Ionic Liquid-assisted Fabrication of Nanocellulose from Cotton Linter by High Pressure Homogenization

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Nanocellulose (NC) was prepared from cotton linter using ionic liquid (IL) 1-butyl-3-methylimidazolium hydrogen sulfate ([Bmim]HSO₄) as both swelling agent and catalyst followed by high-pressure homogenization. Evidence suggested that the IL played a significant role with respect to hydrolysis of the linter cellulose. The effects of various reaction conditions on the NC preparation were investigated in this study. The successful conversion of the cotton to NC was analyzed, which showed that the prepared NC had a uniform rod-like shape that was 50 nm to 100 nm in diameter and 500 nm to 800 nm in length. The characterization of the NC by X-ray diffraction and thermogravimetric analysis revealed that the crystalline cellulose I structure was retained in the NC and it showed stable thermal properties. The recycled ionic liquid exhibited a slightly decreased cellulose hydrolysis ability. The application of [Bmim]HSO₄ as both a catalyst and swelling agent introduced an effective and environmentally friendly method for NC production.

Keywords: Nanocellulose; Ionic liquids; High-pressure homogenization; Recycling

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INTRODUCTION

Cellulose, which is composed of β -1-4-linked D-glucopyranose repeating units, is a linear polysaccharide consisting of six-membered ring structures with many hydrogen bonds (Hassan *et al.* 2012). It has been widely used as the source of energy and for the building materials due to its biocompatible, biodegradable, and non-toxic properties. But, cellulose is insoluble in water and common organic solvents, which limits its functionalization in the aqueous phase. Nanocellulose (NC) is a type of cellulose with nanoscale particles that can form a uniform and stable suspension in water (Atalla and Vanderhart 1984; Hult *et al.* 2003; Kobayashi *et al.* 2011). This subject is currently under very intensive investigation due to its various attractive properties such as high purity, large specific surface area, and the unique mechanical and optical properties (Duong and Nguyen 2016). Therefore, it has potential for use in a wide range of applications including nanocomposite materials, electronic devices, environmental protection, tissue engineering, and cosmetics.

NC is generally divided into three categories according to size and preparation method, cellulose nanocrystals (CNC), cellulose nanofibrils (CNF), and bacterial nanocellulose (Klemm *et al.* 2011). The concentrated sulfuric acid hydrolysis method (Purkait *et al.* 2011) is the earliest method for preparing CNC, but the recovery of waste acid liquid is difficult. CNF is commonly produced by mechanical fibrillation from commercial pulp fibers (Hassan *et al.* 2012; Tingaut *et al.* 2012; Dwivedi *et al.* 2014). The mechanical treatments usually involve high-pressure mechanical treatment of cellulose to

defibrillate the fibers and then separate nano-sized cellulose. However, special equipment and a high energy consumption are generally required for its preparation (Han and Yan 2010).

Ionic liquids (ILs), a new type of green solvent or swelling agents, has been considered as an ideal alternative to separate cellulose nanowhiskers from cellulosic matrices under less harsh conditions (Mahmoudian et al. 2012). The unique properties of ILs, such as a low toxicity, non-flammability, recyclability, and high chemical and thermal stabilities make them a promising media to separate NC from cellulosic sources. Li and Taubert (2009) first produced rod-like nanowhisker-based materials by injecting a mixture of chloroauric acid (HAuCl₄) and cellulose dissolved in IL into aqueous sodium borohydride (NaBH₄). ILs can act as catalysts in cellulose hydrolysis to obtain highcrystallinity CNC. The imidazole ILs with HSO4⁻ or Cl⁻ anion, such as 1-butyl-3methylimidazolium hydrogen sulphate ([Bmim]HSO₄) and 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) were reported to be the most suitable for that purpose. Zhao et al. (2017) also used [Bmim]HSO₄ as a catalyst and solvent and enzymatically esterified to produce CNC. The facile one-pot method was simple and environmentally friendly. Tan et al. (2015) synthesized rod-shaped CNC with high crystallinity by swelling microcrystalline cellulose (MCC) with [Bmim]HSO₄. The effects of synthesis parameters on the catalytic ILs hydrolysis process of CNC from MCC were also investigated (Iskak et al. 2017). Results showed that increasing the reaction temperature and time exerted positive effect on the properties of CNC. Unlike mineral acids, ILs can be recovered and reused after cellulose regeneration by common laboratory methods (Man et al. 2011). By evaporating the anti-solvents, the recovery rate of [Bmim]Cl can exceed 99.5% (Gutowski et al. 2003; Quan et al. 2010).

In order to obtain uniform size of NC, physical treatment often has been combined with ILs to separate NC from cellulose (Alvarez-Guerra et al. 2014; Ahmad et al. 2016). Han (2013) prepared regenerated cellulose nanoparticles including both elongated fiber and spherical structures from MCC using [Bmim]Cl followed by high-pressure homogenization process for 10 passes. The crystal structures of cellulose were transformed from cellulose I to II with decreased crystallinities during the ILs treatment. Wang (2015, 2017) reported the homogeneous isolation of NC from cotton and eucalyptus pulp by high pressure homogenization for up to 50 cycles in [Bmim]Cl. Li (2012) pretreated the bagasse with [Bmim]Cl and the dissolved bagasse cellulose were cyclically processed 50 times in a high pressure homogenizer to separate the NC. The combination of physical treatment could greatly reduce the particle size distribution, but the number of mechanical process cycles still needs 50 times to obtain satisfactory particle size, when natural biomass used as raw material. Compared with [Bmim]Cl, [Bmim]HSO₄ exhibits higher catalytic capability due to its stronger acidity (due to proton from [HSO₄]⁻) (To 2012). Moreover, the less viscous [Bmim]HSO₄ favored the catalytic activity in which the mobility of ions are improved. The stronger acidity (active acid sites) with low viscosity acidic ILs are wellsuited and more effective for catalyzing hydrolysis of cellulose to accelerate the fracture of glycosidic linkages to produce more NC (Liu et al. 2013). Thus, it is expected that the homogenization cycles or process time will be reduced when [Bmim]HSO₄ is used.

In this study, [Bmim]HSO₄ was utilized as dual functions of swelling and catalyzing to induce hydrolytic cleavage of glycosidic bonds of cotton cellulose. The subsequent 10~60 min high pressure homogenization process was coupled to obtained NC with rod-like shape. The effects of the reaction parameters on the NC yield and crystallinity were investigated, and the recovery and reuse of IL were also investigated. The structural and

physicochemical properties of the NC were studied using X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscope (SEM), transmission electron microscope (TEM), atomic force microscopy (AFM), and thermogravimetric analysis (TGA). The low complexity of process and less time-consuming process were strongly augmented by using [Bmim]HSO₄ as catalyst and swelling agent, thus suggesting that the process is suitable for evaluation in a production facility.

EXPERIMENTAL

Materials

Cotton linter was obtained from Gauke Cotton Supplies Co. Ltd. (Fu Jian, China). The IL [Bmim]HSO₄ with a melting point of 28 °C and molecular weight of 236.29 was purchased from Cheng Jie Chemical Co. Ltd. (Shanghai, China). All of the other reagents and chemicals used were of analytic grade and used as received.

Preparation of Nanocellulose

Hydrolysis of cotton cellulose in IL

Defatted cotton cellulose was first cut into pieces, and then it was washed with ethanol and distilled water to remove impurities before use. The cotton cellulose with different mass fraction was added into [Bmim]HSO₄ with continuous mechanical stirring and heated to 80~120 °C. After reacting for 2 h, the suspension was sonicated for 30 min and then poured into an excess of acetone and off-white precipitates formed immediately. After being stirred for about 10 min, the precipitates were filtered under vacuum and washed repeatedly with acetone. Subsequently, the filtered products were re-dispersed in distilled water for washing and then centrifuged at room temperature for 10 min with 10,000 rpm (CTK48 Superspeed Centrifuge, Xiangyi centrifuge instrument Co., Ltd., CN) to further remove the residual IL. This washing and centrifuging procedure was repeated for 3~5 times. After that, the precipitates was dialyzed using DI-water until the conductivity of the mixture approached that of DI-water, indicating near-complete IL removal. The obtained IL-treated cellulose were designated as IL-C.

Homogenization process

The IL-C was uniformly dispersed in ultrapure water to form a uniform aqueous phase dispersion. The final concentration of the cellulose aqueous suspension was about 1% (w/w)). And then The IL-C suspension was homogenized by a high pressure homogenizer (UK-12, Union-Biotech (Shanghai) Co., Itd., CN) under an operating pressure ranging from 25-100 MPa for 10-60 min. After homogenization process, the turbid supernatant was collected and the NC yield (NY, %) was gravimetrically obtained after freeze-dried according to Eq. 1,

$$NY(\%) = (M_1/M_0) \times 100\%$$
(1)

where M_1 is the mass of the dried NC and M_0 is the mass of the initial mass of the dried cotton (g).

Recovery of ionic liquid

The collected IL/solvent mixture was passed through a chromatography column, which was packed with activated carbon (5 cm in length), thin layer chromatography silica gel (diameter \geq 38 µm; and 1.0 cm in length), column chromatography silica gel (100 mesh to 200 mesh; 3 cm in length), and cotton (1.0 cm in length) from top to bottom. The column had a diameter of 5 cm and height of 50 cm. After passing through the column, the mixture was concentrated in a rotary evaporator to remove the solvent under vacuum (70 °C and - 0.1 MPa), and then vacuum-dried for 24 h. The recycled IL was reused to dissolve and hydrolyze cellulose with the same operation conditions as using the fresh IL. The reuse-recovery cycles were repeated five times, and the recycled ILs were labelled as 1st-IL, 2nd-IL, 3rd-IL, 4th-IL, and 5th-IL.

Characterization

The crystal structure and crystallinity of the raw cotton cellulose, RCe, and NC were measured using a Min Flex 600 X-ray diffractometer (Rigaku, Tokyo, Japan) equipped with Cu K α radiation at 40 kV and 40 mA in range of 5° to 40° with a 0.02° resolution. The crystallinity index (CrI) was calculated using Segal's method as described at Eq.2 (Segal *et al.* 1959),

$$\operatorname{CrI}(\%) = \frac{I_{200} - I_{am}}{I_{200}} \times 100\%$$
(2)

where I_{200} is the maximum intensity of the peak at $2\theta=22.5^{\circ}$ that corresponds to the crystalline plane and I_{am} represents the intensity of diffraction peak at $2\theta=18^{\circ}$, which is attributed to amorphous cellulose.

The FTIR spectra for the cellulosic samples were recorded using a Fourier transform infrared (FTIR) instrument (Nicolet iS10, ThermoFisher, Waltham, USA) in the range of 4000 cm⁻¹ to 400 cm⁻¹ at a resolution of 4 cm⁻¹. Dried samples were ground and mixed with KBr powder and then compressed to form an ultra-thin pellets.

Thermogravimetric analysis (TGA) was performed on a Simultaneous Thermal Analyzer (STA449C/6/G, Germany) in order to characterize the thermal stability of the samples. Approximately 6 mg of each sample was heated from room temperature to 600 °C at a heating rate of 10 °C/min under nitrogen atmosphere.

The surface morphology and diameter of samples were investigated by scanning electron microscope (SEM) on a Nova NanoSEM 230 (FEI, Hillsboro, USA) at an acceleration voltage of 5.0 kV. The samples were sputter coated with gold to prevent charging.

The morphologies of the NC samples were also analyzed by atomic force microscopy (AFM) (Bruker Multimode 8, Karlsruhe, Germany). Samples were diluted to solids consistency of 0.01wt% and cast on a clean mica substrate, and then air-dried overnight at room temperature. The samples were then analyzed with a scanning probe microscope.

The dimension of NC samples was determined by transmission electron microscope (TEM) (FEI, TECNAI G2F20, USA) operating at 10 kV. A drop of the diluted suspension of samples was dropped on the copper grid and dried at room temperature.

The proton nuclear magnetic resonance (¹H NMR) analysis of the fresh and recycled ILs was performed using a Bruker AMX-300 MHz instrument with chloroform-d (CDCl₃) as a solvent.

The particle size distribution of the NC was measured with a NanoBrook Omni (Brookhaven, New York, USA). All of the samples were dissolved in warm distilled water prior to analysis.

A ZYP-1000E (Shanghai Zhaoyi Optoelectronic Technology Co., Ltd., China) polarized optical microscope was used to observe the dissolution process of cellulose in ILs.

The viscosity of ILs were tested using a DV2TLV viscometer (Brookfield, Ringgold, USA) at a speed of 150 rpm and room temperature.

RESULTS AND DISCUSSION

Effect of Hydrolysis Temperature

Temperature is considered to be one of the important factors that influence the hydrolysis of cellulose. It notably affected not only the yield but also the crystallinity of NC. The effect of hydrolysis temperature on the crystallinity index and yield of NC at different temperature (80, 90, 100, 110, and 120 °C) is shown in Fig. 1. The yield (NY) increased significantly with increasing temperature initially, which meant that the hydrolysis reaction was increased as the temperature was increased, giving 33.1% yield at 100 °C. It is expected that the dissociation of ion pairs of [Bmim]HSO₄ into individual [Bmim]⁺ cations and [HSO₄]⁻ anions is promoted by high temperature, leading to an increase in the diffusion coefficient of [H]⁺ ions, which go into the interspaces of 1,4-linked β -D-glucose units and disrupt intermolecular hydrogen bonds between the units (Jin *et al.* 2012; Hu *et al.* 2013). Moreover, when the temperature was increased, IL became less viscous, which would enhance the movement rate of [H]⁺ ions and then accelerate the hydrolysis of cellulose and improve the yield of CNC. However, higher temperature (≥ 100 °C) would cause excessive degradation of cellulose, resulting in decrease in both the CrI and NY.



Fig. 1. Effect of the temperature on the CrI and NY for a condition of 10% cellulose concentration, 100 MPa and 60 min for high homogenization process

On the other hand, the variation trend of crystallinity with temperature was the same as that of yield. CrI increased with temperature initially and then gradually decreased when heated beyond 100 °C. The first increase in the crystallinity with increasing temperature is attributed to the increase in $[H^+]$ ions, which facilitated the hydrolytic cleavage of glycosidic bonds, and individual crystallites are then released (Li *et al.* 2009). Therefore, higher crystallinity of NCC is obtained at high temperature hydrolysis reaction with BmimHSO₄ because the removal of amorphous parts essentially increased the crystallinity of the remaining NC (Man *et al.* 2011). The subsequent decrease in crystallinity is presumably due to the hydrolysis of crystalline components taking place at higher temperature after the removal of amorphous fractions. In addition, excessive hydrolysis of cellulose into glucose monomers suggesting loss of NC, also leading to decrease in its crystallinity indirectly.

Effect of the CE Concentration

Cellulose concentrations (expressed in mass ratio of cotton to IL) also influenced the crystallinity of NC greatly. Effects of the cellulose concentration on the CrI and NY are presented in Fig. 2. It is apparent that the crystallinity and yield of NC increased first and then declined gradually with the increase in cellulose concentration. The highest crystallinity and yield were obtained at 10%. The initial increase in the crystallinity and yield of NC is attributed to the greater number of [HSO4]⁻ anions present in the system. Lower cellulose concentration implies the presence of a higher concentration of IL. The gradual reduction in both of crystallinity and yield is mainly attributable to the weakening of the catalytic effect as well as swelling ability of [Bmim]HSO4 with increasing cellulose concentration. Besides that, the more viscous and supersaturated state of [Bmim]HSO4 ascribed to the increase of cellulose would affect the diffusion of anions into the fibers, and thus slow down or halt the hydrolysis reaction.



Fig. 2. Effect of the cellulose concentration on the CrI and NY at 100 °C and 2 h for hydrolysis, 100 MPa and 60 min for high homogenization process

Effect of the Homogenization Process

The size and size distributions of NC were directly impacted by the homogenization pressure and time (Table 1). The average size and polydispersity index (PDI) of NC at

different pressures and process times are shown in Table 1. It could be seen that the average size of NC exhibited a significant reduction from 681 to 210 nm with an increase in pressure from 25 to 100 MPa. The decrease in average size was principally due to the stronger shearing and impact forces on cellulose caused by higher pressure (Kreze and Malej 2003). The PDI of NC dispersions was no more than value of 0.3 during the homogenization process, implying the stable and narrow particle size distribution of NC. The effect of the processing time on the NC size was also evaluated. It appeared that the processing time had little effect on the NC size, but greatly impacted the size distribution. A longer processing time may result in a more uniform size distribution.

Pressure (MPa)	PDI (%)	Average Size (nm)	Time (min)	PDI (%)	Average Size (nm)
25	0.26	681	10	0.44	264
50	0.25	513	20	0.35	262
75	0.27	347	40	0.29	232
100	0.24	210	60	0.24	210

Table 1. Effect of Homogenization on the Size and Polydispersity of the NC

Conditions: Cellulose concentration 10%, 100 °C and 2h for hydrolysis; 100 MPa or 60 min homogenization process

XRD Analysis

XRD analysis was conducted to determine the changes in crystallinity and crystallite size of cotton cellulose, IL-C and NC prepared by [Bmim]HSO₄ combined with high pressure homogenization. The XRD patterns of the cellulose, IL-C, and NC are presented in Fig. 3.

The presence of the (110), (110), (200), and (040) crystallographic planes of typical cellulose I structure, respectively, are apparent from Fig. 3, where NC and IL-C exhibited similar diffraction peaks as cotton cellulose at $2\theta = 14.8^{\circ}$, 16.4° , 22.6° , and 35.5° (Li *et al.* 2012). The preservation of cellulose I structure was found in both RCe and NC, suggesting that the crystal integrity of cellulose had been maintained.



Fig. 3. XRD spectra of the cellulose, IL-C and NC

In some literature, the transformation from cellulose I to cellulose II can be found for regenerated cellulose from 1-butyl-3-methyl imidazolium chloride ([Bmim]Cl). This change might be ascribed to the dissolution and regeneration in [Bmim]Cl (Quan *et al.* 2010; Han *et al.* 2013). However, in current study, cellulose just swelled in [Bmim]HSO4, making the hydrolysis of cellulose a heterogeneous process. During the [Bmim]HSO4 mediated hydrolysis, the amorphous regions of cellulose were selectively hydrolyzed, removed and dissolved in IL, whereas the crystalline structure was preserved as crystalline regions retained in NC. Therefore, the calculated CrI of IL-C was higher than that of cellulose. But further mechanical treatment of RCe would lead to a slight decrease in crystallinity (Wang *et al.* 2017).

Morphology Analysis

The surface morphology of the NC was determined by SEM, TEM, and AFM analysis. Figure 4 shows the FESEM images of cotton cellulose, IL-C and NC. Figure 4 (a) indicates that the pristine cotton cellulose primarily consisted of bundles of aggregated cellulose fibrils with irregular shape and relatively large size of about 20 µm. Obviously, the pristine cellulose had a significantly larger diameter than the other specimens with rough surface morphology and low aspect ratio. After treatment with [Bmim]HSO₄, IL-C showed a nano-scale sized fibrous network with a smooth surface, as shown in Fig.4 (b). As presented in Fig. 4 (c), the aggregated structure of cellulose was broken down to a greater extent when high pressure homogenization was conducted. NC exhibited a cylindrical-shape crystal with a diameter of 50 nm to 100 nm and length of 500 nm to 800 nm. These substantial changes were attributed to the hydrolytic cleavage of the glyosidic bonds of the cellulose during the hydrolysis and the subsequent fibril separation from the fibrous network to form individual cellulose crystallites by mechanical treatment. Corresponding TEM and AFM images of NC are also presented in Fig. 4 (d), (e), and (f), which further confirm that rod-like NC are obtained from cotton cellulose using ILmediated hydrolysis assisted mechanical method.



Fig. 4. SEM images of the Cellulose (a), IL-C (b) and NC (c); TEM images of IL-C (d) and NC (e); AFM images of NC (f)

FTIR Analysis

Further chemical information was obtained by comparing the FTIR spectra of cellulose, IL-C, and NC. The results are presented in Fig. 5. As shown in Fig. 5, all cellulosic samples were almost identical, which indicate no changes in the functional groups. Characteristic peaks at 1424 cm⁻¹ (CH₂ scissoring), 1163 cm⁻¹ (C-O stretching or O-H bending) and 897 cm⁻¹ for C₁ vibrational mode, respectively suggest that the native cellulose I allomorph is preserved (Li and Taubert 2009; Han *et al.* 2013). It can be concluded that the ionic liquid-assisted homogenization process had no influence on the chemical composition of cellulose, even though the significant change in morphology was observed.



Fig. 5. FTIR spectra of the cellulose, IL-C, and NC

TGA and DSC Analysis

The thermal properties of pristine cellulose and NC samples were analyzed by TGA and differential scanning calorimetry (DSC) at temperatures ranging from room temperature to 600 °C at a rate of 10 °C/min under nitrogen flow. The decomposition profiles of the cellulose and NC are presented in Fig. 6a. Both samples had an initial small amount of weight loss at the temperature below 100 °C, corresponding to the evaporation of water loosely bound to the surfaces of samples. The onset thermal degradation temperature (T_{onset}), maximum weight loss temperature (T_{max}), weight loss at T_{onset} (WL), and char yield (CY) determined from curves of the cellulose and NC are summarized in Table 2.

For the pristine cotton, a typical decomposition trend with a T_{onset} of 305 °C was observed, and this coincided with a large mass loss, resulting in 20.2% CY at 550 °C. The T_{max} occurred at 365 °C. The NC exhibited significantly different thermal behavior than the original cotton, showing more gradual thermal transitions that began at a relative lower T_{onset} of 240 °C with a relatively higher CY of 25.7% and T_{max} of 417 °C, respectively. The results clearly showed that the cellulose had a slightly higher thermal stability compared with the NC. A decrease in the thermal stability after acid hydrolysis treatment has been discussed in the literature and has been found to be typical of sulfuric acid-hydrolyzed cellulose (Shankar and Rhim 2016). However, the NC samples displayed a higher T_{onset} compared with the other nanocellulose prepared using sulfuric acid hydrolysis reported in the literature (Ping and Hsieh 2010; Yue *et al.* 2012; Feng and Hsieh 2013). The overall improvement of the thermal stability performance of the NC samples was mainly because of the less adhesion of sulfate groups on the surface of the NC during IL-mediated hydrolysis (Wang *et al.* 2007). Additionally, the lower T_{onset} values were attributed to the smaller fiber dimensions that led to a higher surface area being exposed to heat and to the partial disruption of the cellulose crystal structure (Shankar and Rhim 2016; Nepomuceno *et al.* 2017).

The thermal difference between the CE and NCC was also revealed by the DSC curves (Fig. 6b), in which the cellulose sample showed a one-step pyrolysis process, while the NC sample exhibited a two-step pyrolysis process. This difference may have been because of the different decomposition-gasification processes for the samples (Ping and Hsieh 2010; Liu *et al.* 2016).



Fig. 6. TGA (a) and DSC (b) curves of the cellulose and NC

Table 2. Comparisons of the T_{onset} , T_{max} , WL, and CY at 500 °C for the CE, NCC, and CNCs from the Literature

Sample	T _{onset} (°C)	WL (°C)	T _{max} (°C)	CY (%)
Cellulose	303	7.7	365	20.2
NC	240	5.3	417	25.7
	172 (Liu <i>et al</i> . 2016)	5.1	385	23.4
CNC	221 (Rosa <i>et al</i> . 2010)	3.5	333	22.6
	180 (Ucar <i>et al</i> . 2013)	10.2	346	15.8

Recovery and Reuse of the Ionic Liquids

The used IL was recycled *via* a reduced pressure distillation method. The fresh IL and the recovered IL after used for 1, 2 and 5 times were characterized by FTIR. As shown in Fig. 7, the spectra of the recovered ILs look identical to the spectrum of fresh IL except for the presence of the broader peak within 3400~3600 cm⁻¹ and the extra tiny peak around 1000 cm⁻¹ in 5th-IL spectrum. The presence of broad band around 3400 cm⁻¹ for recovered IL is assigned to the intermolecular hydrogen bonds between IL and water due to the water retained in recovered IL. The extra tiny peak at 1000 cm⁻¹ might be ascribed to the trace amount of sugar remained in the recovered IL (Anjos *et al.* 2015). Purity of the recovered ILs was also ascertained with ¹H NMR, and the spectra are presented in Fig. 8. In both fresh and recovered ILs, the same characteristic ¹H signals for the [Bmim]HSO₄ (a~i) as well as the identical signal integration and splitting pattern are observed. However, with

the increase of cycles numbers, signals of detected impurity is more obvious, especially the moisture protons appeared at a $\delta = 1.75$ ppm.

The above results implied that the main chemical compositions of the recovered ILs is unchanged.

The activity of the recycled IL was confirmed from the maintained high yield of NC production upon reuse. Table 3 calculated the NY of NC upon reuse, the recovery percentage (RP) and viscosity of the recovered ILs. It was observed that all of the index, including NY, RP and viscosity showed a little decrease as the number of cycles increased.



Fig. 7. FTIR spectra of the fresh and recycled ILs



Fig. 8. ¹H NMR spectra of the fresh IL (a), 1st-IL (b), 2nd-IL (c), and 5th-IL (d)

Sample	Fresh IL	1st-IL	2nd-IL	3rd-IL	4th-IL	5th-IL
NY/%	33.1	30.6	30.4	28.9	29.1	27.4
RP/%	100	91.51	91.65	90.32	90.84	91.27
Viscosity/mPa-s	180.8	178.3	175.2	172.1	167.9	165.4

Table 3. Properties of Recovered Ionic Liquid

Polarizing microscopy (POM) was further used to compare the hydrolysis behavior of fresh and 5th-IL specimens, and the results are presented in Fig. S1. It is shown that after stirring for 2 h, no visible particle was observed in fresh IL, while for the 5th-IL, there was still a small amount of black eyeshot detected. These results indicated that there was a small decrease in the hydrolysis efficiency for the 5th-IL, which mainly can be ascribed to the presence of water in the recycled ILs.

CONCLUSIONS

- 1. Nanocellulose (NC) from cotton linter was obtained *via* IL-assisted high-pressure homogenization treatment. The IL [Bmim]HSO₄ here was used as both solvent and catalyst.
- 2. The hydrolytic reaction temperature, cellulose concentration, high-pressure homogenization time and pressure played an important role in the formation of NCC.
- 3. Compared with cotton linter, the basic cellulose I structure and chemical composition were preserved with higher degree of crystallinity and slight decrease in thermal stability. The obtained NC was found to have a rod-like shape with a diameter of 50 nm to 100 nm and length of 500 nm to 800 nm.
- 4. The IL was recycled by reduced pressure distillation and was then reused for cellulose dissolution. More than 90% of IL with trace amount of residues was successfully recovered and reused at least 5 times, where the NY of NC obtained by using the recovered ILs showed a slight drop compared with that by using fresh one. It is expected that the IL-assisted method can provide an environmentally friendly approach for the extraction of NC from cellulose materials.

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APPENDIX

The POM photographs of cellulose dissolution in the ILs (Fig. S1) can be found in the Appendix.



Fig. S1. POM photographs for cellulose dissolution in fresh IL for 0h (a), 1 h(b), 2 h(c) and 5th-IL for 0h (d), 1 h(e), 2 h(f) and 4 h(g) under the conditions of 5% cellulose concentration, 100 °C.