Ionic liquid-assisted nanocellulose preparation from microcrystalline cellulose

Gamal Abdalla Suliman Haron,1 Hilmı Bin Noh,1,2 Muhammad Moniruzzaman1,2*

1Department of Chemical Engineering, Universiti Teknologi PETRONAS, 32610 Bandar Seri Iskandar, Perak, Malaysia
2Center of Research in Ionic Liquids (CORIL), Universiti Teknologi PETRONAS, 32610 Bandar Seri Iskandar, Perak, Malaysia

* E-mail: m.moniruzzaman@utp.edu.my

Abstract. Nanocellulose (NC) has generated interest from the scientific community because of their biodegradability, and unique physiochemical characteristics. In this study, ionic liquid 1-butyl-3-methylimidazolium hydrogen sulfate [Bmim][HSO₄] combined with high ultrasonication is used to prepare NC from microcrystalline cellulose (MCC). The investigation by atomic force microscopy (AFM) revealed that the obtained NC had a rod-like shape with average particle diameter and length of 0.77±0.28µm, 2.11±0.65µm respectively. Fourier transform infrared spectroscopy (FTIR) characterization exhibited that the prepared NC maintained the cellulose type I structure and the recovered IL (97%) composition remained intact as the pure IL. Therefore, it is expected to develop a green approach to produce nanocellulose with high quality using ILs.

1. Introduction
Nanocellulose (NC) has grabbed the attention of industry and academia due to its several attractive properties like high aspect ratio, stiffness, and surface area (1)(2)(3). The application of NC is widely seen in areas such as nanocomposites (4), strong transparent films (5), biodegradable packaging materials (6). Cellulose the monosaccharide which composed of β-1,4-linked D-glucopyranose rings is the primary source of NC production. These rings are linked together through the glucosidic oxygens point. The complex hydrogen-bonding networks are responsible for the tough and high stiffness of cellulose fibrils (7)(8). For these reasons, the choice of tailor-made reinforcing fibers into biopolymers is of central importance (9).

The extraction of NC from cellulose is carried out via two main ways acid hydrolysis and mechanical processing. In acid hydrolysis, a huge amount of wastewater can be generated from the washing process in addition to that the yield is low because some parts can be converted to sugars in an acid environment (10). In contrast, the main drawback of mechanical processing is high energy

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consumption. To overcome this issue, mechanical techniques were combined with other kinds of pretreatment ways (8)(10). Thus, the development of an environmentally benign NC medium can be achieved using ILs.

Ionic liquids (ILs) are a group of salts in a liquid state at room temperature. Most of ILs consist of inorganic anions and organic cations which possess unique features such as high polarity, thermal, chemical stability and special hydrophobicity/hydrophilicity, negligible vapor pressure, and nonflammability (11)(10). Cation and anion like Bmim+, Cl- respectively can associate with the oxygen atoms of H-O-H bonds, and the hydroxyl proton of H-O-H bonds respectively. These interactions can lead to the destruction of the extensive hydrogen bonding network among cellulose chains, resulting in the dissolution of cellulose (12)(13). For example, Lee et al. employed a high-pressure homogenizer for cellulose nanofibrils preparation from microcrystalline cellulose (MCC). After 10 passes, the diameter of the fibrils was in the range from 28 to 100 nm (14). NC was also prepared from pulps of eucalyptus which had a diameter varying from 20 nm to 100 nm (15). However, the homogenizer severely altered the physicochemical features of NC for instance, lower crystallinity and thermal stability. This is probably due to the rupture of the entangled molecular chain networks as well as the mechanical degradation of long-chain molecules during homogenization (15). Pang et al (16) isolated NC with a rod-like shape and diameter of 15–22 nm and 220–300 nm in length. It was also revealed that the thermostability of NC was greatly enhanced compared to that prepared by the traditional acid hydrolysis. Ultrasonic treatment of cellulose in ILs can offer a potential and efficient technique for NC preparation with high crystallinity, yield and thermal stability.

To the best of the author’s knowledge, up to now, only a few researchers focused on the coupling of the green and designer solvent ionic liquids with the mechanical techniques mainly, high-intensity ultrasonication. In this study, the preparation of nanocellulose from microcrystalline cellulose by combing IL [Bmim][HSO4] and ultrasonication were investigated. Fig1 shows the ionic liquid used in the current study.

2. Experimental

2.1. Materials
Microcrystalline cellulose (MCC) with a degree of polymerization (DP) of 150 and particle size of 50 µm and IL 1-butyl-3-methylimidazolium hydrogen sulfate [Bmim][HSO4] were purchased from Sigma Aldrich deionized water.

![1-butyl-3-methylimidazolium hydrogen sulfate [BMIM]HSO4](image)

Figure 1. IL [Bmim][HSO4]

2.2. Nanocellulose preparation
10% MCC was added slowly to the ionic liquid in a round-bottom three-neck flask then the mixture was stirred by magnetic stirrer at 200 rpm 90°C for 120minutes. Afterward, the mixture was quenched by adding cold deionized water until an off-white precipitate was formed. Then, the mixture was sonicated by [Sonic & Materials, INC, U.S.A] at room temperature for 20mintues at 40% amplitude
and 20kHz. Consequently, nanocellulose was isolated by washing the mixture three times using centrifugation at 2000rpm for 15 minutes. Then the aqueous mixture of NC and IL was introduced to a high-speed centrifuge (13000 rpm) for 20 minutes to isolate NC. Afterward, the mixture of IL and deionized water introduced to a rotary evaporator to evaporate the water and recover the ionic liquid. The obtained NC was freeze-dried for subsequent analysis. Fig.2 illustrates the overall steps of nanocellulose preparation.

![Flowchart](image)

**Figure 2.** Overall steps of NC preparation

3. Characterization of nanocellulose

3.1. Atomic force microscopy (AFM)

A small amount of NC suspension was left to dry for 24h on glass surface before measurements in tapping mode with an AFM Olympus (OMCL-AC type 3 series) equipped with a rectangular cantilever with a tetrahedral probe (L=55, W=31, 35). Dimensions and images of NC were analyzed with MountainsLab software.

3.2. Fourier transform infrared spectroscopy

The functional groups of the samples were measured by Thermo Scientific (NICOLET is5) FTIR spectrometer with the wavenumber between 4000 and 5000 cm⁻¹ and the resolution of 4 cm⁻¹. Two mini-KBr plates were used to place the sample of MCC and NC then pressed into a thin disk. While the ILs samples were placed directly on the ATR sample holder.

4. Results and discussion

4.1. AFM analysis

As depicted in Fig.3A, NC with rod-like shape was successfully prepared from MCC. The aqueous suspension of NC was unstable causing huge agglomeration thus making the visualization of the individual crystals more challenging. And this phenomenon can be attributed to the surface electrical charge (17). For example, Gonçalves and co-workers (18) prepared cellulose nanowhiskers (CNWs) with IL 2-hydroxyethylammonium hydrogen sulfate [2-HEA][HSO₄]. The produced CNWs had a zeta potential of 19.1±0.5 mV which formed stable aqueous suspension. In this study, the average particle diameter and length were 0.77±0.26µm and 2.11±0.65µm respectively. This relatively bigger dimension is probably due to a lack of process optimization which is currently being conducted in our lab.
4.2. FTIR analysis

From figure 4A, it can be seen that both samples (MCC, NC) showed similar chemical compositions. The spectra region of 3600–3200 cm\(^{-1}\) indicating O–H stretching vibrations and the peak at 2895 cm\(^{-1}\) is the stretching vibration of C-H. At 1640 cm\(^{-1}\) region, the presence of the absorbed water assigned by the bending of O-H bond. The bending vibration of CH2 at the group C6 appeared at 1430 cm\(^{-1}\) (19). The peak of the asymmetric stretching of C–H groups of polysaccharides appeared at 2369 cm\(^{-1}\). The C–O stretching and C–H vibration of cellulose molecule peak was detected at 1055 cm\(^{-1}\) while the peak at 900 cm\(^{-1}\) was associated with the C–H vibration of β-glycosidic linkages between glucose units in cellulose (10). It can be concluded that the preparation of nanocellulose by [Bmim][HSO\(_4\)] ionic liquid did not affect the chemical composition of native cellulose. As shown in figure 4B, the chemical composition of the regenerated [Bmim][HSO\(_4\)] remained identical to the pure IL except for the extra peak around 3600-3200 cm\(^{-1}\) which assigned to the hydrogen bonding. This peak comes from the small trace of water present in the mixture (20)(21). This successful regeneration of IL (97%) confirms the practicality of utilizing ILs for NC production.
Figure 4. FTIR spectra of MCC and NC A) FTIR spectra of pure [Bmim][HSO\textsubscript{4}] and regenerated [Bmim][HSO\textsubscript{4}].
5. Conclusion
Nanocellulose with average particle diameter and length of 0.77µm and 2.11µm respectively was successfully prepared using IL [Bmim][HSO₄] combined with ultrasonication. The rod-like shape of NC was revealed by AFM analysis. FTIR characterization showed that NC maintained the cellulose type I structure and the recycled IL (97%) remained unchanged. However, further characterizations are needed to explain the agglomeration of the particles and the relatively big particle size.

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