easily recovered and causes less equipment corrosion (Du et al., 2016; Li et al., 2015). Different from CNCs, CNFs have long flexible fiber networks and consists of alternating crystalline and amorphous cellulose domains. CNFs are mainly produced by 2,2,6,6-tetramethylpiperidine-1-loxy (TEMPO)-mediated oxidation or mechanically induced deconstructing strategies. The CNFs obtained by TEMPO-mediated oxidation are more uniform and can be well dispersed in aqueous phase (Habibi, Chanzy, & Vignon, 2006). Yet, mechanical approaches (like high-pressure homogenization, microfluidization, ultrasonication, high-speed blending, grinding, and cryocrushing) always need intensive energy consumption and yield CNFs products with varied particle size (Jiang & Hsieh, 2013). Moreover, mechanical refining can also be considered as a promising method to produce CNFs. Karande, Bharimalla, Hadge, Mhaske, and Vigneshwaran (2011) reported the production of CNFs from cotton by a disc refiner, which has been widely adopted in the modern pulp industry. PFI refiner is a laboratory pulping instrument, which can be used to simulate the effect of commercial disc refiner (Xu et al., 2014), but it is rarely applied for the isolation of nanocellulose.

In the present study, the characterization of nanocellulose isolated from bleached CCR using four different approaches (i.e. sulfuric acid hydrolysis, FA hydrolysis, TEMPO mediated oxidation and PFI refining, respectively) was reported. To our best knowledge, FA hydrolysis and PFI refining approach have not been comprehensively compared with other typical methods (i.e. sulfuric acid hydrolysis and TEMPO-mediated oxidation) in literature. The aim of this work is to use the sustainable bleached CCR as the starting material and investigate the effects of the extraction processes on the key properties of the resulting nanocellulose and thereby provide a set of information for the better use of the nanocellulose product for the development of new nanomaterials.

2. Materials and methods

2.1. Materials

CCR was a gift from ShengQuan Group, China. The main components of CCR were 63.5% cellulose, 2.7% xylan, 25.8% lignin and 2.1% ash based on oven-dried weight, determined according to the National Renewable Energy Laboratory (NREL) procedure (Sluiter et al., 2011). Analytical grade chemicals, including sulfuric acid, FA, ferric chloride, sodium hypochlorite, *tert*-butanol, uranyl acetate and sodium bromide, were purchased from Sinopharm, China. TEMPO was purchased from Sigma Aldrich. All the chemicals were used as received.

2.2. Preparation of nanocellulose

The CCR was treated with an aqueous 3% (w/w) NaOH solution for 3 h at 100 °C, and then washed until neutrality with tap water. Subsequently the insoluble residue was further bleached with sodium hypochlorite (0.02 g per gram CCR) at 80 °C for 2 h and the pH value of solution was adjusted to 12 by addition of sodium hydroxide before the bleaching. The resulting solid was also washed until neutrality with tap water. The bleached CCR was air-dried and stored at room temperature for extraction of nanocellulose. The solid content throughout these treatments was about 5 wt%. The bleached CCR were mainly composed of 95.2% cellulose, 1.0% lignin and 1.1% ash based on oven-dried weight.

2.2.1. Sulfuric acid hydrolysis

Sulfuric acid (64 wt%) preheated to 45 °C was added to CCR at a liquid-to-solid ratio of 20 mL/g under vigorous stirring (Jiang & Hsieh, 2015). The hydrolysis time was 60 min which was found to be the optimal time. The hydrolysis process was stopped by 8-fold cold deionized water. The suspension was washed at least 6 times followed by centrifugation (10,000 rpm for 5 min) to remove excess sulfuric acid. Then, the suspension was dialyzed against deionized water until the pH value remained unchanged.

2.2.2. FA hydrolysis

The procedure was based on our previous study with slight modifications (Li et al., 2015). Briefly, CCR and 0.5% hydrochloric acid (based on the total weight of acid in the mixture) was mixed with 88% FA at a liquid-to-solid ratio of 30 mL/g, and then placed in an oil bath at 95 °C for 30 min with magnetic stirring at 500 rpm. Upon

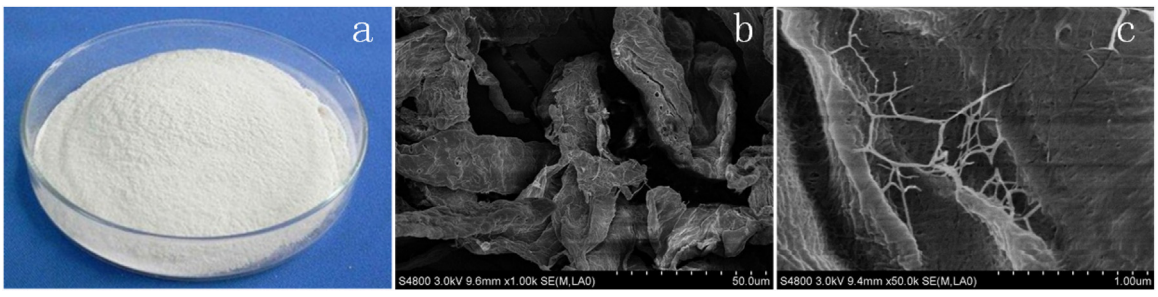

Fig. 1. Photograph (a) and SEM images (b and c) of bleached CCR.