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A novel approach for the preparation of nanocrystalline cellulose by using phosphotungstic acid

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ABSTRACT

In this work, a sustainable and green process to prepare nanocrystalline cellulose (NCC) from bleached hardwood pulp was demonstrated. Rod-like nanocrystalline cellulose with the size of 15–40 nm in width and hundreds of nanometers in length was obtained through $H_3PW_{12}O_{40}$ (HPW)-catalyzed hydrolysis of bleached pulp fibers under the mild reaction conditions. Thermogravimetric analysis revealed that the resulting NCC exhibited much higher thermal stability than the partially sulfated NCC (prepared by sulfuric acid). In addition, the concentrated HPW could be easily recovered and recycled through the extraction with diethyl ether, and the recovered HPW could be reused for several rounds of cellulose hydrolysis without activity lost. These fundamental studies are of crucial importance for the development and application of NCC products/NCC-based biomaterials with good thermal stability.

1. Introduction

Cellulose is one of the most abundant biodegradable polymers and it has been widely used as the reinforcing element in fiber-thermoplastic composite materials at industrial scale in recent years (Eichhorn et al., 2001; Hebeish, Farag, Sharaf, & Shaheen, 2013). Nanocrystalline cellulose (NCC) prepared from acid hydrolysis of natural cellulose, is typically a rod-like cellulose whisker which is 5–70 nm in diameter and hundreds of nanometers in length (Klemm et al., 2011). The size variation of NCC is highly dependent upon the origin of raw material as well as the preparation methods and conditions. Due to its nano-scale dimension, NCC has many superior properties compared to the general cellulose, such as, high aspect ratio and crystallinity, excellent optical properties and great mechanical strength (Abraham et al., 2012; Habibi, Lucia, & Rojas, 2010; Kovacs et al., 2010; Lavoine, Desloges, Dufresne, & Bras, 2012). Therefore, NCC has many potential applications, particularly for the production of value-added materials (Shen, Song, Qian, & Ni, 2011). For example, nanopaper based on nanofibrillated cellulose has excellent optical transparency, high mechanical properties (tensile strength of 208 MPa and Young's modulus of 20 GPa) and high gas barrier properties compared to the traditional paper and plastic substrates (Huang et al., 2013; Yousefi, Nishino, Faezipour, Ebrahimi, & Shakeri, 2011). Chiral nematic NCC confined within a silica host is an ideal precursor for mesoporous carbon material, which can be used as an effective electrode material for super capacitors and selective sensors (Shopsowitz, Hamad, & MacLachlan, 2011). The nano-dimension and strength of NCC make it an ideally reinforcing material for fibrin to provide a new type of biomaterial for artificial vascular graft applications (Brown, Hu, Abu Lail, & Zhang, 2013).

The common method to prepare NCC is hydrolysis of cellulose by mineral acids, including sulfuric acid (Beck-Candanedo, Roman, & Gray, 2005; Fan & Li, 2012; Tang, Yang, Zhang, & Zhang, 2014; Wang et al., 2012), hydrochloric acid (Yu et al., 2013), phosphoric acid (Camarero Espinosa, Kuhnt, Foster, & Weder, 2013), and their mixtures (Teixeira, de Oliveira, Mattoso, Corrêa, & Paladin, 2010). Although this method is simple, some issues need to be addressed, such as serious equipment corrosion, large water usage and generation of a great amount of waste. Recently, many studies have been focused on the optimization of hydrolysis parameters, the avoiding of corrosion and the reduction of waste disposal. In these studies, the substitution of strong liquid acids by solid acids has been investigated for environmental and sustainable reasons. For example, previous work reported a cation exchange hydrolysis method to prepare NCC with a yield of 50%, and the solid cation exchange resin can be regenerated by a post-treatment procedure (Tang, Huang, Ou, Chen, & Chen, 2011). The major advantages of solid acid hydrolysis are the easy recovery of solid acid from the reaction mixture, the less corrosion and the relatively safe working environment

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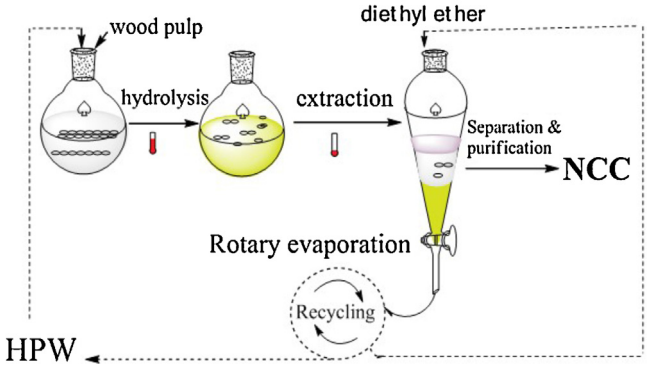

Fig. 1. The overall procedure for the preparation of NCC by using HPW (HPW: phosphotungstic acid, $H_3PW_{12}O_{40}$).

(Huang & Fu, 2013; Trolliet, Coudurier, & Védrine, 2001). However, the limited contact between solid acid and cellulose significantly increases the hydrolysis time. Previous studies have demonstrated that phosphotungstic acid ($H_3PW_{12}O_{40}$, HPW) has abundant Bronsted acid sites which can break the β-1, 4-glycosidic bonds in cellulose. Hence, it is an alternate catalyst of traditional mineral acids for the hydrolysis of cellulose into glucose (Drago, Dias, & Maier, 1997; Li et al., 2012; Shimizu, Furukawa, Kobayashi, Itaya, & Satsuma, 2009). Therefore, it is expected that NCC can be produced by HPW through controlling hydrolysis parameters, and the HPW can be easily recycled. In this work, a sustainable route to prepare NCC from hardwood pulp by HPW hydrolysis was reported, and the recovery and reuse of the concentrated HPW were demonstrated as well.

2. Experimental

2.1. Materials.

The bleached hardwood pulp was obtained from Shandong Chenming Paper Co., Ltd., China. The chemical composition of wood pulp was analyzed according to Technical Association of Pulp and Paper Industry (TAPPI) standards, and the results are shown in Table 1 (Two replicates were conducted and the average was reported). Sulfuric acid, ethanol, diethyl ether, tetrahydrofuran and phosphotungstic acid ($H_3PW_{12}O_{40}$, HPW) were purchased from Sinopham Chemical Reagent Co., Ltd. All chemicals were of analytical grade and used as received.

2.2. Preparation of the nanocrystalline cellulose (NCC) suspension

The overall procedure for the preparation of NCC by using HPW is given in Fig. 1. The starting wood pulp (0.5 g) was added to 40 mL HPW ($H_3PW_{12}O_{40}$) solution with the desired concentration varied from 50% to 85%. The mixture was heated at 90 °C in an oil bath with mechanical stirring for the required time (15–30 h). Upon completion, the reaction was stopped by rapidly cooling the reactor in an ice bath to room temperature. Then, the resulting mixture was extracted twice with superfluous diethyl ether. As HPW could be completely extracted from water phase by diethyl ether, and HPW and diethyl ether could form a composite with large specific gravity (this composite could not be dissolved in diethyl ether or in water), three layers were formed after standing. The lowest layer (formed by diethyl ether and HPW) was collected, and the HPW was recovered after the complete evaporation of diethyl ether. After being dried at 45 °C overnight, the recovered HPW could be reused for a second run of hydrolysis as the fresh HPW with the same procedure as described above. The upper layer was the excess diethyl ether with lower specific gravity (0.7134 g/cm^3, probably mixed with a very small amount of water). To verify the component of the upper layer, FTIR-ATR analyses of pure diethyl ether and the upper layer were carried out, and the results are shown in Fig. S1. It can be seen that the upper layer had similar FTIR spectrum pattern with pure diethyl ether except for the peaks at around 3432 and 1643 cm^{-1}, which were associated with the mixed small amount of water. The upper layer was decanted and the diethyl ether could be recovered by simple evaporation. The middle layer mainly contained water and NCC, as well as the degraded sugars (as tested, the concentrations of glucose, xylose, and arabinose were 0.629 g/L, 1.519 g/L, and 0.028 g/L, respectively. Furfural substances were undetected.). The middle layer was centrifuged (6000 rpm) for 15 min at room temperature, and the supernatant was decanted. Ethanol (40 mL) was added to the precipitation from the middle layer, followed by 5 min of mixing and centrifugation (2000 rpm × 15 min) to remove unreacted cellulose. The suspension was washed with ethanol to remove excess acid and diethyl ether, and the NCC was collected for further centrifugation at 12,000 rpm for 15 min. After that, the NCC was washed by deionized water, and the washing/centrifugation cycles were repeated twice. Finally, the NCC water suspension was obtained.

For comparison, the sulfated NCC (s-NCC) was prepared by using 64% H_2SO_4 with the solid to liquid ratio of 1:20 at 55 °C for 1 h. The hydrolysis reaction was stopped by diluting 10-fold (volume) with deionized water. After setting, the clear top layer was decanted off and the remaining cloudy layer was centrifuged at 6000 rpm for 15 min at room temperature. The resulting cellulose gel was washed with deionized water and centrifuged again at 6000 rpm for 15 min. The procedure of washing and centrifugation was repeated three times. Subsequently, the resulting precipitate was dialyzed with a cellulose dialysis membrane with 12–14 kDa molecular weight cut off against deionized water until neutralization. At last, the obtained suspension was stored in a cool room for further studies.

2.3. Dispersion studies.

The dispersibility of the obtained NCC and s-NCC was observed by preparing NCC and s-NCC dispersions with water, ethanol, and tetrahydrofuran, respectively, at the concentration of 5 mg/mL. All samples were simultaneously sonicated for 10 min and the dispersibility was investigated by taking pictures of the obtained suspensions immediately after sonication and after standing for 12 h and 48 h, respectively.

2.4. Drying of the NCC suspensions

Direct water evaporation: the 2% NCC suspension was placed in an oven at 40 °C for overnight. Freeze-drying: the 0.04% and 1% NCC suspensions were first frozen under −20 °C and then placed into a vacuum-freeze dryer for 2 days.

2.5. Characterization.

2.5.1. Scanning electron microscopy (SEM)

The wood pulp before and after hydrolysis was subjected to observation by using a scanning electron microscope (Hitachi S-4800, Japan) at 3.0 kV. Surface of the sample was coated with gold under vacuum before observation.

2.5.2. Transmission electron microscopy (TEM)

Dilute NCC suspensions with the concentration of 0.01% were deposited on carbon-coated TEM grids. After the samples were completely dried, the images were taken using a field emission H-7600 electron microscope (Japan) at 100 kV.