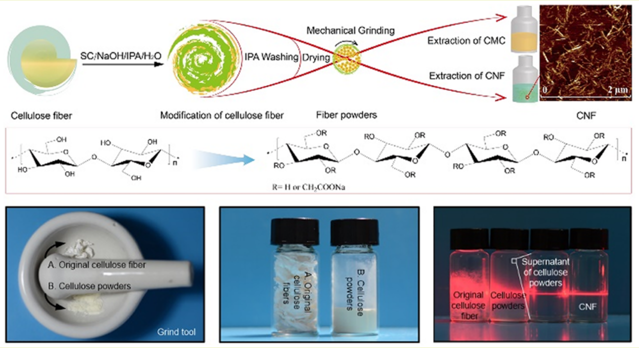
ACS Sustainable Chemistry & Engineering
Research Article
pubs.acs.org/journal/ascecg

Integrated Production of Cellulose Nanofibers and Sodium Carboxymethylcellulose through Controllable Eco-carboxymethylation under Mild Conditions

Lingfeng Su, Yanghao Ou, Xiao Feng, Meiyan Lin, Jun Li, Detao Liu,* and Haisong Qi*

State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510640, China

ABSTRACT: In the past few decades, the preparation of cellulose nanofibers (CNF) has been restricting its application in industrialization. A fast and green preparation method is urgently needed to promote the industrialization process. In this paper, eco-carboxymethylation of cellulose was first used to enable the carboxymethylation of eucalyptus wood dissolving pulp (EWDP) and then we introduced a new idea of isopropanol alcohol (IPA) washing followed by drying to disintegrate chemical modified fibers into dried nanometer-sized cellulose powders. The cellulose powders were transferred into CNF with a width of 18 nm and length of several hundred nanometers after high-pressure homogenization. The powder form of cellulose provided more chances for fibrillation which resulted in low energy consumption and high yield of CNF. The obtained CNF were employed to prepare nanopaper and conductive nanopaper by vacuum filtration. The fabricated nanopaper exhibited a high optical transmittance of 92% with a maximum tensile stress of 107.5 MPa. However, the optical transmittance of conductive nanopaper slowly decreased to 68% when the square resistance reached 18 Ω/sq. This novel route for preparing CNF was low toxicity, environmentally friendly and solved the blocking of the high-pressure homogenization process. The fabricated transparent flexible conductive nanopaper with smooth surface, high transmittance, high strength and good conductivity has great potential in the field of optoelectronics.



KEYWORDS: *Eco-carboxymethylation, Cellulose nanofibers, Nanopaper, Conductive nanopaper, Silver nanowires*

INTRODUCTION

As a renewable biomass resource, plant cellulose has been a part of people's life since antiquity.[1] It deserves special attention due to its abundance, renewability, lightweight, recyclability, biodegradability and many other interesting properties and characteristics.[2] The growing demand for environment sustainability has encouraged research into biodegradable polymers in order to minimize the negative impacts of conventional polymers. Industrial ecology, eco-efficiency, and green chemistry are presently directing the developments of the new materials, products, and processes. Under these circumstances, cellulose nanofibers, or more specifically its main derived components of such cellulose nano crystalline, bacterial cellulose and electrospining cellulose nanofibers, with at least one dimension in nanoscale (1−100 nm), has been found to be applied as advanced substrates[3] in fabricating packaging, coating, papermaking, electronics and devices such as OLED substrate[4,5] and solar cells.[6,7] The simple structure of cellulose is fully known, and the rich hydroxyl groups in the cellulose molecule (six in each repeat unit) enable facile formation of hydrogen bonds with high stiff structures, which prevents the effective isolation of cellulose nanofibers from the cell wall. As the main building material out of which woods are made, the research in the extraction methods of cellulose has not stopped since its discovery. There are many methods applied to prepare cellulose nanofibers, such as mechanical method (including high-pressure homogenization,[8] grinding,[9] refining,[10] extrusion,[11] blending,[12] ultrasonication,[13] ball milling with ultrasonification[14] and so on. In 1983, Turbak et al.[8] and Herrick et al.[15] were the first to patent a new process to produce cellulose nanofibers by repeatedly passing a liquid suspension of fiber cellulose through a high-pressure homogenizer until the cellulose suspension become substantially stable. The process converted the cellulose into cellulose nanofibers without substantial chemical change, but production of cellulose nanofibers using only mechanical disintegration requires high energetic cost.[16] Several strategies have been proposed to obtain fibers that are less stiff and cohesive before sending to mechanical fibrillation process, thus decreasing the energy needed for fibrillation. There are three alternatives employed: (1) limit the hydrogen bonds inside fibers, and/or (2) add a repulsive charge that is different to the original cellulose molecular chains, and/or (3) decrease the degree of polymerization (DP) or the amorphous

Received: September 5, 2018
Revised: December 6, 2018
Published: January 22, 2019

DOI: 10.1021/acssuschemeng.8b04492

link between individual cellulose fibers. From this point, biological and chemical pretreatments (including enzymatic hydrolysis,[17] TEMPO mediated oxidation,[18] carboxymethylation,[19] acetylation[20] pretreatment and so on) are taken into consideration. The high-pressure homogenization together with biological and chemical pretreatments greatly decreased the energy consumption and reduced difficulty by solving the blocks of the head of the high-pressure homogenizer. Other cellulose nanofibers have different formation mechanisms compared with mechanical methods with or without biological and chemical pretreatments. Bacteria cellulose (BC) is high-purity cellulose generated by different bacteria in aqueous culture media that contains a sugar source with a DP ranging from 3000 to 9000 and a distinct crystallinity of 80−90%. The generating time of BC ranges from few days up to 2 weeks depending on the processes employed.[21] BC is generated in the form of twisting ribbons with cross sections of 3 to 4 nm × 70 to 140 nm, and usually the obtained BC has a length of more than 2 μm.[22] Researchers usually focus on finding different bacterium and the postmodification of BC film. The high-purity and the dense networks of BC with different surface modification would obtain special functions like desirable contact angle,[23] and give it a broad prospect in food packing[24] and some other fields. Electrospun cellulose nanofibers (ECNF) are considered to be applied most likely in industrial production with controllable diameter and length. To produce ECNF, cellulose is first dissolved in an appropriate solvent. Then, a high voltage is applied to a droplet of cellulose solution to overcome the surface tension and to form a jet of the solution. While it passes through air, the solvent evaporates, forming a filament, which is collected on an electrically grounded target.[25] This electro-spinning process makes it possible to fabricate complex three-dimensional shapes and even different material microcapsules.[26] In 2005, Ma et al.[27] used acetone/DMF/trifluoroethylene as a dissolving media and had produced ECNF with a diameter ranging from 200 nm to 1 μm. In 2013, Xuan et al.[28] determined that cellulose was difficult to dissolve in ordinary solvents and electrospin into CNF directly, so cellulose was modified into cellulose acetate (CA) nanofibers and CA nanofibers were prepared by electrospinning and then subjected to alkali treatment to obtain CNF. In 2014, He et al.[29] improved the solution of cellulose in DMAc-LiCl and produced ECNF for tissue engineering. The preparing methods of cellulose nanofibers have developed rapidly over the past years; however, research efforts on isolating cellulose nanofibers have still encountered numerous problems, such as energy-extensive consumption, serious pollution, high cost, time-consuming and single product (only cellulose nanofibers). Thus, it is necessary to explore new methods to solve these problems.

Among the typical strategies for fabricating nanoscale-sized cellulose-based materials, the cellulose nanofiber, generated by mechanical isolation of cellulose with or/and without biological and chemical pretreatments is arguably the most versatile and easily scalable method.

In this research, we demonstrated a process to prepare cellulose nanofibers by both a novel partial carboxymethylation of eucalyptus wood dissolving pulp (EWDP) carried out through a solvent media process and two mechanical processes including fine grinding after drying and high-pressure homogenization. The carboxymethylation of EWDP was carried out by treating plant fibers in H_2O/isopropyl alcohol (IPA)/NaOH/$ClCH_2COONa$ to increases the anionic charges through the formation of carboxyl groups on the surface of the cellulose nanofibers. The carboxymethylation treatment made the fibrils highly charged and easier to liberate. Followed by a washing process with IPA and drying process, the chemical modified fiber was fine-ground into cellulose powders with a concentrated small size. After the extraction of CMC by water, a 30 min high-pressure homogenization was employed to prepare CNF. This new method for preparing CNF had the following advantages: (1) the carboxymethyl cellulose with low degree of substitution (DS) can be carried out easily by industrial production; (2) the washing process only consumed a little of IPA and it was recyclable during the drying process; (3) the chemical modified and IPA washed fiber could be ground into cellulose powders easily with low energy consumption and the highly concentrated small size of 49.1 μm contributed a lot in preventing the blocking of the high-pressure homogenization process; (4) benefited in the harsh cross section of cellulose powders, the fibrillation of cellulose powders became easier and it increased the yield of CNF after high-pressure homogenization.

■ EXPERIMENTAL SECTION

Materials. Eucalyptus wood dissolving pulp (EWDP) was purchased from Guangzhou Chenhui Pulp & Paper Trading Co., Ltd. with a solid content of 33%, and it was heated under 105 °C for 4 h until oven dry. Sodium hydroxide (NaOH, AR, 99.7%) and isopropyl alcohol (IPA, AR, 99.7%) were both provided by Guangdong Guanghua Sci-Tech Co., Ltd. Sodium chloroacetate (SC, AR, 98.0%) was bought from Shanghai Macklin Biochemical Co., Ltd.

Carboxymethylation of Eucalyptus Wood Dissolving Pulp. The carboxymethylation section used oven dry EWDP as the starting material. First, 2 g NaOH was added into 50 g of deionized water and continuously stirred after NaOH totally dissolved. After that, 150 g of IPA was immediately added to prepare the reacting environment. Then, 2 g of oven dry EWDP was successively added to the mixed solvent to complete alkalization activation of EWDP fiber through continuously stirring for 1 h under room temperature (20−25 °C). 75 g of mixed solvent was removed and 2 g of SC was added into the mixed solvent after the pretreatment of NaOH. Finally, carboxymethylation of EWDP fiber was completed by continuously stirring under 60 °C at a low speed (150−300 rpm) for a certain time ranging from 30 min to 2 h. After the carboxymethylation process finished, the reacting solvent was filtered and removed and the fiber filter cake was dispersed by IPA and washed 2 to 3 times, the sample was named IPA-washed fibers. It is worth noting that the fiber gradually agglomerated and hardened in the IPA washing process, and the fiber needed to be fully dispersed to ensure adequate washing by gradually reduce the temperature of the washing solution. To make it different, IPA was replaced by water to wash fiber filter cake and the sample was named water-washed fibers. Both IPA-washed fibers and water-washed fibers were dried at 75 °C until oven dry (usually it would take no more than 1 h).

Fabrication of Cellulose Powders. The fabrication of cellulose powders was based on previous experiments. Oven dry IPA-washed fibers were ground by a mortar and pestle. After the grinding process, the cellulose powders were passed through a 100-mesh sieve in order to get better separation of cellulose powders from coarse fiber. The sample was named IPA-washed cellulose powders. The IPA-washed cellulose powders were washed by deionized water and passed through a polyester film of 22 μm twice and deionized water was also used to wash cellulose powders with the help of dialysis membrane (molecular weight of 8k−10k) overnight. In the last washing step, 95 wt % alcohol was utilized to prevent water-washed cellulose powders from clumping together and being difficult to disperse again. The sample was named water-washed cellulose powders.

DOI: 10.1021/acssuschemeng.8b04492

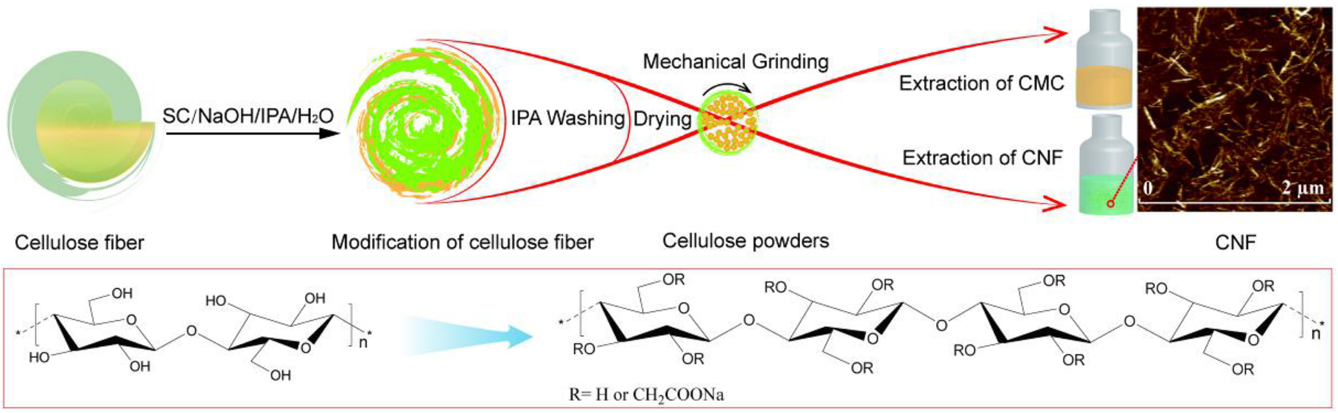


Figure 1. Schematic illustration of the process for preparing cellulose powders and cellulose nanofibers.

Fabrication of Cellulose Nanofibers (CNF). Water-washed cellulose powders were added to 500 mL of deionized water and stored for use. CNF was achieved by high-pressure homogenization (nano DeBEE, US) for a cycle of 20 min and high-speed centrifugation at 5,000 rpm for 30 min. The high-pressure homogenization process can stop in advance as long as the water-washed cellulose powders dispersing liquid become clarified. The concentration of CNF was measured through evaporation of quantitative CNF suspension.

Fabrication of Nanopaper and Conductive Nanopaper. Nanopaper was manufactured through vacuum-filtration under the vacuum degree of 0.1 MPa using a membrane filter with a diameter of 5 cm and pore size of 22 μm. The obtaining of conductive nanopaper was similar to nanopaper with an extra step of adding different concentrations of Ag NWs suspension to the surface of the wet nanopaper. Both nanopaper and conductive nanopaper were dried at 60 °C.

Characterization. *Scanning Electron Microscopy (SEM).* The surface appearance and the relative content of C/O/Na/Cl of the original fibers, IPA-washed fibers, IPA-washed cellulose powders, and water-washed fibers were measured with the help of scanning electron microscopy (SEM, EVO 18, Germany). The samples were first dispersed in 95 wt % alcohol, and then the dispersing solution was dropped on clean mica film and dried at room temperature. The mica films with samples were glued to a steel support and covered with a gold layer.

Atomic Force Microscopy (AFM). The appearance of CNF, nanopaper and conductive nanopaper was observed with the help of atomic force microscopy (AFM). CNF suspensions were diluted to 0.05% with deionized water and then dropped on clean silicon wafer and dried at room temperature. The nanopaper and conductive nanopaper were glued to a silicon wafer by double faced adhesive tape.

Degree of Substitution (DS). Degree of substitution of water-washed cellulose powders was measured in reference to an ashing method[30] with some optimization. 1 g of water-washed cellulose powders was burned at 300 °C for 3 min and 800 °C for 30 min to ash, and the ash was dissolved in 0.1 mol/L HCl solution. The DS was measured through acid–base titration by 0.1 mol/L NaOH solution. The titration end point was given out by pH meter with pH = 6–8. The calculation of eqs 1 and 2 was given as follows

$$B = \frac{V_1c_1 - V_2c_2}{m} \tag{1}$$

$$\mathrm{DS} = \frac{0.612B}{1 - 0.080B} \tag{2}$$

where B stands for the carboxymethyl molar number in each gram water-washed cellulose powders, mmol/g. V_1 stands for volumetric value of standard HCl titration solution, mL. c_1 stands for the concentration of standard HCl titration solution, 0.1 mol/L. V_2 stands for volumetric value of standard NaOH titration solution, mL. c_2 stands for the concentration of standard NaOH titration solution, 0.1 mol/L. m stands for the quantity of the water-washed cellulose powders, g.

Infrared Analysis (FT-IR). Infrared analysis (FT-IR) of original fibers and water-washed fibers with different carboxymethylation times was measured in the spectral range from 400 to 4,000 cm^{-1} using a TENSOR27 from Bruker Inc. The fibers were comminuted and mixed with KBr separately. The concentration of KBr was 10% in every sample.

X-ray Diffraction (XRD). Degree of crystallinity of original fibers, fiber powders with different carboxymethylation times and nanopaper fabricated from CNF was measured by X-ray diffraction (D/max-3A, Japan) with an angle ranging from 4° to 40°.

Ultraviolet–visible Spectroscopy (UV–vis). The transmittance of nanopaper and conductive nanopaper was measured by ultraviolet–visible spectroscopy (UV–vis, DU 7HS, USA) with wavelength ranging from 400 to 800 nm. The thickness of nanopaper and conductive nanopaper was 35–40 μm.

Mechanical Property. Mechanical property of nanopaper and conductive nanopaper was measured by tensile compressive material testing machine (INSTRON 5565, USA) with the stretching velocity of 5 mm/min. The samples were cut into rectangular strips with length of 4 cm and width of 0.5 cm. The test data was taken into consideration only when the fracture position was in the middle of the paper strip.

Resistance of Conductive Nanopaper. The conductivity of different conductive nanopapers was measured by a four probe resistance tester (KDY-1). The samples were all cut into square pieces of 1 cm^2 and tested multiple times to take the average data.

■ RESULTS AND DISCUSSION

There were three hydroxyl groups on every glucose unit, which limited the degree of substitution (DS) of carboxymethyl group between 0 and 3. Functional groups transferring from hydroxyl group to carboxymethyl group would increase the steric hindrance between every cellulose molecular chain. The carboxymethylation process under alkaline conditions also cut cellulose long chain into short ones, which helped in preparing CNF. This was because NaOH was good at alkalization and swelling plant fibers up, together with peeling reaction and alkaline degradation, which made it easier for chemiosmosis and reaction of SC. The mechanism of reaction was that cellulose was converted into alkalized cellulose according to eq 3:

$$\text{Cell–OH} + \text{NaOH} \rightleftharpoons \text{Cell–ONa} + \text{H}_2\text{O} \tag{3}$$

Alkalized cellulose had a much better reactivity, which made the carboxymethylation of cellulose with SC much easier. SC

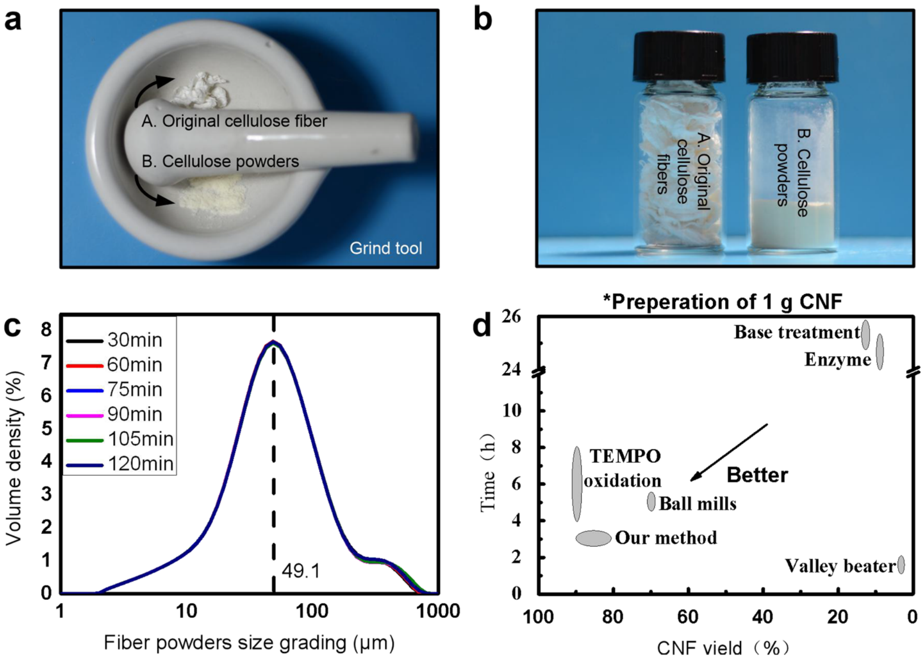


Figure 2. (a) Grind tool used to grind IPA-washed fibers into IPA-washed cellulose powders. (b) The 1 g of original fibers (A) and 1 g of IPA-washed cellulose powders (B). (c) Size grading of IPA-washed cellulose powders treated with grind tool shown in panel a. (d) Producing time of 1 g CNF with different methods.

was usually used to produce carboxymethyl cellulose. The mechanism of carboxymethylation was indicated by eq 4:

$$\text{Cell–ONa} + \text{ClCH}_2\text{COONa} \rightarrow \text{Cell–OCH}_2\text{COONa} + \text{NaCl} \tag{4}$$

The side reaction was indicated by eq 5:

$$\text{ClCH}_2\text{COONa} + \text{NaOH} \rightarrow \text{HOCH}_2\text{COONa} + \text{NaCl} \tag{5}$$

This reaction must be continued under the basic environment. In addition, it was named Williamson ether synthesis.

Fibers had the potential to be transferred into CNF. In this research, as the fabrication process shows in Figure 1, fibers were invoked as the starting material. Fibers were treated with sodium hydroxide in order to form alkalized fiber, which owned a higher reactivity. The degree of modification should be controlled to obtain a suitable degree of carboxymethylation, which both help to separate cellulose from each other and reserve a certainly high yield after chemical and mechanical treatments. The change of the fundamental group would influence the crystalline region so that cellulose was easier to obtain. With carboxymethyl groups present on cellulose chains, fibers were easier to be made into nanosized ones. It made the EWDP fibers more convenient for high-pressure homogenization so as to reduce energy consumption. There was about one-third water in the reacting system: part of hydrogen bonds would be broken, and the drying process took out most water and IPA inside fibers, which meant fewer hydrogen bonds between cellulose molecular chains. During the carboxymethylation process, water-soluble sodium carboxymethyl cellulose (CMC) dissolved in water and adsorbed inside the fibers; this process caused the morphological change greatly. The cellulose powders were produced by grinding, which meant that there must be full of gaps in the two sides of the cellulose powders. This structure contributed to high-pressure homogenization, which raised the yield of CNF instead of debris and declined the energy consumption during high-pressure homogenization.

The grind tool is shown in Figure 2a. Compared to original fibers, IPA-washed fibers were easier to be ground into cellulose powders, and there was no need for any complex process. The 1 g original fibers (A) as well as 1 g IPA-washed cellulose powders (B) are shown in Figure 2b: the cellulose powders were smaller than the original fibers. As shown in Figure 2c, compared to original fibers whose average length was no less than 1 mm, IPA-washed cellulose powders had a concentrated size distribution at 49.1 μm on any dimension. There was only 10% cellulose powders beyond 153 μm that could be screened easily by 100 mesh if necessary. The feature of small size as well as low concentration of powders suspension during the high-pressure homogenization process not only solved the blocking problem of mechanical treatment but also reduced time consumption, energy consumption and promoted yield during producing CNF by using traditional methods. The existence of cellulose powders with large size was due to incomplete reaction, grinding process and different crystalline structures of fibers. As shown in Figure 2d, our method had a comparatively better side in treating time and CNF yield compared with TEMPO oxidation,[31] ball milling,[32] enzyme treatment and base treatment.[33] Different pretreatment with the same homogenization post-treatment would differ in energy consumption. According to the general energy consumption studied by Ankerfors,[34] 2% (w/w) carboxymethylated NFC, which has been produced by one-time homogenization at 1600 bar, would cost 2221 kWh/tonne. Under this condition, A Naderi[35] averaged out eq 6:

$$\text{EC}_{p,n}(\text{kWh/tonne}) = \frac{2221 \times 2 \times p \times n}{1600 \times 1.2} \tag{6}$$

In this equation, p and n stand for the applied homogenization pressure and the number of passes through the homogenizer,

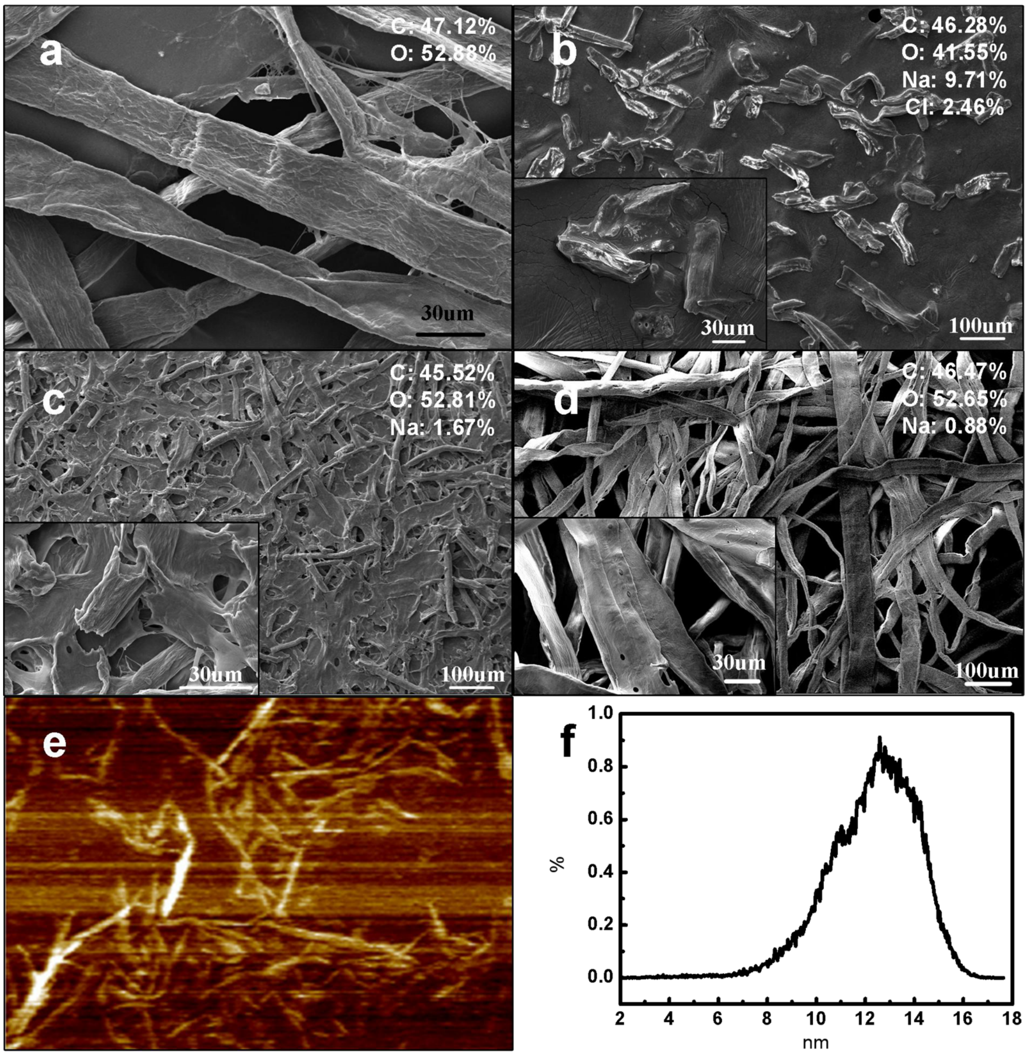


Figure 3. (a) SEM image of original fibers. (b) SEM image of IPA-washed cellulose powders. (c) SEM image of water-washed cellulose powders. (d) SEM image of water-washed fibers. (e) AFM image of CNF. (f) Depth distribution of CNF in Figure 3e.

respectively. In our study, the pressure was set to 100 bar, and the number of passes through homogenizer was set to 3–4, so the energy consumption was about 694–925 kWh/tonne. Its lower than nonpretreatment bleached kraft pulp (12 000–70 000 kWh/tonne), nonpretreatment sulfite pulp (27 000 kWh/tonne) and TEMPO or enzyme pretreatment (~20 000 kWh/tonne).[36,37] Although the TEMPO oxidation pretreatment is the best method so far in quality, it is much expensive than SC and IPA used, giving the carboxymethylation pretreatment a broad prospect.

The most brilliant breakthrough in this work was that fibers were very easy to be ground into cellulose powders by grinder. In Figure 3, the original fibers, IPA-washed cellulose powders, water-washed cellulose powders and water-washed fibers were made into paper, separately. Figure 3a showed the original fibers of EWDP. The fibers were several microns in length and diameter and the surface was rough with some micro fibrils attached to the large long fibers. As shown in Figure 3b, accompanied by a carboxymethylation process, micro fibrils disappeared and numerous crystal particles were attached to the surface of IPA-washed cellulose powders, while others may be embedded in holes of fibers. The crystal particles were shown as the white part. Referring to the reacting mechanism of carboxymethylation of cellulose, the carboxymethylation happened primarily in noncrystalline areas irregularly distributed in the fiber. After IPA washing, the byproduct $HOCH_2COONa$ as well as NaCl, which does not dissolve in IPA, formed the crystal particles. These crystal particles acted as scissors and became one of the reasons that caused fibers to be cut easier into cellulose powders. Another reason was that the hydrogen bonds decreased thanks to fewer fibrils and the barrier of crystal particles. From Figure 3c, compared with Figure 3b, it was obvious that there were no crystal particles in water-washed cellulose powders. This was because the crystal particles were water-soluble. The wash not only retained the small size after grinding but also purified it and exposed more fibrils for homogenization. Compared to the complete original fibers, the structure of water-washed cellulose powders must be easier, energy saving and reduced the risks of blocking of homogenizer head during homogenization in the same situation. The little holes of particles adsorbed made it easy for fibrillation to get CNF. If it were washed with water but not IPA, fibers would exhibit different properties after drying. The most intuitional phenomenon was that fibers were hard to grind into cellulose powders. The fibers were still too big in length and diameter to go through homogenizer head, and the

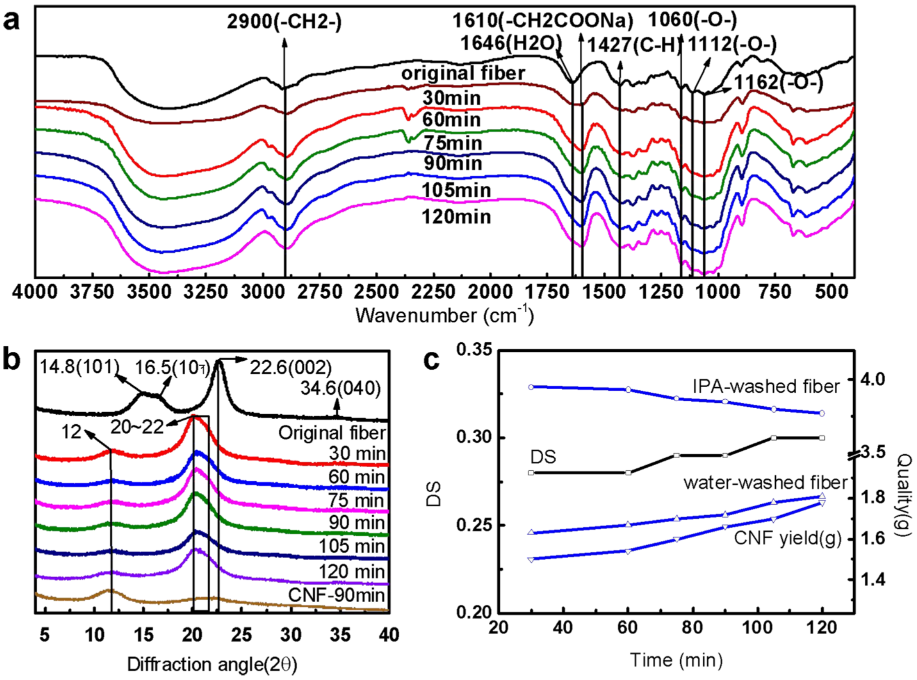


Figure 4. (a) FT-IR curves of cellulose with different modification time. (B) XRD curves of original fibers and fibers with different modification times. (C) DS-CNF Yield-IPA-washed-water-washed−time curves of cellulose with different modification times.

surface of water-washed fibers was much smoother than original fibers shown in Figure 3a. This structure would make it hard for cutting down and fibrillation, which would result in blocking. Instead, they intertwined into a piece of paper during filtering. As shown in Figure 3d, the surface of water-washed fibers was so smooth that even grain and grain holes were filled with tiny composite and these tiny composite glued neighboring fibers together. The structure of mutual bonding obtained higher binging force that made it difficult to disperse and grind the fibers through mechanical action.

Further study of the relative element content of four different materials is shown in Figure 3. IPA-washed cellulose powders had higher content of Na and Cl, and the C/O ratio was higher than those of the other three due to the existence of IPA and residual NaCl and $HOCH_2COONa$. The C/O ratio of water-washed cellulose powders was higher than that of water-washed fibers, and the content of Na was lower in the meanwhile. This could be explained that although most soluble carboxymethylcellulose was washed away during washing with deionized water, there were more CNF lost after it was made into powder form.

The CNF prepared by homogenization was showed in Figure 3e, the length of CNF was about several hundred nanometers and the diameter was about 10−20 nm. Figure 3f shows the depth distribution of the whole part in Figure 3e, which was calculated by nanoscope analysis. The data centrally distributed between 10 and 15 nm; the curve could also indirectly indicate the diameter distribution of CNF.

FTIR analysis showed the changes of functional groups of fibers before and after carboxymethylation. As shown in Figure 4a, the curves of cellulose powders treated with different times were similar to each other and had little difference presented with original fiber. Referring to known materials, wavenumbers 1060, 1112 and 1162 cm^{-1} stand for −O− of stretching vibration of −OH groups of cellulose, stretching vibrations of ether bonds in cellulose molecules and stretching vibrations of ether bonds (C−O−C) on cellulose skeleton, respectively. 1427 cm^{-1} stands for C−H, 1610 cm^{-1} stands for carboxylate COO− ($-CH_2COONa$), 1646 cm^{-1} stands for the absorption peak of adsorbed water in the cellulose and 2900 cm^{-1} stands for $-CH_2-$. The C−H characteristic absorption peak could be found in both original fibers and modified fibers. However, COO− characteristic absorption peak could be found only in the curves of modified fibers. It was concluded that the reacted fiber had a $-CH_2COO-$ group, which could be defined as carboxymethyl cellulose. Figure 4b shows the X-ray diffraction patterns of the fibers. The original fibers exhibited the typical cellulose I crystalline form with peaks located in 22.6°, 16.2° and 14.8°.[38] Whereas the modified fibers showed the typical cellulose II crystalline form, with peaks located in 12° and 20°−22°.[39] This indicated that the crystalline form of fibers changed during the modification of fibers.[40] The average crystallinity of original EWDP was about 44% while the IPA-washed fiber powders before washing by deionized water and homogenization was as high as 90%. This result explained why the IPA-washed fibers were easier to be ground into fiber powders. The average crystallinity of CNF-90 min (the carboxymethyl modification time of original fibers was 90 min) decreased to about 45−55% (the crystallinity increased as the modification time increased) because the homogenization process broke some crystalline regions by fibrillation of fiber powders. The solvent media process toward the production of carboxymethyl cellulose was fully studied. According to the ratio of water and IPA showed in the study of Zhuomei,[41] the proportioning was set at 70 wt % IPA in order to get CMC with DS of 0.4. However, the efficiency and evenness of the modification process in actual operation was not as high as the reference value and the washing and filtration processes caused some loss of CNF with high DS, which also made a great contribution to the practical DS being lower than theoretical data. According to the study of Heinze et al.,[42] the different reaction time and NaOH concentration

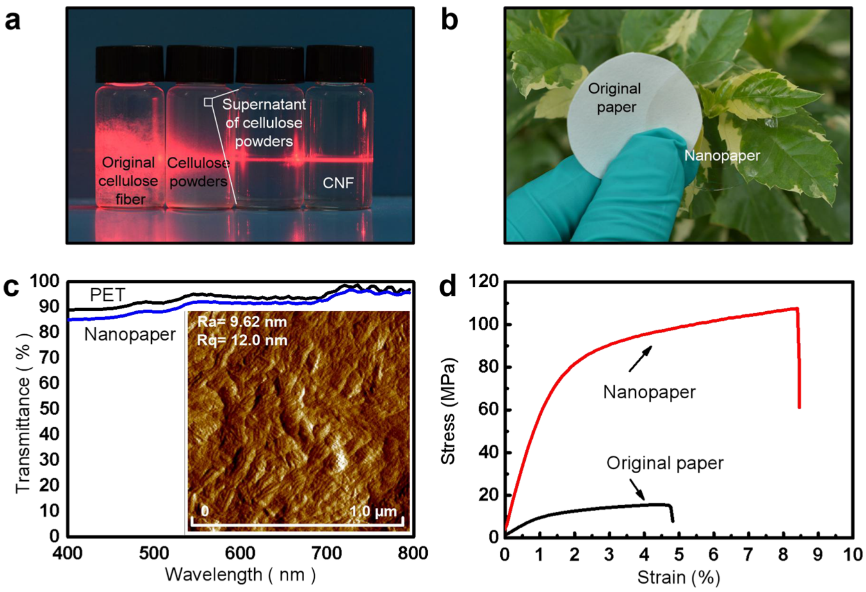


Figure 5. (a) Digital image of original cellulose fibers, cellulose powders suspension, the supernatant of cellulose powders suspension and CNF suspension. (b) Digital image of original paper and nanopaper. (c) Optical transmittance of PET and nanopaper and AFM image of nanopaper. (d) Stress−strain curves of original paper and nanopaper.

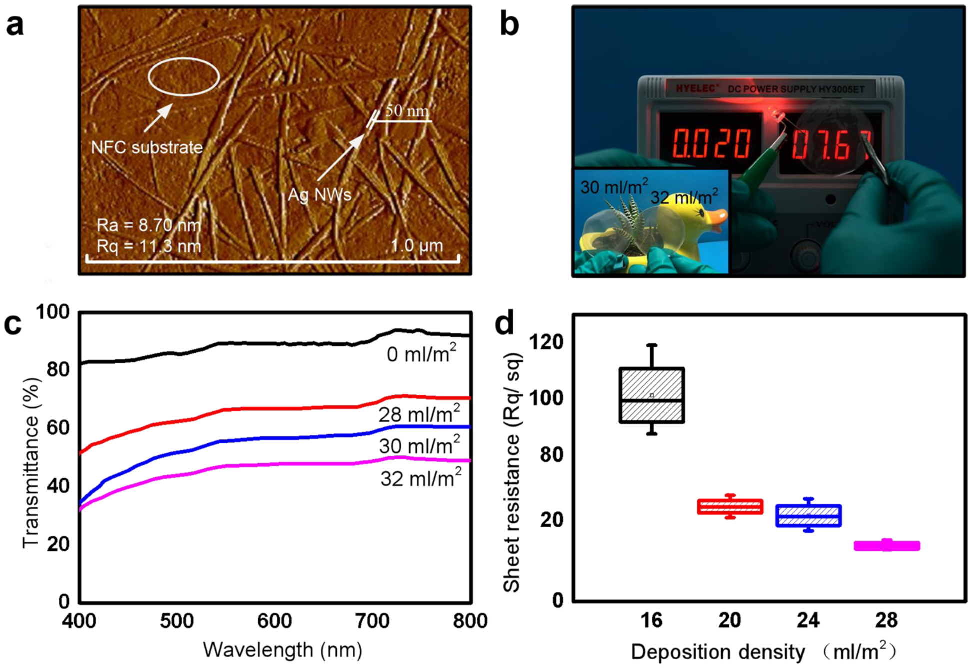


Figure 6. (a) AFM image of conductive nanopaper. (b) Digital image of conductive nanopaper. (c) Transmittance curves of original nanopaper and conductive nanopaper with different contents of Ag NWs. (d) Sheet resistance of conductive nanopaper with different contents of Ag NWs.

would lead to a different DS and yield of CMC, and the reaction was more uneven in IPA, so a 75 wt % IPA proportioning was taken into consideration. The DS of fibers after modification was around 0.28. Although DS value was 0.28, cellulose powders were redispersible. As shown in Figure 4c, the yield of CNF stayed at a high level. The highest yield indicated that the best modification time was about 110 min.

Figure 5a shows that as the size of fibers gradually decreased, the transparency of the dispersion increased. Under the light of a laser lamp, original fibers were visible and the cellulose powders were smaller than original fibers. The supernatant of cellulose powders showed a pure Tyndall effect, which indicated that there were CNF in the supernatant of cellulose powders solution but with low concentration. The concentration of CNF increased after high-pressure homogenization. As the digital images show in Figure 5b,c, compared with original paper, nanopaper had a high transparency up to 93%, similar to the light transmittance of PET film. Pure CNF were transparent in the visible region, only the large scale of cellulose, air inside cellulose and paper gaps would lead to low transparence. The high transparency of nanopaper was mainly due to the smooth surface (with R_q = 12.0 nm and R_a = 9.62 nm), small size of CNF and less air inside the nanopaper. Moreover, this nanopaper exhibited a high tensile strength up to 107.5 MPa, which was about 7 times higher than that of the original paper (Figure 5d).

The conductive nanopaper had a smooth surface (R_q = 11.3 nm and R_a = 8.70 nm) as shown in Figure 6a. The Ag NWs were stiff and combined with CNF closely. Ag NWs partly inserted into the surface of nanopaper to form conductive nanopaper. This structure would prevent Ag NWs from washing away. A good dispersion of Ag NWs would not only render nanopaper a stable conductivity but also a fine surface roughness and transparency. The digital image of conductive nanopaper is shown in Figure 6b; the power supply was loaded at both ends of the conductive nanopaper, and the indication of the voltage and current was displayed behind. The conductive nanopaper was highly transparent with high resistance. The detail data of transparency and resistance curves are shown in Figure 6c. It was obvious that as the content of Ag NWs increased, the conductivity of conductive nanopaper increased as well, but their transparency decreased. At light wavelength of 550 nm, as Ag NWs added, transparency of conductive nanopaper decreased to 65%, 55%, 45% when Ag NWs added up to 32 mL/m^2. This phenomenon was because Ag NWs had a different light refractive index with cellulose as well as air and the large size of Ag NWs also contributed to it. When the content of Ag NWs was down to 16 mL/m^2, it was hard to form an intact conductive network. As Ag NWs increased up to 20 mL/m^2, the conductivity of conductive nanopaper tended to be stable and decreased to the lowest of 18 Ω/sq, shown in Figure 6d.

CONCLUSIONS

The innovation of this work was that it provided a two-step route to fabricate nanosized fibers. The first step was to prepare cellulose powders with concentrated size distribution around several micrometers before further use. The alkalization and carboxymethylation process would transfer original fibers to carboxymethyl cellulose. However, the DS depended on the ratio of isopropyl alcohol and water. A low DS of 0.3 was taken into consideration to get a higher yield of cellulose nanofiber. Chemical modified fibers that washed with IPA or water would lead to a different result. In this research, we used IPA to wash chemical modified fibers because they were more convenient to dry and be ground into powders. The second step was to disperse dried cellulose powders in water and carry out a high-pressure homogenization process. The size of cellulose powders was small enough to go through the head of a high-pressure homogenizer with a diameter of 90 μm. Cellulose powders could not be used to make a film because of too much fiber debris without fibrillation. The high-pressure homogenizer acted as a beating machine and increased the yield of cellulose nanofibers. After 20 min of a high-pressure homogenization process, CNF solution separated from the obtained nanosized fibers with the help of high-speed centrifugation. The nanopaper and conductive nanopaper fabricated from CNF prepared also showed great properties with tensile strength up to 107.5 MPa, light transmittance up to 93% and low sheet resistance of 18 Ω/sq with smooth surface (the best R_a = 8.70, R_q = 11.30). This work highlights the potential for effort to further research properties and uses of microfibers, CNF, nanopaper and conductive nanopaper.

AUTHOR INFORMATION

Corresponding Authors

*D. Liu. E-mail: dtliu@scut.edu.cn.
*H. Qi. E-mail: qihs@scut.edu.cn.

ORCID

Lingfeng Su: 0000-0001-6585-5315

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was financially supported by Guangzhou Science and Technology Plan Project (Grant No. 201704030066), Guangdong Province Youth Science and Technology Innovation Talents (Grant No. 2014TQ01C781), Science and Technology Planning Project of Guangdong Province, China (Grant No. 2016B090918074), and the Fundamental Research Funds for the Central Universities, South China University of Technology (Grant No. 2017ZD087), and Guangdong Province Science Foundation for Cultivating National Engineering Research Center for Efficient Utilization of Plant Fibers (2017B090903003).

REFERENCES

(1) Azizi Samir, M. A. S.; Alloin, F.; Dufresne, A. Review of Recent Research into Cellulosic Whiskers, Their Properties and Their Application in Nanocomposite Field. *Biomacromolecules* **2005**, *6* (2), 612−626.

(2) Saito, T.; Kimura, S.; Nishiyama, Y.; Isogai, A. Cellulose Nanofibers Prepared by TEMPO-Mediated Oxidation of Native Cellulose. *Biomacromolecules* **2007**, *8* (8), 2485.

(3) Syverud, K.; Stenius, P. Strength and barrier properties of MFC films. *Cellulose* **2009**, *16* (1), 75.

(4) Ummartyotin, S.; Juntaro, J.; Sain, M.; Manuspiya, H. Development of transparent bacterial cellulose nanocomposite film as substrate for flexible organic light emitting diode (OLED) display. *Ind. Crops Prod.* **2012**, *35* (1), 92−97.

(5) Pinto, E. R. P.; Barud, H. D. S.; Silva, R. R.; et al. Transparent composites prepared by bacterial cellulose and castor oil based polyurethane as substrate for flexible OLEDs. *J. Mater. Chem. C* **2015**, *3* (44), 11581−11588.

(6) Nogi, M.; Karakawa, M.; Komoda, N.; Yagyu, H.; Nge, T. T. Transparent Conductive Nanofiber Paper for Foldable Solar Cells. *Sci. Rep.* **2015**, *5*, 17254.

(7) Hu, L.; Zheng, G.; Yao, J.; et al. Transparent and conductive paper from nanocellulose fibers. Energy Environ Sci. *Energy Environ. Sci.* **2013**, *6* (2), 513−518.

(8) Turbak, A. F.; Snyder, F. W.; Sandberg, K. R. Microfibrillated cellulose, a new cellulose product: Properties, uses and commercial potential. *J. Appl. Polym. Sci.: Appl. Polym. Symp.* **1983**, *37*, https://www.osti.gov/biblio/5062478.

(9) Wang, Q. Q.; Zhu, J. Y.; Gleisner, R.; Kuster, T. A.; Baxa, U.; Mcneil, S. E. Morphological development of cellulose fibrils of a bleached eucalyptus pulp by mechanical fibrillation. *Cellulose* **2012**, *19* (5), 1631−1643.

(10) Karande, V. S.; Bharimalla, A. K.; Hadge, G. B.; Mhaske, S. T.; Vigneshwaran, N. Nanofibrillation of cotton fibers by disc refiner and its characterization. *Fibers Polym.* **2011**, *12* (3), 399−404.

(11) Ho, T. T. T.; Abe, K.; Zimmermann, T.; Yano, H. Nanofibrillation of pulp fibers by twin-screw extrusion. *Cellulose* **2015**, *22* (1), 421−433.

(12) Nakagaito, A. N.; Ikenaga, K.; Takagi, H. Cellulose nanofiber extraction from grass by a modified kitchen blender. *Mod. Phys. Lett. B* **2015**, *29* (06n07), 1540039.

(13) Cheng, Q.; Wang, S.; Rials, T. G. Poly(vinyl alcohol) nanocomposites reinforced with cellulose fibrils isolated by high intensity ultrasonication. *Composites, Part A* **2009**, *40* (2), 218−224.

(14) Zhao, H. P.; Feng, X. Q.; Gao, H. Ultrasonic technique for extracting nanofibers from nature materials. *Appl. Phys. Lett.* **2007**, *90* (7), 073112.

(15) Herrick, F. W.; Casebier, R. L.; Hamilton, J. K.; Sandberg, K. R. Micro-fibrillated Cellulose: Morphology and accessibility. *J. Appl. Poly. Sci.: Appl. Poly. Symp.* **1983**, *37*, 797−813.

(16) Nechyporchuk, O.; Belgacem, M. N.; Bras, J. Production of cellulose nanofibrils: A review of recent advances. *Ind. Crops Prod.* **2016**, *93*, 2−25.

(17) Jayant, M.; Rashmi, J.; Shailendra, M.; Deepesh, Y. Production of cellulase by different co-culture of Aspergillus niger and Penicillium chrysogenum from waste paper, cotton waste and baggase. *J. Yeast Fungal Res.* **2011**, *2* (2), 24−27.

(18) Saito, T.; Okita, Y.; Nge, T. T.; Sugiyama, J.; Isogai, A. TEMPO-mediated oxidation of native cellulose: Microscopic analysis of fibrous fractions in the oxidized products. *Carbohydr. Polym.* **2006**, *65* (4), 435−440.

(19) Aulin, C.; Ahola, S.; Josefsson, P.; et al. Nanoscale cellulose films with different crystallinities and mesostructures–their surface properties and interaction with water. *Langmuir* **2009**, *25* (13), 7675−7685.

(20) Tingaut, P.; Zimmermann, T.; Lopezsuevos, F. Synthesis and Characterization of Bionanocomposites with Tunable Properties from Poly(lactic acid) and Acetylated Microfibrillated Cellulose. *Biomacromolecules* **2010**, *11* (2), 454−464.

(21) Gatenholm, P.; Klemm, D. Bacterial Nanocellulose as a Renewable Material for Biomedical Applications. *MRS Bull.* **2010**, *35* (3), 208−213.

(22) Brown, E. E.; Laborie, M. P. G. Bioengineering Bacterial Cellulose/Poly(ethylene oxide) Nanocomposites. *Biomacromolecules* **2007**, *8* (10), 3074−3081.

(23) Bhanthumnavin, W.; Wanichapichart, P.; Taweepreeda, W.; Sirijarukula, S.; Paosawatyanyong, B. Surface modification of bacterial cellulose membrane by oxygen plasma treatment. *Surf. Coat. Technol.* **2016**, *306*, 272−278.

(24) Frone, A.; Panaitescu, D.; Chiulan, I.; et al. Surface Treatment of Bacterial Cellulose in Mild, Eco-Friendly Conditions. *Coatings* **2018**, *8* (6), 221.

(25) Lim, Y. M.; Gwon, H. J.; Jeun, J. P.; Nho, Y. C. *Preparation of Cellulose-based Nanofibers Using Electrospinning*; InTech; 2010, DOI: 10.5772/8153.

(26) Kwak, D. H.; Lee, E. J.; Kim, D. J. Bioactivity of cellulose acetate/hydroxyapatite nanoparticle composite fiber by an electrospinning process. *J. Nanosci. Nanotechnol.* **2014**, *14* (11), 8464−8471.

(27) Ma, Z.; Kotaki, M.; Ramakrishna, S. Electrospun cellulose nanofiber as affinity membrane. *J. Membr. Sci.* **2005**, *265* (1), 115−123.

(28) Xuan, X.; Zhu, S.; Pan, Z. Preparation and alkali treatment of electrospun CA nanofibers. *J. Textile Res.* **2013**, *34* (9), 6, http://www.fzxb.org.cn/EN/Y2013/V34/I9/6.

(29) He, X.; Xiao, Q.; Lu, C.; et al. Uniaxially aligned electrospun all-cellulose nanocomposite nanofibers reinforced with cellulose nanocrystals: scaffold for tissue engineering. *Biomacromolecules* **2014**, *15* (2), 618−627.

(30) Zeng, H.; Li, Z. Novel method on the determination of DS of CMC. *J. Cellulose Sci. Technol.* **1996** (4), 38−43, http://en.cnki.com.cn/Article_en/CJFDTotal-XWSK199604005.htm.

(31) Fang, Z.; Zhu, H.; Yuan, Y.; et al. Novel Nanostructured Paper with Ultrahigh Transparency and Ultrahigh Haze for Solar Cells. *Nano Lett.* **2014**, *14* (2), 765−773,.

(32) Zhang, L.; Batchelor, W.; Varanasi, S.; Tsuzuki, T.; Wang, X. Effect of cellulose nanofiber dimensions on sheet forming through filtration. *Cellulose* **2012**, *19* (2), 561−574.

(33) Tibolla, H.; Pelissari, F. M.; Menegalli, F. C. Cellulose nanofibers produced from banana peel by chemical and enzymatic treatment. *LWT - Food Science and Technology* **2014**, *59* (2), 1311−1318.

(34) Ankerfors, M. *Microfibrillated cellulose: Energy-efficient preparation techniques and key properties*; KTH Royal Institute of Technology, 2012; URN urn:nbn:se:kth:diva-102949.

(35) Naderi, A.; Lindström, T.; Sundström, J. Repeated homogenization, a route for decreasing the energy consumption in the manufacturing process of carboxymethylated nanofibrillated cellulose? *Cellulose* **2015**, *22* (2), 1147−1157.

(36) Graveson, I. Low energy method for the preparation of non-derivatized nanocellulose. U.S. Patent US 20150158955 A1, 2016.

(37) Eriksen, Ø.; Syverud, K.; Gregersen, Ø. The use of microfibrillated cellulose produced from kraft pulp as strength enhancer in TMP paper. *Nord. Pulp Pap. Res. J.* **2008**, *23* (3), 299−304.

(38) Zhigan, L. Study on natural cellulose crystallinity determinated by the technology of XRD peak separation. *China Measurement Test* **2015**, *41* (2), 38−41.

(39) Li, G. Studies on the Preparation and Characterization of Nano-Crystal CelluloseII. *J. Cellulose Sci. Technol.* **2002**, *10* (2), 12−19.

(40) Zhang, L.; Zhang, J.; Zhou, N. Preparation Process Optimization and Characterization of Carboxymrthyl Pine Cellulose with High Degree of Substitution. *Journal of Zhejiang Sci-Tech University (Natural Sciences)* **2014**, *31* (11), 610−616.

(41) Zhuomei, L. Carboxymethyl Celluloses I. Synthesis. *Oilfield Chem.* **1987**, No. 04, 318−326.

(42) Heinze, T.; Pfeiffer, K. Studies on the synthesis and characterization of carboxymethylcellulose. *Angew. Makromol. Chem.* **1999**, *266* (1), 37−45.