

Review Article

Recent Strategies in Preparation of Cellulose Nanocrystals and Cellulose Nanofibrils Derived from Raw Cellulose Materials

Hongxiang Xie^{1,2,3}, Haishun Du⁴, Xianghao Yang¹ and Chuanling Si^{1,2,3}

¹Tianjin Key Laboratory of Pulp and Paper, Tianjin University of Science and Technology, Tianjin 300457, China

²State Key Laboratory of Pulp & Paper Engineering, South China University of Technology, Guangzhou 510640, China

³Key Laboratory of Industrial Fermentation Microbiology of Ministry of Education and Tianjin Key Lab of Industrial Microbiology, Tianjin University of Science and Technology, Tianjin 300457, China

⁴Department of Chemical Engineering, Auburn University, Auburn, AL 36849, USA

Correspondence should be addressed to Chuanling Si; sichli@tust.edu.cn

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The recent strategies in preparation of cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs) were described. CNCs and CNFs are two types of nanocelluloses (NCs), and they possess various superior properties, such as large specific surface area, high tensile strength and stiffness, low density, and low thermal expansion coefficient. Due to various applications in biomedical engineering, food, sensor, packaging, and so on, there are many studies conducted on CNCs and CNFs. In this review, various methods of preparation of CNCs and CNFs are summarized, including mechanical, chemical, and biological methods. The methods of pretreatment of cellulose are described in view of the benefits to fibrillation.

1. Introduction

Cellulose is the most abundant natural polymer and can be sustainably produced from various biomass. The global annual output of cellulose is approximately 75 to 100 billion tonnes [1]. The development and utilization of cellulose is of great significance to the sustainable development of human society, especially the energy scarcity in the future. Nanocelluloses (NCs) could be produced by the degradation of cellulose from various sources of biomass and have many unique properties, such as high specific surface area, high aspect ratio, high tensile strength and stiffness, low density, and low thermal expansion coefficient [2]. Recently, the application of NCs has attracted great attention [2–5]. NCs include cellulose nanocrystals (CNCs), cellulose nanofibrils (CNFs), bacterial cellulose (BC), and electrospun cellulose nanofibers (ECNFs). CNCs and CNFs are more common than the other NCs. This is because CNCs and CNFs are gained by disintegration of raw cellulose materials into nanosize particles (top-down process), while BC and ECNFs are produced by a build-up of nanofibers from low molecular weight sugars by bacteria and electrospinning,

respectively. This review will focus on CNCs and CNFs, while BC and ECNFs will not be covered. There is a significant difference between CNCs and CNFs in terms of dimension and crystallinity. CNCs are highly crystalline and usually have a length less than 500 nm, while CNFs are made up of amorphous and crystalline cellulose chains and have a length of up to several microns. Both of them have immense potential in the manufacture of renewable and biodegradable materials [6, 7]. They have been applied in the fields of biomedical engineering, food, sensor, packaging, optical and electronic devices, and so on [8–10]. Previous reviews have summarized their source, chemistry, and applications [2, 11–25]. The present review mainly focuses on the advances in preparation of CNCs and CNFs in order to display a clear development direction for the preparation of CNCs and CNFs.

2. Preparation of Cellulose Nanocrystals

CNCs have high crystallinity with diameter less than 100 nm and length less than 500 nm, which are formed through intra- and intermolecular interaction of cellulose macromolecules

in a hydrogen bond way. CNCs are usually obtained through acid hydrolysis or enzymatic hydrolysis of cellulose pulp. The acid hydrolysis processes need to go through very harsh reaction conditions which usually require concentrated acid, while the enzymatic hydrolysis process requires really long time. These are mainly determined by the inherent stable structure of the materials that have been explained in a related review [5]. During the hydrolysis process, the amorphous regions of cellulose are more easily invested by acid compared to the crystalline regions, leading to first degradation of amorphous regions, while the crystalline regions are retained. Finally, whisker-like CNCs are obtained.

In retrospect, the first successful preparation of CNCs was in 1947 through hydrolyzing cellulose with hydrochloric acid and sulfuric acid by Nickerson and Habrle [26]. In 1951, Rånby prepared the stable CNCs colloidal suspensions through sulfuric acid hydrolysis of wood fiber [27]. In 1953, Mukherjee and Woods proved that the acicular particles obtained by sulfuric acid hydrolysis possessed nanometer size by X-ray technology and electron microscope and found that their crystal structure was the same as that of raw cellulose material [28]. Subsequently, Marchessault et al. found that the CNCs colloid suspension had birefringence [29]. After that, some new methods to prepare CNCs appeared gradually, such as enzymatic hydrolysis, oxidative degradation, ionic liquid, solid acid hydrolysis, organic acid hydrolysis, and sub-critical hydrolysis, as shown Table 1. These will be described in the following sections.

2.1. Mineral Acid Hydrolysis. The mineral acid hydrolysis is the most common method for the preparation of CNCs. Various cellulose sources have been used for the preparation of CNCs by mineral acid hydrolysis [30–55], such as tomato peel [30], oil palm biomass [31], rice husk [33], and waste cotton cloth [34]. The typical mechanism is that the hydrogen ions from acid can easily invade the loose amorphous regions of cellulose to break the 1,4- β -glycoside bonds, resulting in the hydrolysis of amorphous regions, while the crystalline region of cellulose could be retained in the process which is attributed to the inherent compact structure that prevented the permeation of the acid. Therefore, the relatively complete crystalline structure of CNCs can be obtained by the hydrolysis of mineral acid. The principle diagram of preparation is shown in Figure 1 [5].

The typically used mineral acids are sulfuric acid [30–33, 37, 38, 40–43, 56, 57], hydrochloric acid [58, 59], phosphoric acid [35, 60], hydrobromic acid [61], and their mixed acids [34, 36]. Sulfuric acid is the most typically used as it produces a negative surface charge on the particles which leads to more stable suspension. In general, the hydrolysis process needs the sulfuric acid concentration to be 60–65%, reaction temperature to be 40–50°C, and reaction time to be 30–60 min. However, the yield of CNCs is very low (less than 30 wt.%) due to the excessive degradation. Fan and Li optimized the sulfuric acid hydrolysis conditions with cotton pulp as raw material, and the yield of CNCs reached to 63.8% [62]. Chen et al. found that the yield of CNCs could be significantly improved by decreasing the concentration of sulfuric acid and prolonging reaction time. For example,

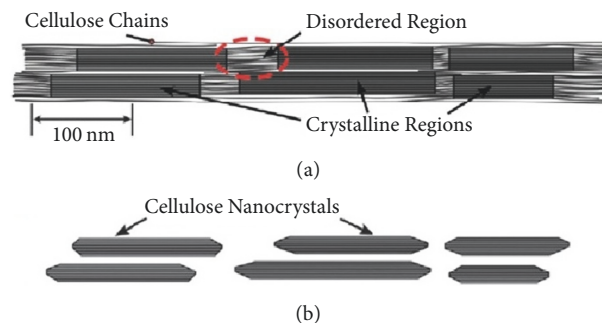


FIGURE 1: Schematic diagram of CNCs prepared by acid hydrolysis: (a) idealized cellulose microfibril showing one of the suggested configurations of the crystalline and amorphous regions and (b) CNCs after acid hydrolysis dissolved the disordered regions. Adapted from [5].

the yield of CNCs could reach to 75.6% when 58 wt.% sulfuric acid was used at 56°C for 210 min [56]. CNCs from sulfuric acid hydrolysis have poor thermal stability due to the sulfate group which is a significant barrier for thermal process in composites [63]. The thermal stability of CNCs can be improved through neutralization with NaOH [58, 64, 65]. The morphology of CNCs can be also modified by controlling the reaction conditions. The spherical CNCs with average dimension of 35 nm could be obtained by using 63.5% H_2SO_4 to hydrolyze microcrystal cellulose under the ultrasonic treatment combined with mechanical stirring for 3 h [66]. Azrina et al. also reported a similar condition for the preparation of spherical CNCs. This reaction was carried out with 64% (w/v) H_2SO_4 solution at 45°C for 2 h in an ultrasound bath. In this reaction, the spherical CNCs with an average diameter of 30–40 nm were extracted from oil palm empty fruit bunch pulp [67].

Hydrochloric acid also was commonly used for the preparation of CNCs. The typical acid concentration, reaction temperature, and reaction time are 2.5 N–6.0 N, reflux temperature, and 2–4 h, respectively [58, 59]. Due to the lack of charge on the surface of CNCs, the CNCs prepared by hydrochloric acid are easily flocculation in water. But the thermal stability of CNCs by HCl is higher than that by H_2SO_4 (see Figure 2). Yu et al. used hydrochloric acid to treat raw cellulose materials under hydrothermal conditions. The crystallinity of the resultant CNCs was 88.6% with high yield of 93.7% [58]. The maximum degradation temperature was 363.9°C which was determined by TGA analysis. Cheng et al. reported an inorganic chloride/hydrochloric acid system for extracting CNCs from microcrystalline cellulose (MCC) under hydrothermal conditions [68]. Four inorganic chlorides including $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, AlCl_3 , and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ were investigated in this work. The research showed that the hydrolysis process was promoted significantly by inorganic chlorides especially ferric chloride via accelerating degradation of the amorphous region of cellulose.

Phosphoric acid, which belongs to middle strong acid ($\text{pK}_a = 2.12$), could be used for the manufacture of CNCs

TABLE 1: Introduction of various preparation methods of CNCs including major chemical reagents, typical conditions, yield, thermal stability, and some other advantages/disadvantages.

Method	Major chemical reagents	Typical conditions [ref.] ^a	Yield ^b (%)	T_{\max}^c (°C)	Other advantages/disadvantages	Ref. ^d
Mineral acid hydrolysis	H_2SO_4 , HCl, H_3PO_4 , HBr	64 wt.% H_2SO_4 , at 45°C for 30 min [30].	15.7	253.2	It is difficult to treat waste acid. H_2SO_4 has a serious corrosion problem to equipment. The CNCs have excellent suspension stability. [35–75]	
		6 M HCl, 110°C, 3 h [58].	80	347.2	It is difficult to treat waste acid. HCl has a serious corrosion problem to equipment. The CNCs have bad suspension stability.	
Solid acid hydrolysis	Cation exchange resin (NKC-9), Phosphotungstic acid	75 wt.% Phosphotungstic acid, at 90°C for 30 h [77].	60	350	Phosphotungstic acid could be recovered through extraction with ethyl ether and is low corrosion to equipment. [76–79]	
Organic acid hydrolysis	Formic acid, oxalic acid, Maleic acid, <i>p</i> -toluenesulfonic acid	0.015 M $FeCl_3$, 88 wt.% HCO_2H , at 95°C for 6 h [63]. Melt oxalate dihydrate, at 110°C for 2 h, then, sonicated for 18 min [91, 93].	75 80.6	355 360	Formic acid could be recovered by reduced pressure distillation and is low corrosion to equipment. Oxalate dihydrate could be recovered by crystallization and is low corrosion to equipment. [63, 80, 91–101]	
Enzymatic hydrolysis	Cellulase	20 u/mL complex enzymes (cellulase : xylanase = 9 : 1), at 50°C for 5 h [104].	13.6	--	This method is environment-friendly, but the cost is very high. [81, 102–105]	
Oxidation degradation	$(NH_4)_2SO_5$, $NaIO_4$, $NaClO_2$	1 mol/L $(NH_4)_2SO_5$, at 80°C for 16 h [110].	35	330.9	Carboxylation CNCs could be produced. A large number of oxidants were consumed in the process. [106–117]	
Ionic liquid	[BMIM] HSO_4 , [BMIM]Cl, [EMIM][OAc], TBAA/DMAc	[BMIM] HSO_4 , at 70–90°C for 1 h [119].	--	260	Ionic liquid could be reused. It has advantage to preparing functional CNCs. However, ionic liquid is very expensive at present. [82, 118–125]	

TABLE I: Continued.

Method	Major chemical reagents	Typical conditions [ref.] ^a	Yield ^b (%)	T_{\max}^c (°C)	Other advantages/disadvantages	Ref. ^d
Transition metal catalysis	Cr(III), Fe(III), Al(III), Ni(II), Co(II), Mn(II)	Solid-liquid ratio was 1 : 30 and 0.8 M $\text{Cr}(\text{NO}_3)_3$ was adopted at 80°C for 1.5 h [126].	83.6	344	Transition metal could be used to enhance the hydrolysis reactivity and reduce the amount of acid.	[68, 126–129]
Subcritical water	--	H_2O , 120°C and 20.3 MPa for 60 min [130].	21.9	345	The method is environment-friendly. The cost of preparing CNCs was estimated to be 0.02 \$/kg. The CNCs have bad suspension stability.	[83, 130]
DES	Choline chloride/Oxalic acid	Choline chloride/Oxalic acid dihydrate = 1 : 1 (Molar ratios), at 100°C for 6 h, then Mechanical disintegration with microfluidizer [131].	78	300	DES is recoverable, biodegradable, and environmentally friendly. However, the reaction degree is low, so it needs follow-up mechanical treatment to get the CNCs products.	[131]
AVAP	Sulfur dioxide/Ethanol	$\text{SO}_2/\text{EtOH}/\text{H}_2\text{O}$, 130–165°C [84].	24	--	AVAP method could produce hydrophobicity and morphology adjustable CNCs. The method is low cost and has been used for industrial production of CNCs.	[84, 132]

^a[ref.]: the reference of typical conditions; ^bYield: the details come from the reference of corresponding typical condition; ^c T_{\max} : the max decomposition temperature, the details come from the reference of corresponding typical condition; ^dRef.: the reference of corresponding method of preparing CNCs.

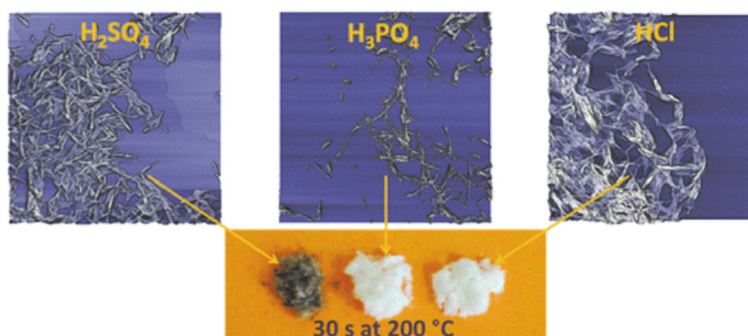


FIGURE 2: Schematic diagram of thermal stability contrast of CNCs from sulfuric acid hydrolysis, hydrochloric acid hydrolysis, or phosphoric acid hydrolysis [69].

with high thermal stability and stable suspension [69] (see Figure 2). Lu et al. reported a mechanochemical approach to manufacture bamboo cellulose nanocrystals (BCNCs) [70]. In this process, the bamboo cellulose pulp was chemically treated by phosphoric acid. Finally, short rod-like BCNCs with the length of 100–200 nm and the width of 15–30 nm were obtained. The crystalline structure transformed from cellulose I to cellulose II, and the crystallinity index declined from 66.44 to 59.62%, while the thermal stability became lower.

Hydrobromic acid (HBr) hydrolysis conditions assisted with ultrasonication to prepare CNCs were investigated by Sadeghifar et al. [61]. When the hydrolysis process was carried out at 2.5 M HBr under 100°C with sonication for 3 h, CNCs could be obtained at a yield of 60%. Moreover, Sucaldito and Camacho used HBr to hydrolyze fresh water green algae to achieve the highly crystalline CNCs (crystallinity index of 94.0%) [71]. The resultant CNCs have an average diameter of 20.0 (± 4.4) nm, and the decomposition temperature reached 381.6°C.

Spherical CNCs could be also prepared by using a mixed acid system assisted with ultrasonication from MCC [64, 72–74]. The mixed acid system is a mixture of sulfuric acid (98%, w/w), hydrochloride (37%, w/w), and H₂O at a ratio of 3:1:6 (v/v) which was reported by Zhang et al. [72]. The process was carried out at 80°C by ultrasonicator heating for 8 h. The diameters of produced cellulose nanoparticles are in the range of 60–570 nm. The hydrolysis condition offered by Wang et al. was that the ratio of sulfuric acid (98%, w/w), hydrochloride (37%, w/w), and H₂O was still 3:1:6 (v/v), while the ultrasonic treatment was at 50 Hz for 10 h [73]. The resultant spherical CNCs suspension with the dimension of 10–180 nm showed liquid crystalline property when the concentration was above 3.9%. A mixed acid system of hydrochloric acid and nitric acid (HCl/HNO₃) could be used to prepare carboxylated cellulose nanocrystals (CCNCs) from MCC [75]. When the reaction was carried out under the mixed acid (HCl/HNO₃ = 7:3 (v/v)) concentration being 4 M at 110°C for 3 h, the resultant CCNCs were rod-like morphology (176 \pm 6 nm length and 11 \pm 2 nm width) and had excellent suspension stability and good thermal stability.

Overall, mineral acid hydrolysis method to produce CNCs is a simple method and has gone to pilot scale (quite

a few around the world) and even demonstration plant (1 tonne/day at CelluForce, Canada). However, there are still some disadvantages in this method. First, the corrosion problem of the equipment is serious which leads to the insufferable cost of production. Furthermore, a large amount of waste acid and other pollutants will be produced in the process of acid hydrolysis, and it is very difficult to dispose and recover. So it is very necessary to develop green and low-cost CNCs production technologies [13].

2.2. Solid Acid Hydrolysis. Tang et al. reported a cation exchange resin hydrolysis method for the preparation of CNCs [76]. By hydrolyzing MCC with cation exchange resin (NKC-9), an optimum yield (50.04%) was achieved with a ratio of resin to MCC (w/w) being 10 and at 48°C for 189 min. The results showed that the diameter of CNCs was about 10–40 nm and the length was 100–400 nm. The crystallinity of resin-CNCs was higher than that of H₂SO₄-CNCs. In addition to the recoverable ability of cation exchange resin, the cation exchange resin-catalyzed hydrolysis is a promising approach for manufacturing of CNCs. Liu and coworkers reported the phosphotungstic acid (HPW) catalyzed-hydrolysis method with bleached hardwood pulp as raw material. CNCs with the diameter of 15–40 nm were given, which had high thermal stability and stable dispersion in aqueous phase [77]. The process is shown in Figure 3. The reaction was carried out with 75 wt.% phosphotungstic acid at 90°C for 30 h; the yield of CNCs was up to 60%. Phosphotungstic acid could be recovered through extraction with available ethyl ether. Because this method is a solid/liquid/solid three-phase reaction, the reaction efficiency is low and the reaction time is relatively long compared with the mineral acid hydrolysis method. Further research results showed that the reaction time was significantly shortened under the optimal conditions, and the obtained CNCs had a high crystallinity index (79.6%) with a 84% yield [78]. Torlopov et al. also reported a CNCs preparation process using phosphotungstic acid/acetic acid system to destruct cotton cellulose [79]. The resulting CNCs have high-crystalline structure and rod-like morphology.

Compared with the classic mineral acid hydrolysis method, solid acid hydrolysis method has mild condition and low corrosion to equipment, and the solid acid can be

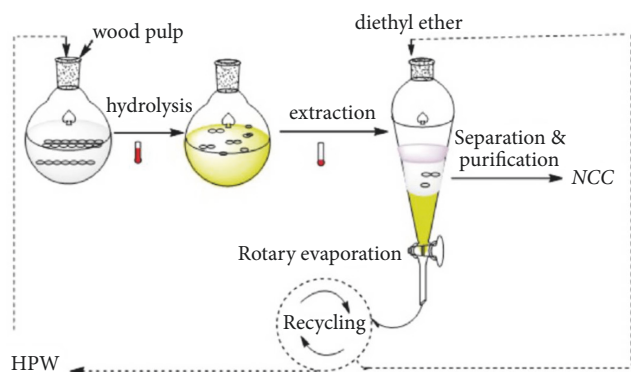


FIGURE 3: The overall procedure for the manufacture of CNCs by using HPW (HPW: phosphotungstic acid, $\text{H}_3\text{PW}_{12}\text{O}_{40}$) [77].

recycled. Moreover, the yield of CNCs is higher. However, the reaction efficiency is low and the reaction time is pretty long. Appropriate physical approach (such as microwave and ultrasound assisted) or suitable catalyst could be used to improve the reaction efficiency. At present, solid acid hydrolysis method to prepare CNCs is still in the stage of laboratory research.

2.3. Organic Acid Hydrolysis. Recently, organic acid hydrolysis was presented to produce NCs due to the fact that the organic acid is mild, recyclable, and environment-friendly and of low corrosiveness. However, in order to improve the efficiency of hydrolysis, higher temperature and longer reaction time are necessary because of the weak acidity of organic acid. Li and coworkers reported a two-step strategy to produce CNCs from bleached chemical pulp under mild conditions [80]. In the first stage, formic acid (FA) was used to hydrolyze the amorphous region of cellulose and release CNCs. In the second stage, the generated CNCs were further oxidized by TEMPO in order to increase the surface charge. The results showed that the CNCs modified by TEMPO have much higher crystalline and much more surface charge. In order to further increase the hydrolysis efficiency, Du et al. introduced the FeCl_3 to the FA system [63]. Figure 4 shows the process flow and the CNCs were obtained from bleached eucalyptus kraft pulp with a high yield (75%). The results showed that the crystallinity index of resultant CNCs could reach 75% when 0.015 M FeCl_3 was used. Moreover, up to 90% FA can be recovered by rotary evaporation, FeCl_3 could be recovered in the form of $\text{Fe}(\text{OH})_3$ precipitation generated by ammonia treatment, and the generated ammonium salt can be used as fertilizer. Thus, the FeCl_3 -catalyzed FA hydrolysis process was more sustainable than the traditional sulfuric acid hydrolysis process.

Then, dicarboxylic acid was used for CNCs production proposed by Chen et al. [91]. Similarly, CNCs usually were obtained at a low yield due to the low reactive activity of dicarboxylic acid. Thus, most of the hydrolyzed products are the insufficiently hydrolyzed fibers which can be used for preparing CNFs through subsequent mechanical disintegration. The advantages of using dicarboxylic acid for the preparation of NCs are that (1) carboxyl groups are

introduced on the surface of CNCs and CNFs, as ester group could have been formed by the reaction of dicarboxylic acids with cellulose [92]; (2) solid dicarboxylic acid (e.g., oxalate and maleic acid) is of low corrosion to equipment and could be fully recovered by using crystallization technology; (3) the resultant CNCs and CNFs are thermally stable which is beneficial for the manufacture of composite. Li and coworkers used molten oxalate dihydrate to treat cellulose fibrils which is a free solvent for the preparation of CNCs [93]. In this process, the hydrolysis and esterification of cellulose could be carried out in one pot. CNCs could be gained in a high yield (80.6 wt.%). Xu and coworkers successfully prepared the CNCs with a mixed acid composed of hydrochloric acid and oxalate. The optimal condition is that the concentration of oxalate is 0.11 M with 10% HCl at 95°C for 4 h. Results showed that CNCs could be obtained with a high yield of 81.5% [94].

Maleic acid was also used for the preparation of CNCs and the pretreatment of cellulose [95–98]. Wang and coworkers reported the preparation of CNCs using maleic acid to hydrolyze cellulose [95]. CNCs were obtained at a low yield, about 5%. The fibrous cellulosic solid residue could be converted to CNFs through the following mechanical disintegration. Bian et al. used concentrated maleic acid to hydrolyze unbleached mixed hardwood kraft pulp. The results were that the lignin-contain CNCs and CNFs were successfully prepared [97, 98]. Bian and coworkers also reported a maleic acid catalyzed-hydrolysis reaction for the preparation of CNCs and CNFs. The bleached eucalyptus pulp and unbleached mixed hardwood kraft pulp were used as the raw materials, and typical operating conditions were acid concentrations of 50–70 wt.% at $100\text{--}120^\circ\text{C}$ for 1–2 h. The results showed that CNCs with the length of approximately 239–336 nm were obtained, and CNFs could be gained by the further mechanical fibrillation of fibrous cellulosic solid residue [99]. Yu et al. reported an approach for extracting carboxylated CNCs by citric acid/hydrochloric hydrolysis of MCC [100]. In this work, rod-like CNCs with the length of 200–250 nm and the width of 15–20 nm were obtained. The CNCs extracted for 4 h had the highest carboxylic group content and high zeta potential value (up to -46.63 mV). By applying organic acid hydrolysis, some interesting functional groups could be introduced to the surface of CNCs through the ester bond between organic acid and CNCs in the hydrolysis process. For example, Boujemaoui et al. used 2-bromopropionic acid, 3-mercaptopropionic acid, 4-pentenoic acid, and 2-propynoic acid, respectively, to catalyze the hydrolysis of raw cellulose materials. Some active functional groups such as Br-, HS-, alkenyl, and alkynyl were grafted on the surface of CNCs correspondingly, which could be beneficial to further modify CNCs despite the very long reaction time (10 days) [101]. Overall, organic acid hydrolysis is more sustainable and environment-friendly than mineral acid hydrolysis for CNCs production. It is believed that the industrialization of CNCs by using organic acid hydrolysis will be realized in recent years.

2.4. Enzymatic Hydrolysis. Cellulase is a multicomponent enzyme system. Its active components include endoglucanases (EG), cellobiohydrolases (CBH), and β -glucosidase

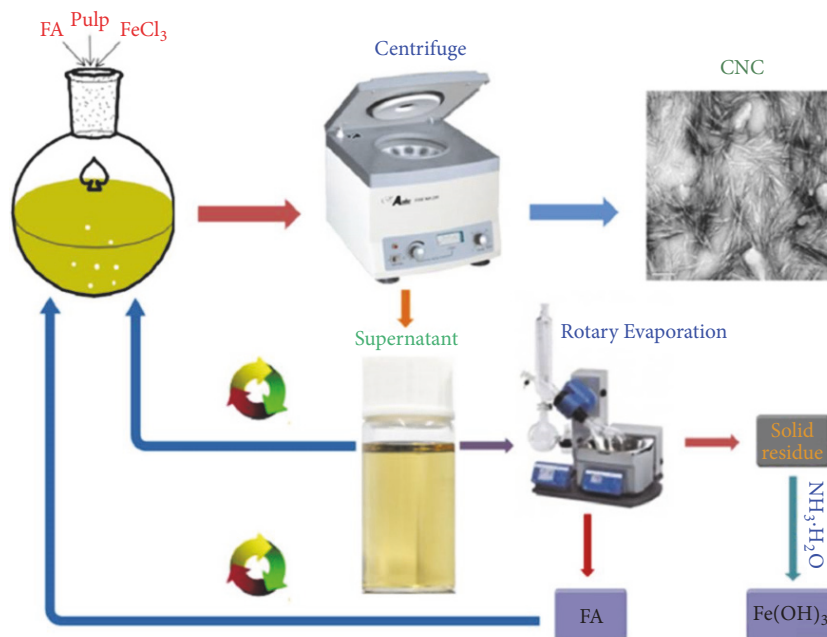


FIGURE 4: Overall flow-process diagram of the preparation of CNCs by FeCl_3/FA hydrolysis [63].

(GB). The action mechanism of each component on cellulose is shown in Figure 5 [14, 81]. EG mainly acts on the amorphous region of cellulose to randomly hydrolyze the β -1,4-glycosidic bond, so the long chain cellulose molecules are truncated into small molecular cellulose in the interior of cellulose; CBH mainly acts on the end of linear cellulose molecular to destroy the crystalline region of cellulose; GB is used to hydrolyze cellulose into glucose [81, 102]. When CNCs are prepared by enzymatic hydrolysis, the destruction of the crystalline area of cellulose by CBH should be avoided as much as possible. Therefore, three components of cellulase should be separated from each other. EG is used to hydrolyze cellulose amorphous regions, and much more crystalline regions are retained in the process. Filson and coworkers successfully prepared CNCs using endoglucanase to hydrolyze recycled pulp [103]. They found that when the endoglucanase was increased to 420 EGU per 1 g pulp and the reaction temperature was at 50°C with microwave heating for 60 min, the CNCs with the diameter of 30–80 nm and the length of 100 nm– $1.8\ \mu\text{m}$ could be obtained, the yield was up to 38.2%, the average zeta potential was $-31.37\ \text{mV}$, and birefringence could be observed for the CNCs dispersion. Chen et al. prepared a spherical nanosized cellulose by the enzymatic hydrolysis of pulp fibers [104]. This research showed that enzymatic hydrolysis of pulp could give spherical CNCs with the diameter of ca. 30 nm, which had excellent monodispersity and uniformity. When the concentration of complex enzymes was 20 u/mL (cellulase: xylanase = 9:1), the yield of CNCs reached to 13.6%. However, when the single cellulase was used, even if the enzyme concentration reached up to 200 u/mL, only a mixture of strip and granular flocculation was obtained. Meyabadi et al. also reported the enzymatic hydrolysis method to produce the spherical CNCs

with waste cotton as raw material combining with sonication [105]. The particle sizes of gained CNCs were less than 100 nm.

Overall, compared with the mineral acid hydrolysis, the enzymatic hydrolysis process for the preparation of CNCs is environment-friendly, while the experimental conditions are harsh, the yield of CNCs is low, and the reaction time is long. Enzymatic hydrolysis of raw cellulose materials is promising for the industrial production of CNCs, so further research of efficient enzymatic hydrolysis is imperative and urgent.

2.5. Oxidation Degradation. The hydroxyl groups on cellulose have high reactivity. They are easily oxidized by strong oxidants to aldehydes, ketones, and carboxyl groups so that their structures are destructed and the degree of polymerization is decreased. Therefore, some scientists have successfully prepared CNCs by use of the oxidation degradation method. Yang et al. adopted two-step oxidation method to prepare CNCs: softwood pulp was firstly oxidized by sodium periodate and then further oxidized by sodium chlorite, and finally two-step centrifugation was implemented to give CNCs (diameter/length, 13 nm/120–200 nm) and microfibrils (diameter/length, 120 nm/0.6– $1.8\ \mu\text{m}$) [106]. The resultant microfibrils could be further translated to CNFs by mechanical agitation. The separated CNCs with carboxyl groups on the surface had a high crystallinity (91%) and high charge density which could form a stable suspension in aqueous phase.

Ammonium persulfate (APS) also could be used to prepare carboxyl CNCs [57, 107, 108]. Hu et al.'s research results showed that the spherical shape particles with diameters of 20–70 nm were obtained by this method, and the crystallinity of CNCs was significantly improved after a series of chemical

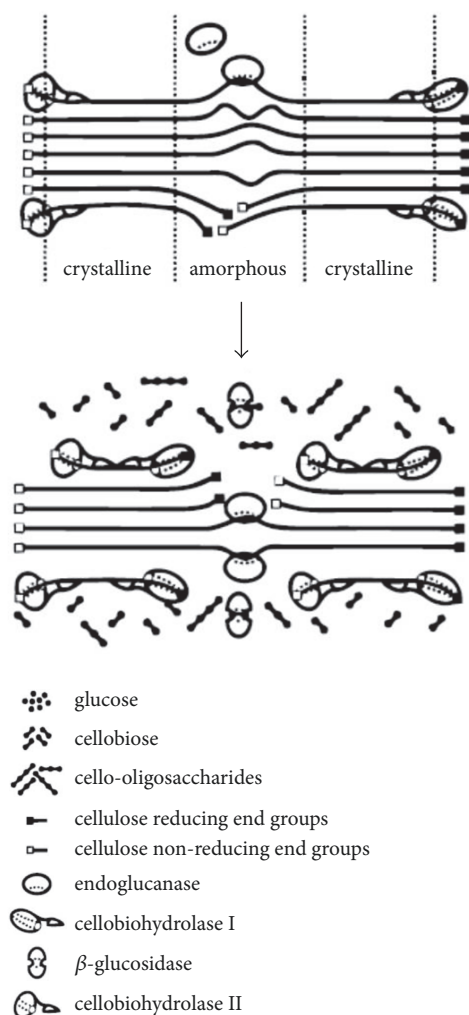


FIGURE 5: Schematic diagram of different cellulase impacts on cellulose, adapted from [81].

treatments [107]. The research results of Mascheroni and coworkers showed that CNCs produced through the APS treatment displayed higher charge densities, crystallinity, clarity of the solution and transparency of the coating compared to the CNCs produced by the H_2SO_4 hydrolysis [108]. Leung and coworkers used the APS to oxidize the flax fibers to produce the surface-carboxylated CNCs [109]. The CNCs were needle-like with diameter of 3.8 nm and length of 150 nm, and the particle size distribution was uniform. In this method, the raw materials (such as hemp, flax, straw etc.) could be used directly for the preparation of CNCs without pretreatment process for the delignification. The reason is that APS has the delignin function in addition to oxidative degradation. Cheng and coworkers prepared the CNCs with 1 mol/L APS aqueous solution to oxidize lyocell fiber at 80°C for 16 h. The prepared CNCs were spherical with the diameter of 35 nm and a great deal of carboxyl groups were introduced on the surface of CNCs. The crystal type of resultant CNCs was cellulose II [110].

TEMPO was also used as oxidation to prepare carboxyl CNCs [111–113]. However, only subfraction of raw cellulose materials was oxidized to CNCs by using TEMPO; the rest of oxidized cellulose had much larger dimensions. It indicated that TEMPO was not as effective as APS on cellulose oxidation. Moreover, CNCs from TEMPO oxidation are highly carboxylated [114, 115], which provides the opportunity for functionalization [116, 117].

Overall, compared with the mineral acid hydrolysis and enzymatic hydrolysis, the yield of CNCs was higher by the oxidation degradation method. However, in the process of reaction, a large number of oxidants were consumed, and the reaction time was longer. Also, a large amount of water and energy need to be consumed which leads to the fact that the cost of CNCs production was very high.

2.6. Ionic Liquid Method. Ionic liquid is a kind of organic salt solution with low melting point (less than 100°C) composed of organic cations and other anions. Compared to the traditional solvent, ionic liquid has advantages in terms of chemical stability, thermal stability, nonflammability, and low vapor pressure. It is also called “green solvent” [118]. In recent years, due to the unique properties of ionic liquid, it has been widely used to dissolve and separate lignocellulose and to prepare CNCs. Man and coworkers treated MCC with 1-butyl-3-methylimidazolium bisulfate ([BMIM]HSO₄) to give CNCs with the diameter of 14–22 nm and the length of 50–300 nm. It was found that, compared with the original MCC, the CNCs remained cellulose I, while the thermal stability was significantly decreased [119]. Mao and coworkers treated MCC with [BMIM]HSO₄ aqueous solution at 120°C for 24 h to give the CNCs at 48% yield [120]. Later, they hydrolyzed softwood, hardwood, and MCC by the optimizing two-stage method with [BMIM]HSO₄ aqueous, and the yield of CNCs was 57.7%, 57%, and 75.6%, respectively, which was close to the theoretical value [121]. Tan et al. used [BMIM]HSO₄ as both catalyst and solvent to prepare CNCs from MCC. Highly crystallized CNCs with diameter of 15–20 nm and length of 70–80 nm were obtained at 90°C [122]. Lazko and coworkers reported another method which is that cotton fibers were infiltrated firstly by [BMIM]Cl at 80°C , and 1–4 wt.% sulfuric acid was added subsequently. Then the reaction was kept for 2–16 h, and the CNCs were successfully prepared with the diameter of about 20 nm and the length of 150–350 nm. The analysis results showed that the CNCs prepared by [BMIM]Cl had less sulfonic group content on the surface than that of [BMIM]HSO₄, and their thermal stability was obviously increased [123]. Iskak et al. used [BMIM]Cl as ionic liquid to prepare CNCs [124]. In this work, they investigated the effects of the reaction time and temperature on the yield, size, and crystallinity index of CNCs. The results showed that CNCs with the particle size of 9 nm and the crystallinity index of 73% were obtained when the reaction time was 30 min. Meanwhile, when reaction temperature was 100°C , CNCs were obtained with a yield of 90% and crystallinity index of 76%. Abushammala and coworkers directly treated wood with 1-ethyl-3-methyl imidazole acetate ([EMIM][OAc]), and the surface acetylated CNCs were successfully prepared in a 44% yield. The type



Novo and coworkers used subcritical water to hydrolyze cellulose for the preparation of CNCs [83, 130]. The subcritical water (120°C and 20.3 MPa for 60 min) possessed higher diffusion, activity, and ionization than common water. With that, cellulose materials could be hydrolyzed partly to provide CNCs at 21.9% yield [83]. The gained CNCs exhibited a high crystallinity index (79.0% determined by XRD), rod-like shape, and good thermal stability. The schematic diagram of the device is shown in Figure 7 [83]. During the experiment, the pressure inside the reactor could be decreased by opening the restrictor valve (due to the loss of a small volume of liquid) or be increased by injecting water with a precision pump. The cost of this method was compared with conventional one. The conventional production stage would produce CNCs with a cost of 1.54 \$/kg, whereas the cost of preparing CNCs by the proposed subcritical treatment would be 0.02 \$/kg. Later, Novo and coworkers systemically

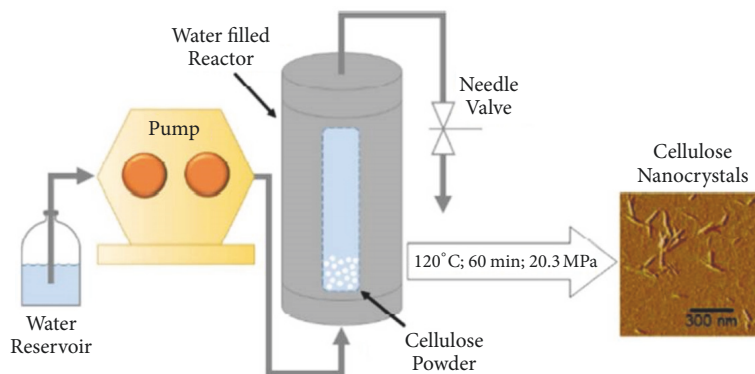


FIGURE 7: Scheme of subcritical water batch setup [83].

studied the effects of subcritical hydrolysis on the yield, crystallinity, hydraulic radius, and color of CNCs [130]. It was found that pressure played an important role in the yield of CNCs, and the temperature had a great influence on the color of CNCs. With the increase of temperature, the stability of CNCs aqueous suspensions was enhanced gradually but still far below the stability of CNCs suspension prepared by sulfuric acid hydrolysis. The main reason is that the surface charge density of CNCs prepared by this method is relatively low. The subcritical water method is very promising for industrial production of CNCs. Although the process requires a reactor that supports high pressures and high consumption of energy, it results in a greener method in terms of water and chemicals consumption reduction, lower effluent generation, and treatability of wastes.

Sirviö and coworkers reported that the deep eutectic solvent (DES) formed by choline chloride and oxalic acid could hydrolyze the wood fiber fine fibers into microfibrils which were microfluidized sequentially to give the CNCs with the diameter of 9–17 nm and the length of 310–410 nm, which had high thermal stability and good dispersion stability in aqueous phase [131]. Compared with sulfuric acid hydrolysis, the preparation of CNCs with DES method has high yield (68–78%) and DES is recoverable, biodegradable, and environmentally friendly. However, the reaction degree is low, so it needs follow-up mechanical treatment to get the CNCs products. At present, the DES method to produce CNCs is in the laboratory study stage.

Nelson et al. reported that American Value Added Pulp- ing technology (AVAP) developed by American Process Inc. (API) could produce NCs from different kinds of lignocellu- losic materials. This technology provides a low-cost way to prepare NCs. It can prepare hydrophilic/hydrophobic CNCs and CNFs by controlling the content of lignin [84]. The process flow chart of nanoscale cellulose prepared by AVAP is shown in Figure 8. In this process, sulfur dioxide (SO_2) and ethanol were used as pretreatment agents to remove lignin, hemicellulose, and the amorphous regions of cellulose from biomass. SO_2 was used as delignifying agent, and ethanol was used as a solvent which could dissolve resins and extractives, assist SO_2 penetrating easily into the wood, and reduce degradation of crystalline cellulose. The final

morphology of NCs was modified by controlling temperature and the time of the pretreatment step. Nelson and Retsina used eucalyptus wood as raw material to produce the CNCs and CNFs using AVAP technology; the resultant CNCs with the diameter of 5–200 nm and the length of 50–500 nm had a high crystallinity of 93% [132]. In addition, AVAP method did not cause swelling and destruction to the crystalline region of cellulose. AVAP method can produce hydrophobicity and morphology adjustable CNCs, which greatly increases the potential application of CNCs in various fields. In April 2015, API started up a nanocellulose production line for production of the full range of AVAP nanocellulose products in Thomaston Georgia for sale under the BioPlus™ trade name.

3. Production of Cellulose Nanofibrils

Cellulose nanofiber [132], nanofibrillar cellulose [133, 134], and cellulose nanofibril [135] are the terms used for nanofib- rillated cellulose [136]. The preparation of CNFs needs strong mechanical machining. However, according to the properties of raw materials and degree of processing, chemical pretreat- ments are carried out before mechanical machining [137]. A fact is that appropriate pretreatments of cellulosic fibers can increase the inner surface, alter crystallinity, and break hydrogen bonds of cellulose [138].

3.1. Mechanical Method. Mechanical approaches to prepare CNFs include homogenizing [139–144], grinding [145], twin- screw extrusion [146], cryocrushing [147], and high-intensity ultrasonication [148–151]. Among them, homogenizing and grinding are the most commonly used for the preparation of CNFs and the most effective for the scaling production of CNFs at present. At the same time, other methods have been also developed in order to find a more favorable solution for the industrial production of CNFs.

3.1.1. High Pressure Homogenization. Homogenizers and microfluidizers are typical equipment for the preparation of CNFs. They can disintegrate cellulose fibers into CNFs by high pressure homogenization. The process is that cellulose pulp is passed through a minute gap between an impacting

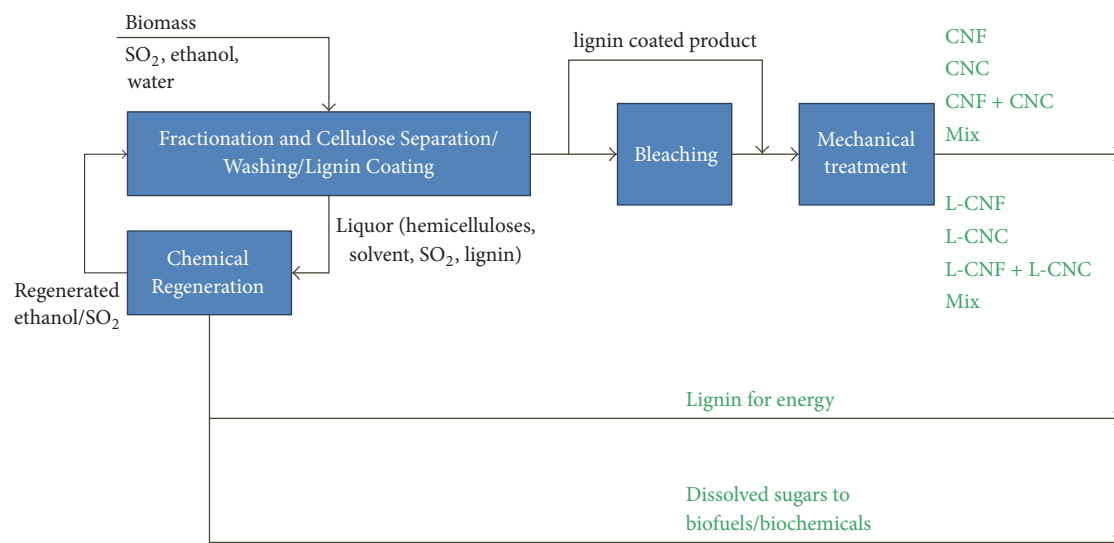


FIGURE 8: A simplified process flow diagram of the AVAP NCs process [84].

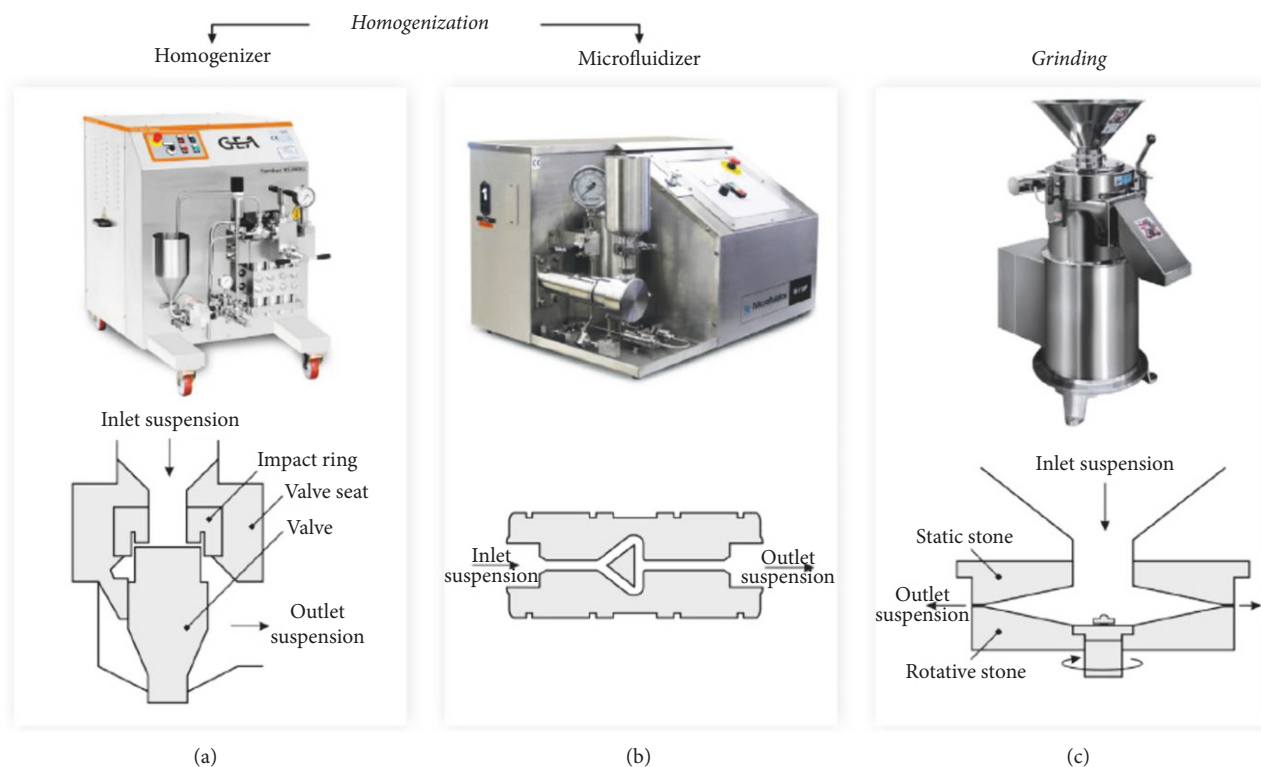


FIGURE 9: The most applied mechanical treatment processes used in the fabrication of CNFs and their schematic diagram: (a) homogenizer, (b) microfluidizer, and (c) grinding. The photographs were adapted from [14], <https://www.niro-soavi.com>, <https://www.microfluidicscorp.com> and <http://www.masuko.com>.

and the homogenizing valve (see Figure 9 [14]) under high pressure and high velocity conditions, making the fibers sheared and to ensure cellulose fibrillation. Turbak et al. and Herrick et al. used high pressure homogenizer to treat 2 wt.% wood pulp for the first time in 1983 to produce CNFs with a diameter of less than 100 nm [152, 153]. And then, homogenizers were widely used for the preparation of CNFs

[139, 154–158]. The main disadvantages include the following: (1) the high energy consumption for homogenization process could reach up to 70 MW h/t [159]; (2) the clogging of the system occurred frequently when using long fibers as raw materials [160]. However, when some pretreatment techniques (e.g., enzymatic, oxidation, and carboxylation) [87, 161, 162] were adopted, this energy consumption value was

reduced significantly to 2 MW h/t, and the clogging problem could be solved as well [163].

3.1.2. Grinding Method. Ultrafine friction grinding is another common technique for the preparation of CNFs. The commonly used equipment is Supermasscolloider grinder (see Figure 9). Taniguchi and Okamura used Masuko's colloider grinder for the first time to grind 5–10 wt.% cellulose materials for 10 times and successfully prepared CNFs with diameter of 20–90 nm [164]. Since then, this method has attracted wide attention [165–170]. Gane et al. determined that adding kaolin or calcium carbonate is helpful for accelerating grinding in the grinding operation and will provide composite of CNFs and a mineral [171, 172]. The working principle is that cellulose materials are sent to the grinding area consisting of a movable disc and a fixed disc, and the process of high-speed grinding and shearing was carried out to give CNFs lastly. Compared to the high pressure homogenization method, grinding method has the advantages of high efficiency, large capacity, low energy consumption, and being less prone to material clogging. However, because of the strong mechanical force in the grinding process, the fiber damage is more serious. As a result, the CNFs property is not well, such as low crystallinity and inferior thermal stability, which leads to the low physical strength of CNFs and the enhancement effect of material not as good as CNFs prepared by high pressure homogenization.

3.1.3. Ball Milling. Ball milling technique is also used for the production of CNFs. In this process, cellulose in a way of suspension can be disintegrated by the high energy collision between the balls (e.g., ceramic, metal, or zirconia) in a hollow cylindrical container while the container rotates. Zhang and coworkers studied the possibility of preparing CNFs from once-dried bleached softwood kraft pulp suspension by ball milling and investigated the effect of milling conditions [173]. The results showed that the size of milling ball had a decisive influence on the morphologies of produced nanocellulose (fibrous morphologies or particulates). In addition, ball-to-cellulose mass ratio was very important as well as milling time for the controlling of fiber morphology. Alkali pretreatment was helpful for weakening hydrogen bonds and eliminating small particles. But the fibrous morphology was easily damaged in this process. When cerium-doped zirconia balls with diameter of 0.4–0.6 mm were adopted and without alkaline pretreatment, CNFs with diameter of 100 nm could be obtained within 1.5 h. Kekäläinen et al. used ball milling technology to mill never-dried bleached hardwood kraft pulp with high solid contents ($\geq 50\%$) to give CNFs with the diameter of 3.2 nm and the bundles of nanofibrils with the diameter of 10–150 nm [174].

3.1.4. Twin-Screw Extrusion Method. Twin-screw extrusion is another method for CNFs production. In the preparation process, cellulose pulp is fibrillated by two corotating, intermeshing screws mounted in a closed barrel. The advantage of twin-screw extrusion is that CNFs can be obtained with high solid contents (25–40 wt.%), which is very beneficial for transportation and storage [146]. The twin-screw extrusion

process of the composites from thermoplastic starch and TEMPO-oxidized cellulose fibers was studied by Cobut and coworkers [175]. The CNFs with the diameter of ca. 30 nm were obtained during extrusion process. Hietala and coworkers studied this process for the bleached cellulose from softwood flour (particle size of 200–400 μm) as raw materials [176]. The result was that CNFs were not gained; however, fibers with good dispersion in the starch matrix were given. Ho and coworkers studied this method for the preparation of CNFs from never-dried refined needle-leaf bleached kraft pulp [146], and the resultant CNFs were obtained at a solid content of 45 wt.%. Overall, twin-screw extrusion method is promising for the scale production of CNFs.

3.1.5. Cryocrushing Method. Cryocrushing method for the preparation of CNFs was studied by Dufresne and coworkers for the first time. The process is that water swollen cellulosic fibers were frozen firstly by liquid nitrogen and subsequently crushed by mortar grinding. Under mechanical impact, the pressure on the cell walls derived from ice crystals caused cell wall to break and release cell wall fragments [177]. Sain and coworkers studied the fibrillation of agricultural crops using cryocrushing method [156, 178, 179]. The results showed that the CNFs with the diameter of 50–100 nm and the crystallinity of 48% could be obtained, and the soybean stock nanofibers could be dispersed in acrylic oligomer emulsion as good as in water [156, 180].

3.1.6. Blending Method. Uetani and Yano successfully prepared CNFs by using the high-speed blender to shear never-dried bleached softwood pulp [181]. The resultant CNFs had a uniform diameter of 15–20 nm when 0.7 wt.% cellulose pulp suspension was blended at 37,000 rpm. Jiang and Hsieh blended the cellulosic fibers suspension at 37,000 rpm and 97°C under different time conditions (up to 2 h) to give the NCs with bimodal size distribution: (i) one was with the diameter of 2.7 nm and the length in range of 100–200 nm; (ii) the other was with the diameter of 8.5 nm and the length with few micrometers [182]. Nakagaito and coworkers improved the blender bottle, and the results showed that the time was halved for fibrillation process [183].

3.1.7. Aqueous Counter Collision. Aqueous counter collision (ACC) is another technology for CNFs preparation. Under high pressure, two jets of cellulose suspensions collide against each other, leading to wet pulverization of cellulose and liberation of CNFs. Kose et al. prepared CNFs from the previously homogenized bacterial cellulose aqueous suspension at a concentration of ≤ 0.4 wt.% using ACC method. The process was carried out under the ejecting pressure of 200 MPa for 80 passes [184]. The result was that CNFs with the diameter of ca. 30 nm were produced and cellulose I α changed to cellulose I β after ACC. But the crystallinity was still kept at $>70\%$. Kondo and workers reported the preparation of CNFs from MCC by using ACC method [185]. The diameter of CNFs was ca. 15 nm and the length was ca. 700 nm. It is worth noting that in order to avoid clogging, the size of processed cellulosic material should be less than the nozzle diameter (ca. 150 μm).

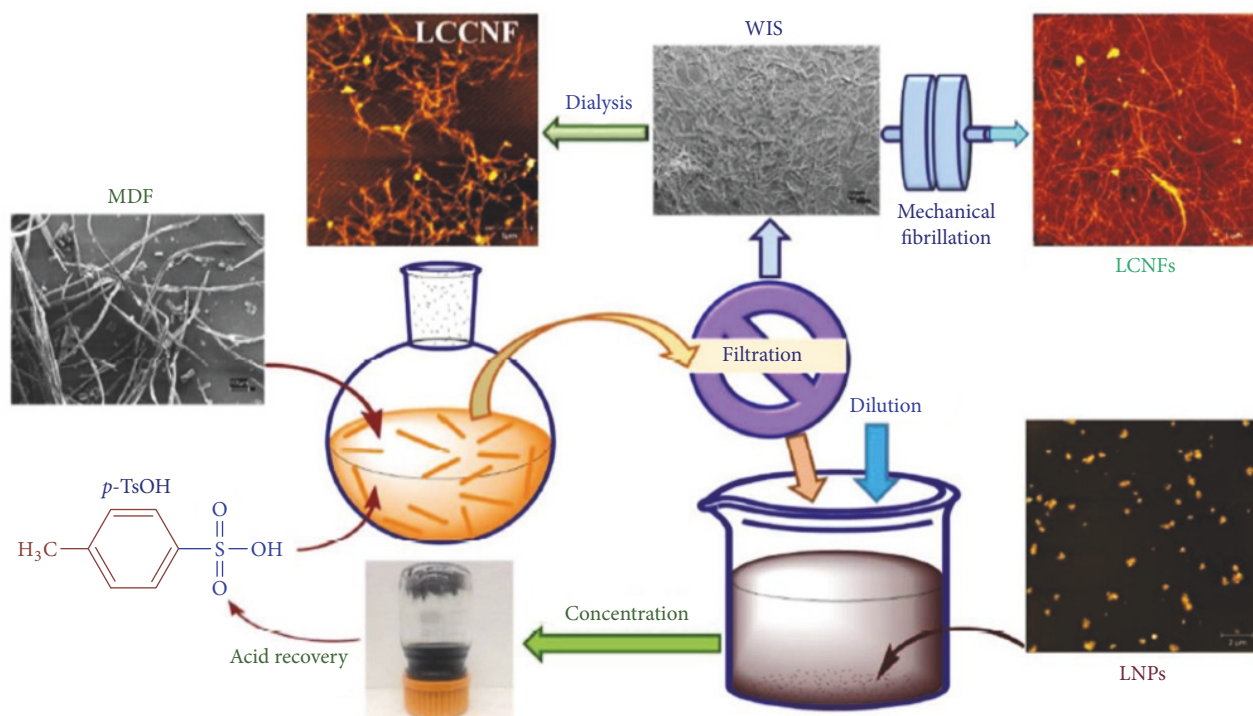


FIGURE 10: Schematic diagram of the preparation of LCNFs and LNPs by using *p*-TsOH pretreatment [85].

3.2. Pretreatments. The high energy consumption of CNFs by mechanical method is the mainly barrier to the scale production of CNFs, and cellulosic raw materials should be of small sizes for some equipment in order to avoid clogging. To solve these problems, a series of pretreatment methods have been developed, such as solvent-assisted pretreatment, enzyme hydrolysis, TEMPO oxidation, periodate oxidation, carboxymethylation, and cationization.

3.2.1. Solvent-Assisted Pretreatments. Traditionally, the cellulose pulp is pretreated by dilute base or dilute acid [158, 186–189]. For instance, bleached kraft bagasse pulp was pretreated with the aqueous solution of 5% NaOH at 50°C for 45 min so as to get rid of the residual hemicellulose and lignin and then was further ground to obtain the CNFs [158]. Degree of polymerization and cellulose content of the resultant CNFs were higher than the ones untreated or hydrolyzed with xylanase enzyme. Lee and coworkers used a low-concentration alkaline solution as pretreatment condition (2 wt.% NaOH solution below 0°C) to produce CNFs. The resulting CNFs with 90 nm diameter had relatively high thermal stability [188]. The maximum thermal decomposition temperature was 343°C, while it was 310°C for the CNFs prepared without the NaOH pretreatment. Since urea and ethylenediamine have the ability to loosen the hydrogen bonds and solubilize cellulose, they could be applied to pretreat cellulose [190]. Before further mechanical disintegration, a microemulsion (surfactant–oil–water systems) including urea or ethylenediamine was applied to treat kraft pulps. It was found that urea and ethylenediamine

pretreatment could effectively accelerate the isolation of CNFs [190].

3.2.2. Organic Acid Hydrolysis Pretreatment. Recently, some organic acids, for example, formic acid and oxalate, were used to facilitate the cellulose. Du and coworkers used highly concentrated formic acid to hydrolyze bleached softwood pulp; then the formic esterified MCC passed through homogenizer without clogging to give CNFs [191]. The resultant CNFs showed high thermal stability (onset decomposition temperature ac. 291°C) and good dispersibility in DMSO, DMAc, and DMF, respectively, due to the introduction of surface formic ester groups. Bian et al. used *p*-toluenesulfonic acid (50–80 wt%) for the rapid and nearly complete dissolution of wood lignin at 80°C for 20 min (see Figure 10) [85]. In this process, the birch wood fiber fractions were hydrolyzed to lignocellulosic solid residue (LCSR) that was subsequently fibrillated into lignocellulosic nanofibrils (LCNFs). The dissolved lignin could be precipitated as lignin nanoparticles (LNPs) by diluting the concentration of *p*-TsOH to less than 10%, and the *p*-TsOH could be recovered by using commercially proven crystallization technology. The dicarboxylic acid was also used as the pretreatment of lignocellulose to prepare lignin containing cellulose nanocrystals (LCNCs) and LCNFs by Bian et al. [98]. The resultant LCNCs and LCNFs were less carboxylated compared to those lignin-free CNCs and CNFs. Therefore, they had lower charges. Overall, organic acid hydrolysis is an efficient pretreatment method, which is recycle and has low corrosion to equipment, and ester groups or carboxyl groups are grafted onto the surface of cellulose in the pretreatment process.

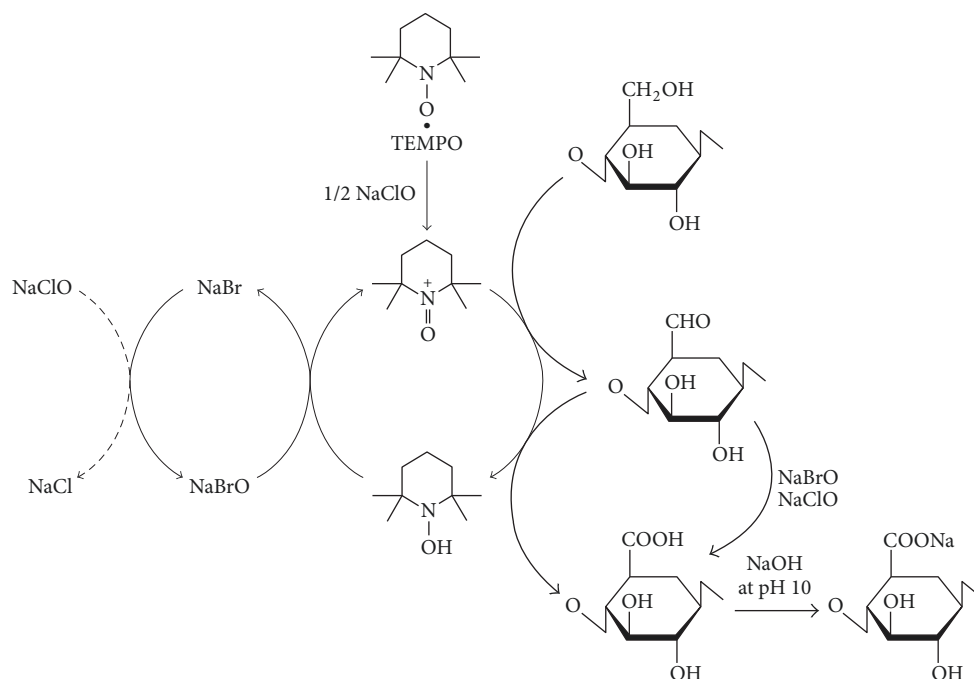


FIGURE 11: Regioselective oxidation of C6 primary hydroxyls of cellulose to C6 carboxylate groups by TEMPO/NaBr/NaClO system in water at pH 10–11 [86].

3.2.3. Enzyme Hydrolysis. The hydrolysis of cellulose can be catalyzed by some enzymes and the fibrillation can also be enhanced. The action mechanism of cellulase components to cellulose has been described in Section 2.4 and Figure 5. The enzyme pretreatment has a mild condition and a high selectivity and can make fibers produce holes, peeling, and fine fibrosis, which is conducive to the nanofibrillation of cellulose in subsequent mechanical processes and reduces the probability of blocking the homogeneous valve by cellulose slurry. The enzyme system could be multicomponent enzyme mixture [192–194] or the monocomponent [157, 170, 193, 195–198]. According to the reports, the monocomponent endoglucanase seems to give a better pretreatment effect [170, 199, 200].

3.2.4. TEMPO Oxidation. As we all know that the negatively charged groups (such as carboxyl or carboxymethyl) are introduced into cellulosic fibers and then the delamination of the nanofibrils can be improved, since there is electrostatic repulsion between cellulose nanofibrils with negative charge [201]. The process of 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) radical oxidizing the primary alcohol groups of monosaccharides to carboxylic groups was reported by Davis and Flitsch in 1993 which has become one of the most extensive research topics in the area of oxidation of cellulose [202]. The typical oxidation system for cellulose is TEMPO/NaBr/NaClO [203], which has been extensively used for the pretreatment of raw cellulose materials before mechanical disintegration [22, 189, 204, 205]. The mechanism of oxidation reaction is shown in Figure 11 [86]. Nitrosonium ions ($+N=O$) are generated in situ during the reaction of

TEMPO radicals with the oxidants and they are used to oxidize the cellulose fibers. Consequently, the primary alcohol groups are first oxidized to aldehydes and further converted to carboxyl groups. At the same time, the depolymerization phenomenon of cellulose appears. There are two phenomena which may be caused by cellulose depolymerization: (i) β -elimination could occur owing to C6 aldehyde groups presented in an alkaline environment and (ii) the cleavage of a hydroglucose unit took place owing to the existing of hydroxyl radicals [86, 206]. TEMPO/NaClO/NaClO₂ system was also applied which overcame the depolymerization [207, 208]. The reaction was carried out in the neutral or weakly acidic environment and at 60°C for 72 h. The results demonstrated that most of original DP remained unchanged. TEMPO oxidation pretreatment remarkably reduced the energy consumption for the further mechanical disintegration of cellulose [86, 201, 203, 209–211]. Nelson et al. evaluated that the mechanical energy consumption after TEMPO oxidation was about 570 KWh/t, which was far lower than that of 70000 KWh/t without any pretreatment [84].

3.2.5. Periodate-Chlorite Oxidation. Periodate-chlorite is an effective oxidation system for transferring secondary alcohols of cellulose to carboxyl groups [212]. Liimatainen et al. used this method to oxidize cellulose to promote further mechanical decomposition of cellulose [87]. During the reaction, secondary alcohols of cellulose were firstly converted to aldehydes by sodium periodate, which were further oxidized to carboxyl groups by sodium chlorite (see Figure 12(a)). The CNFs with the diameter of 3–5 nm were obtained through sequential high pressure homogenization for up to 4 passes.

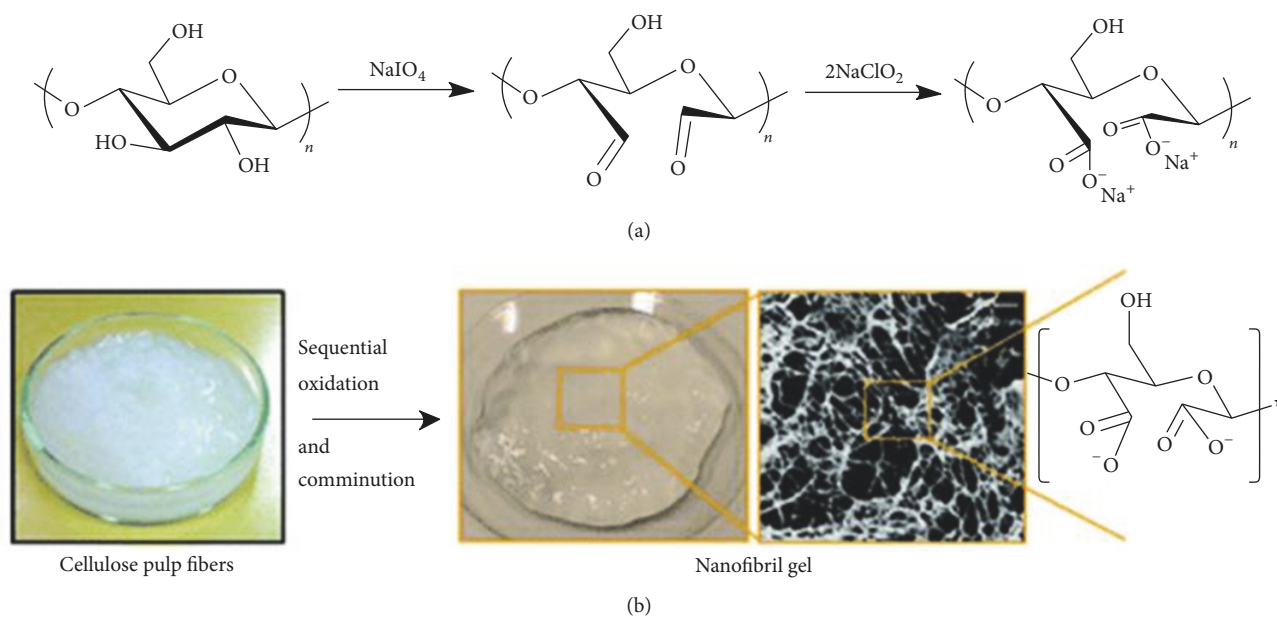


FIGURE 12: Schematic diagrams of cellulose carboxylation via periodate-chlorite: (a) chemical formula for cellulose carboxylation via periodate-chlorite oxidation and (b) preparation of CNFs by periodate-chlorite oxidative system [87].

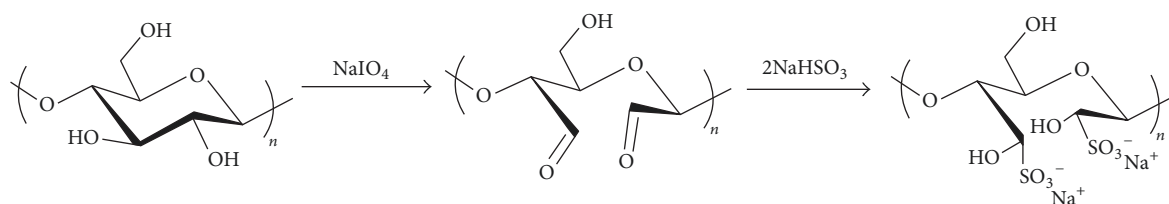


FIGURE 13: Schematic diagram of cellulose sulfonation via periodate-bisulfite treatment.

In this method, the glucopyranose ring was opened to provide 2,3-dicarboxylic acid cellulose (see Figure 12(b)) [87]. Moreover, the strength property of CNFs was not decreased by ring opening reaction [213–215].

3.2.6. Oxidative Sulfonation. Oxidative sulfonation of cellulose is another method for introducing negative charge groups onto the surface cellulose and can be used to enhance the fibrillation process [214, 216]. Liimatainen et al. treated bleached kraft hardwood pulp with periodate and bisulfite (see Figure 13), and CNFs with typical diameter of 10–60 nm were obtained by the following high pressure homogenization for 5 times. In this method, the used periodate could be efficiently recycled, so it is a potential green method for the pretreatment of cellulose [214].

3.2.7. Carboxymethylation. Carboxymethylation is another method for the pretreatment of cellulose. The hydroxyl groups on cellulose could react with 1-chloroacetic acid under strong alkaline conditions to give the carboxymethylation products (see Figure 14(a)). Wågberg et al. reported the production of CNFs from carboxymethylated cellulose by high pressure homogenization [217]. The resultant CNFs had acylindrical cross section with the width of 5–15 nm

and the length of ca. 1 μm . Chen et al. reported the preparation of CNFs by high pressure homogenization of carboxymethylated cellulose raw fibers [88]. In this work, the carboxymethylation pretreatment included two steps: (1) basification of raw oven-dried cellulose fibers by using anhydrous NaOH/dimethyl sulfoxide; (2) further sodium acetoxylation of cellulose raw fibers by using sodium chloroacetate. Then the resultant MCC was extracted by deionized water which was beneficial to the collapse of the cell wall of cellulose fibers. Finally, the pretreated cellulose fiber suspension passed through homogenizer to give the CNFs. The resultant CNFs were used for manufacture of nanopaper which exhibited 90.5% optical transparency. Carboxymethylation pretreatment was also used by other researchers for preparing CNFs [218–222]. Overall, the carboxymethylation method is also a potential green pretreatment technology for the preparation of CNFs.

3.2.8. Cationization. The cationization of cellulose could be used for promoting the nanofibrillation of cellulose. In the process, the cations were introduced on the surface of cellulose by the quaternization of cellulose [223–225]. The fibrillation of cellulose was promoted by the electrostatic repulsion between the quaternary ammonium cations (see Figure 15

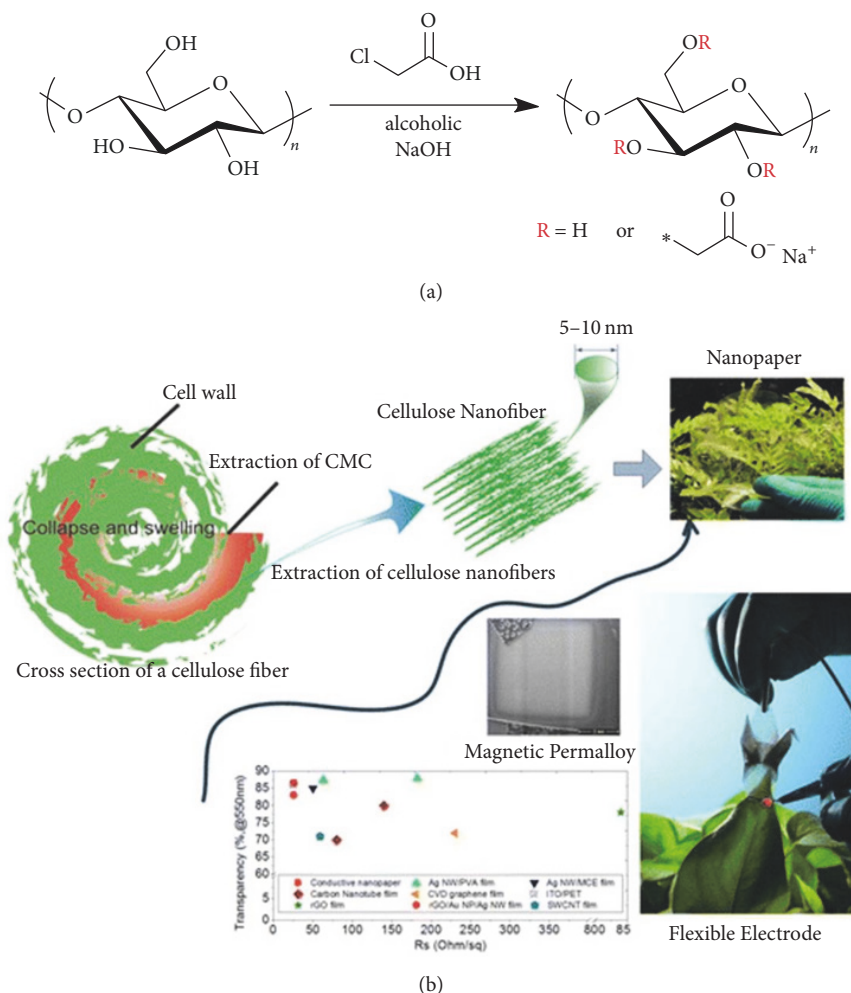


FIGURE 14: Schematic diagrams of (a) chemical formula for carboxymethylation of cellulose by using chloroacetic acid and (b) carboxymethylation pretreatment of cellulose for the preparation of CNFs and the application of resultant CNFs as nanopaper and flexible electrode [88].

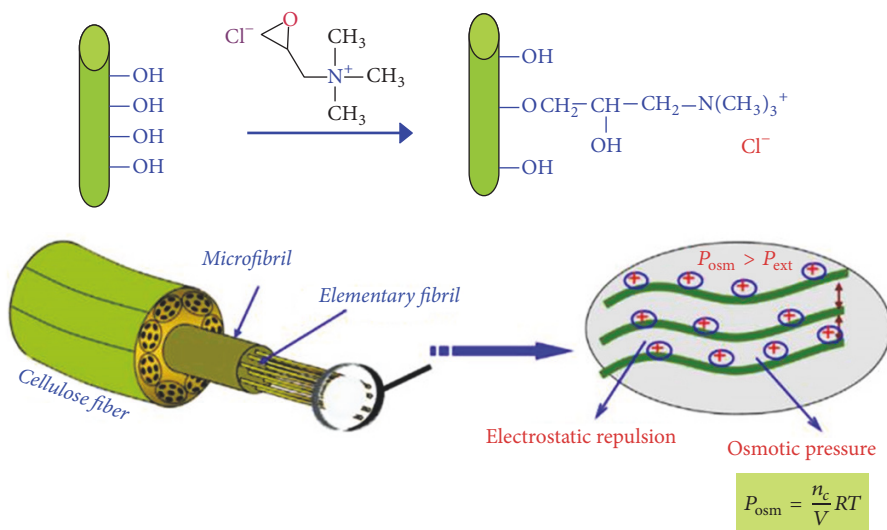


FIGURE 15: Schematic diagram of cellulose cationization using (2,3-epoxypropyl) trimethylammonium chloride [89].

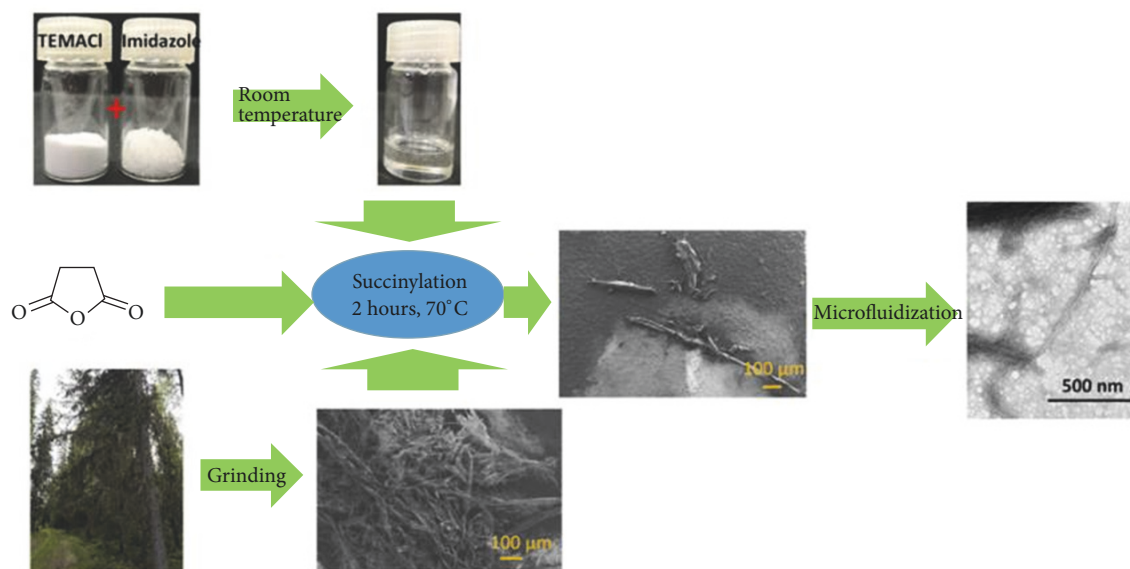


FIGURE 16: Schematic diagram of DES pretreatment for the preparation of anionic CNFs [90].

[89]). This method has been used for preparation of CNFs combination with following mechanical disintegration: (2,3-epoxypropyl) trimethylammonium chloride [89, 226, 227], (2-chloroethyl) trimethylammonium chloride [228], and (2-hydrazinyl-2-oxoethyl)-trimethylazanium chloride [162] were commonly used as cationization reagents. The process was carried out under alkaline environment, for example, NaOH/H₂O/*i*-PrOH, NaOH/DMSO. Recent studies showed that, owing to significant antibacterial properties of cationic CNF film, and without quaternary ammonium leaking to the environment [89, 229], they could be applied into wound healing, food packaging, tissue, and so on.

3.2.9. Ionic Liquids. Ionic liquids could also be used for the pretreatment of cellulose. Li et al. successfully prepared CNFs using 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) to treat sugarcane bagasse combining with the following high pressure homogenization for the first time [230]. Ninomiya et al. also proposed an ionic liquid pretreatment method for the preparation of lignocellulose nanofibers (LCNFs) [231]. In this work, choline acetate as an ionic liquid was used to treat bagasse powder; then LCNFs were obtained through a subsequent mechanical nanofibrillation. However, ionic liquids are expensive, which will hinder the scaling application for the preparation of CNFs.

3.2.10. Deep Eutectic Solvent Pretreatments. Deep eutectic solvent (DES), which is composed of two or more compounds, has lower melt point than any component of its own. Due to its low cost, low toxicity, and recyclability, DES has been widely used in various fields [232]. Sirviö and workers proposed a bio-based DES consisting of urea and choline chloride (molar ratio of 2:1) which could be used to the pretreatment of cellulose pulp [233]. Li and coworkers used the urea-based DES as the pretreatment for the preparation of CNFs [234]. In this work, DES was

composed of urea and ammonium thiocyanate or guanidine hydrochloride and was used to treat wood-derived cellulose fibers. The results showed that the cellulose fibers were well loosened and swelled by both DES systems. Then CNFs with the width of 13.0–19.3 nm were smoothly obtained through further mechanical nanofibrillation without clogging. A method for the preparation of anionic CNFs using DES as reaction medium was proposed by Sirvio and Visanko [90]. As is shown in Figure 16, the DES consisted of triethylmethylammonium chloride (TEMACI) and imidazole was liquid at room temperature. The ground wood pulp with a 27.4 wt% lignin was carboxylated by succinic anhydride during the DES pretreatment process under mild reaction conditions (2 h at 70°C). Then the anionic CNFs could be obtained through the followed microfluidization of carboxylated ground wood pulp. A microwave-assisted DES pretreatment method for fast CNCs production was proposed by Liu and coworkers [235]. It took only a little time (not more than 3 min) for the pretreatment of cotton, and then a high-intensity ultrasonication process was adopted. The resultant CNCs with the diameter of 3–25 nm and the length of 100–350 nm were obtained at a yield of 74.2%. Overall, DES pretreatment is efficient and environment-friendly and is a promising technology for the industrial production of NCs.

4. Conclusions

This review summarizes the preparation methods of CNCs and CNFs. For the preparation of CNCs, promising techniques were discussed besides the conventional mineral acid hydrolysis, such as organic acid hydrolysis, subcritical hydrolysis, AVAP method, and ionic liquid hydrolysis. Most of them have great possibility for further industrialization. However, there are still some problems that need to be solved. For example, the corrosion of equipment is serious and the postprocessing of waste acid is difficult for mineral acid

hydrolysis, the preparation time is long and the technological requirements are rigorous for enzymatic hydrolysis, the reactivity is low for organic acid hydrolysis, there is a great deal of chemical consumption and wastewater treatment for oxidation degradation method, and the yield is low for subcritical water method. Therefore, in order to achieve the industrialization of various CNCs, a lot of research works need to be done. The appropriate catalysts should be developed to reduce the amount of acid or increase the efficiency of organic acid hydrolysis. The subcritical water method should be further improved to be suitable for the industrial production of CNCs. The DES method is promising and more attention should be paid to it. For the preparation of CNFs, various mechanical treatments are discussed, including high pressure homogenization, grinding method, ball milling, twin-screw extrusion, cryocrushing, blending, and aqueous counter collision. Among them, the twin-screw extrusion is the method with the most potential for the preparation of CNFs due to a high solid content of obtained CNFs. In order to reduce energy consumption of mechanical disintegration, the pretreatment of cellulose materials is necessary. Various pretreatment methods are summarized in this review. In this process, some special functional groups could be introduced to the surface of CNFs so that the physicochemical properties could be effectively adjusted.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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