

Review Article

Preparation and Applications of the Cellulose Nanocrystal

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Cellulose widely existed in plants and bacteria, which takes important effect on the synthesis of macromolecule polymer material. Because of its great material properties, the cellulose nanocrystal (CNC) showed its necessary prospect in various industrial applications. As a renewable future material, the preparation methods of the CNC were reviewed in this paper. Meanwhile, the important applications of CNC in the field of composites, barrier film, electronics, and energy consumption were also mentioned with brief introductions. The summarized preparations and considerable applications provided operable ideas and methods for the future high-end and eco-friendly functional composites. Suggestions for potential applications were also discussed.

1. Introduction

Cellulose is a macromolecular polysaccharide composed of glucose. It is also the most diverse and widespread group of polysaccharides in nature. As a kind of natural crystalline macromolecular compound, the cellulose nanocrystal (CNC) widely exists in the plant fibers and the capsular polysaccharide of bacteria [1] and possesses a series of characteristics of high crystallization, high strength, large specific surface, low density, biocompatibility, and biodegradability. Therefore, it is usually utilized in the field of construction, foodstuff, electronics, pharmacy, barrier industry, et al. [2–6].

The main methods for preparing CNC at present are the mechanical process, the chemical process of hydrolysis, the biological process of hydrolysis, and the combined method of the above processes. All the above methods mentioned have their own advantages and disadvantages and also different effects on their applications [7, 8]. This paper presents a summary of the research progress of preparations, modifications, and applications of CNC in all aspects.

2. Methods for CNC Preparations

The plant fibers are usually employed in preparing the CNC for its low price and abundance, whose common size is 0.5–3.0 mm for length and 20–40 μm for diameter [9]. Meanwhile, the size of any one dimensionality of cellulose locating in 100 nm is called the CNC [10]. Therefore, the methods for obtaining the CNC are the processes of decreasing the size of natural cellulose, which includes the process of mechanical, the chemical hydrolysis, the biological hydrolysis, and the combined methods.

2.1. Preparation of CNC via the Mechanical Process. The mechanical process is a physical method for getting the CNC and consists of four ways: homogenization under high pressure, microfluidization, fine grinding, and freezing smashing [11].

2.1.1. Homogenization under High Pressure. Homogenization is a one-step process to make a stable suspension by smashing the solid to form ultrafine particles in the solution [12].

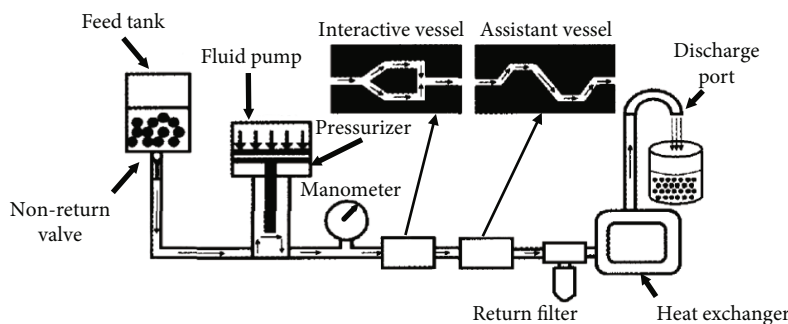


FIGURE 1: Technological process of the microfluidization [20].

Homogenization under high pressure was usually used to produce the microcrystalline cellulose (MCC), where the process of the homogenization under high pressure usually occurred in the homogeneous valve [13]. The raw material was extruded to the adjustable gap between the rod and the seat of the valve (usually $h = 0.1$ mm) by the outside force to accelerate the solution speed to 200~300 m/s. While leaving the gap, the inner press of the mixed solution fell instantaneously [14]. According to Bernoulli's theory [15], the great change of inner press would create an inner shearing force to produce lots of positive holes and the turbulence, which would break the fibers into ultrafine particles.

The method of homogenization under high pressure was first improved in 1980s [16]. Turbak et al. [17] employed the wood fibers to produce the MCC with this method and obtained the stable MCC gel with high viscosity. And then, a series of studies reported its application for the MCC preparation with varieties of raw materials. Khiari [18] utilized chemistry-treated residue of the Badam to produce cellulose nanofibril (CNF) gel at 600 bars for 10 times, and the resulting CNF was one with a diameter of 3~18 nm. Meanwhile, they also indicated that the parameters of production would be the best by holding the reaction temperature at 70~80°C, and the homogenization under high pressure could be applied in the continuous industry production.

Although the method of the homogenization under high pressure possessed several advantages, its development was also limited by its obvious disadvantages. As an energy-intensive process, the homogenization under high pressure utilizes lots of energy, which meant that its energy waste was huge. Meanwhile, its efficiency was unstable because the valve was easily jammed by the long plant fibers. All the above problems prevented its improvement.

2.1.2. Microfluidization. The microfluidization is called microfluidization under high pressure [19], one of the methods for preparing nanomaterials, and its technological process is shown in Figure 1 [20]. The raw slurry was firstly injected and pressurized to about 4000 bars by the fluid pump. It was then forced into a Y-form interactive vessel, where two squirts of liquid with the speed of 1000 m/s met head-on. This impaction would create a huge shear force as well as the void effect, which results in the manufacture of the nanoparticle. Furthermore, the slurry goes through the assistant vessel with several inner zigzags, which results in

more impaction occurring with the cavity walls and consequently smashing the nanoparticles further to obtain more homogeneous CNC.

Li and Liu [21] employed the high-pressure jet machine to prepare the NFC at 103.4 MPa for 12 times with a diameter of 80 μ m of its inner cavity. They indicated that the jet machine with small-bores in its main cavity could improve the relative water content of the prepared MCC. The test result showed that the relative water content of MCC was 1105% prepared by the machine with a diameter of 75 nm of its inner cavity for 10 times. Meanwhile, the MCC size decreased with the homogeneous times increasing and reached 100~200 nm after 5-time microfluidization, when the diameter of the main cavity was 100 nm. Compared to the homogenization under high pressure, the microfluidization had the disadvantage that the cavity was easily jammed by long fibers, and its energy consumption was high. It is not easily applicable in the industry.

2.1.3. Fine Grinding. The method of fine grinding was a novel physical way in preparing the MCC, which was realized by the fine grinder and a commercial grinder as shown in Figure 2. It was obvious that the core components consisted of two discs, the inner and the external, where both discs were covered with grooves with different parameters. The initial step of the process for the MCC preparation was firstly to pour the raw slurry into the gap between two discs, while the external disc remained stationary and the inner disc kept rotating. The relative rotation of the two discs produced the force of crush, shearing, friction, grinding, and tearing to divide the fibers as well as decrease their sizes to obtain the MCC. By controlling the grinding parameters, the MCC with varieties of size levels ended up with low energy consumption; meanwhile, the grinder was easy to clean and maintain. But it was incredibly inefficient, and little application was reported. Li and Liu [21] used the pretreated fibers of the coniferous tree to prepare the MCC by grinding the slurry for 15 times, and the diameter of the obtained MCC was 10~40 nm.

2.1.4. Freezing Smashing. The freezing smashing technique was used in smashing the frozen cellulose fiber with mechanical force to divide the cellulose fibers and produce the CNC. Liquid nitrogen was usually employed as the freezing medium to freeze the cellulose slurry, which could transfer

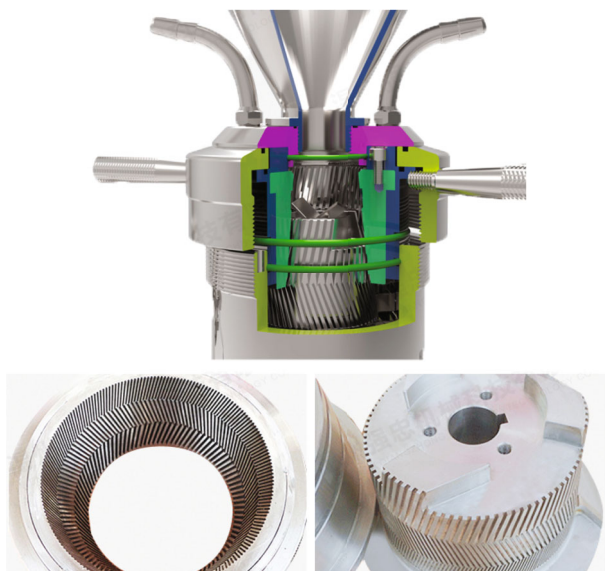


FIGURE 2: A commercial fine grinder.

the fibers from toughness to brittleness under low temperature and subsequently increase its internal stress. The powerful impaction from the mechanical smashing easily broke the structure of the frozen fibers hence dividing it to nanosize [22]. However, its cost was too high while it was also too low to be promoted.

2.2. Preparation of Chemical Process. Although all the above mechanical processes were employed in preparing the CNC, they were not widely applied due to their great energy consumption. Therefore, the chemical process was focused on treating the natural cellulose. As a kind of polysaccharide, the cellulose is made from the glucose molecules, which are connected by the β -1,4-glucosidic bond with each other [23]. Thus, the process of partially breaking glucosidic bonds is the key way to obtaining the CNC, and the chemical hydrolysis offers a case for realizing it [24].

2.2.1. Process of Alkali Hydrolysis. As a kind of natural polymer, the cellulose had the supramolecular structure which made it difficult to be hydrolyzed. However, the alkali had the ability to swell the cellulose as well as break its inner hydrogen bonds [25]. Therefore, the alkali was employed to hydrolyze the cellulose.

Research showed that the crystal form of natural cellulose was transferred from I-form to II-form after treatment with 9 wt% NaOH [26]. Zhang et al. [27] obtained the II-form spherical CNC by treating the cellulose with 5 M NaOH at 80°C and acid solution, successively. Tang et al. [28] used NaClO solution to hydrolyze the microcrystalline cellulose (MCC) to obtain spherical CNC with the diameter of 20~40 nm, and its crystalline was 79.71%. Hagman et al. [29] dissolved the MCC with 2 M NaOH solution and found that the MCC was hydrolyzed to new chains with a lower crystalline degree and kept stable in the solution. Xie et al. [30] investigated the effects of the parameters of the alkali

hydrolysis on the microstructure of the CNC. They showed that the productivity of II-form CNC was 54.50% with an average diameter of 156.9 nm, and its parameter was handling the cellulose with 5 M NaOH solution at 60°C for 2 hours. Although several studies have reported the application of alkali in hydrolyzing cellulose, the alkali was mainly employed in pretreating the cellulose to dissolve the lignin and pectin.

2.2.2. Process of Acid Hydrolysis. The microstructure of the cellulose fiber consisted of discontinuous regions of crystalline cellulose and amorphous cellulose, where the unconfined amorphous region was between two inerratic crystalline regions, and the fiber was made from the repetition of the above structures. Therefore, researches were aimed at how to remove the amorphous regions quickly and keeping the crystalline regions as well.

Liu et al. [31] prepared the CNC from reed pulp with 55 wt% sulfuric acid, using sodium *m*-nitrobenzene sulfonate (SMS) as the cocatalyst. It was indicated that the optimum parameters for the CNC preparation were the reaction at 50°C for 5 hours accompanied with 10 wt% SMS. Compared to the method with two catalysts, sodium dodecyl benzene sulfonate (SDBS) and cupric sulfate simultaneously, the CNC obtained from this process was smaller and more homogeneous, with much higher yield. Wu et al. [32] indicated that the ultrasound-assisted sulfuric acid method could be applied for the preparation of CNC, and its parameters were about 10 nm for diameter and 200~400 nm for length with a crystallinity of 63.3%. Meanwhile, the thermal insulation foam made of the CNC with the freezing-drying method expressed its perfect thermal insulation performance under normal condition.

You et al. [33] used the ultrasonic-assisted method to hydrolyze the MCC with carbon-based phosphotungstic acid as the catalyst. The obtained CNC was rod-like and I-form with a length of 146~862 nm and a diameter of 12~79 nm, whose crystallinity was 76.1%. Sun et al. [34] hydrolyzed the cotton fibers with 63.9% sulfuric acid at 50°C and tested its microstructure, solubility in alkali solution, molecular weight, and other characteristics. It was found that the hydrolysis time of 45~55 min was the optimum time range when the CNC yield was 32.2~41.7%, and the 18% NaOH solution was a perfect indicator for the CNC preparation. The process of acid hydrolysis is widely applied all over the world, but the terrible wastes are unavoidable, wasted solution of acid, alkali, water, and residua. And the novel ways for obtaining the CNC have drawn the attentions all the time.

2.2.3. Process of TEMPO Hydrolysis. The TEMPO is a series of reagents used to oxidize the alcohol and ether, including 2,2,6,6-tetramethylepiperridin-1-oxyl and its ramifications with the structure of 1-oxyl, an oxygen radical. Research showed that the function of the TEMPO was its oxidation effect on the alcoholic hydroxyl group [9]. As an efficient and pollution-free reagent, the TEMPO was employed to produce the CNC, and its common reaction system consisted of the TEMPO, the NaBr, and the NaClO [35].

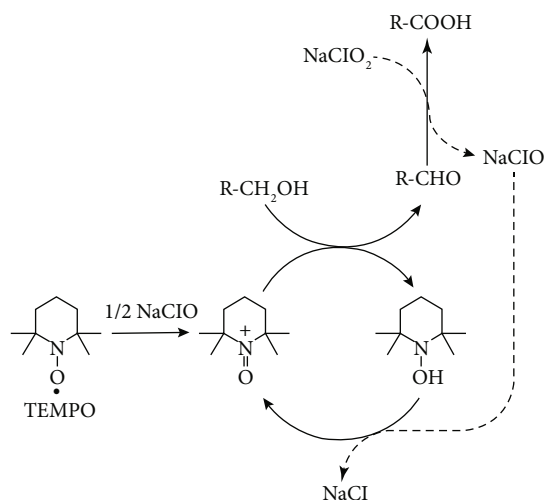


FIGURE 3: Oxidation of primary hydroxyls to carboxyls by the TEMPO/NaClO/NaClO₂ system under weak acidic or neutral conditions [37].

2.2.3.1. Development of TEMPO Reaction System. Research indicated that the process of the TEMPO oxidation of the cellulose was a process where the C6-formyl group was transformed to the C6-carboxyl group [36]. As the main oxidation reagent, the NaClO firstly transformed the NaBr into NaBrO, and the produced NaBrO would oxidize the TEMPO to be a nitroxonium. Nitroxonium underwent oxidation to transform the alcoholic hydroxyl group and produced an aldehyde or carboxylic acid, where its mechanism was displayed in Figure 3 [37].

However, further study showed that the basicity of alkalinity had great effect on the degree of dissociation of the CNC, which might have led to the decrement of the mechanical properties of the CNC, as the strength and flexibility of the nanofibers [38]. Therefore, the present researches of the reaction systems were mainly focused on the adjustment and controlling of the reaction system [39].

Saito et al. [37] replaced the NaBr in the reaction system of the TEMPO/NaBr/NaClO with the NaClO₂ and found the phenomena that the aldehyde groups teemed in the produced CNC surface obtained from the reaction system of the TEMPO/NaBr/NaClO, and it did not occur in the TEMPO/NaClO/NaClO₂ system. This mechanism is shown in Figure 3. Meanwhile, the size of the CNC made from the above reaction system was long for 2 μm and wide for 5 nm; the degree of polymerization was 900, with an optimum reaction pH of 6.8.

Although the system of the TEMPO/NaClO/NaClO₂ displayed its advantages, its disadvantages were also unavoidable, such as its terrible reaction rate and relatively low content of the carboxyl in the CNC. Attentions were drawn to improve the efficiency of the TEMPO/NaClO/NaClO₂ system [40]. Iwamoto et al. [41] employed ten kinds of systems consisting of TEMPO ramification, NaBr, NaClO, and NaClO₂ to compare their efficiencies in preparing the CNC. It resulted that the 4-acetamido-TEMPO and

the 4-methoxy-TEMPO showed their optimum catalytic efficiencies; however, the 4-hydroxyl-TEMPO and 4-oxygen-TEMPO showed the worst efficiencies. In addition, the ultrasonic assistance was usually used in the chemical reaction. Mishra et al. [42] utilized the system of the TEMPO to hydrolyze the cellulose with the ultrasonic assistance, and the productivity of the CNC was raised by about 10%, when the content of the carboxyl was raised by 10~15%. According to the above investigations, it was obvious that the preparations with the system of TEMPO were a pollution-free and efficient way to produce the CNC, which also sketched the contours of its development prospect of the assistance-TEMPO methods.

2.2.3.2. Effect of Treatment on the Dispersion of the CNC. The preparation of the CNC was affected by a series of factors that involved the reaction conditions, the carboxyl content, the homogenization treatment, and other circumstances [43–45], in which the carboxyl content of the CNC controlled the dispersity of the cellulose fiber in water as well as the productivity of the CNC [46].

Hirota et al. [47] indicated that the oxide cellulose fiber obtained with different methods possessed a similar carboxyl concentration of 1.8~2.2 mmol/g on the fiber, which was the maximum content in the undissolved cellulose fibers. On the other hand, low content of the carboxyl in the CNC was against its decentralization in the water. Saito et al. [48] found that the system's viscosity increased quickly with 2~4% solid content; however, the phenomena did not occur while the content was below 1%. In addition, research showed that the CNC solution possessed much more carboxyls and displayed relatively lower viscosity, because of the electrostatic repulsive force among the carboxyls [49, 50]. Okita et al. [43] reported that the TEMPO-CNC dissolved not only in water but also in several organic solvents, and the CNC could also be obtained in the organic solvent just with extremely high energy consumption. The morphology of CNC obtained by four methods is shown in Figure 4 [51].

2.3. Preparation of Biological Fermentation. Usually, the process of chemical hydrolysis is low-cost and convenient for preparing the CNC, but its pollution is terrible since it leaves lots of wasted solutions of acid or alkali, which is difficult to handle and harmful to the environment. Therefore, the non-complicated, efficient, and pollution-free method for preparing the CNC is focused on in recent years. As a perfect solution, the biological process rises in response to the proper time and conditions, which mainly involves the biological hydrolysis.

The CNC was firstly obtained from some specific bacterial cellulose (BC) in 1886 [52], which was so called bacterial nanocellulose (BNC). Several bacteria were discovered and employed in obtaining the BNC, including the Acetobacter, Azotobacter, Achromobacter, and Aerobacter [53]. In fact, the BC was better than plant cellulose in terms of its higher purity, crystallinity (over 60%), degree of polymerization (between 2000 and 6000), and tensile strength [54, 55]. Therefore, the BC was a perfect resource for the BNC.

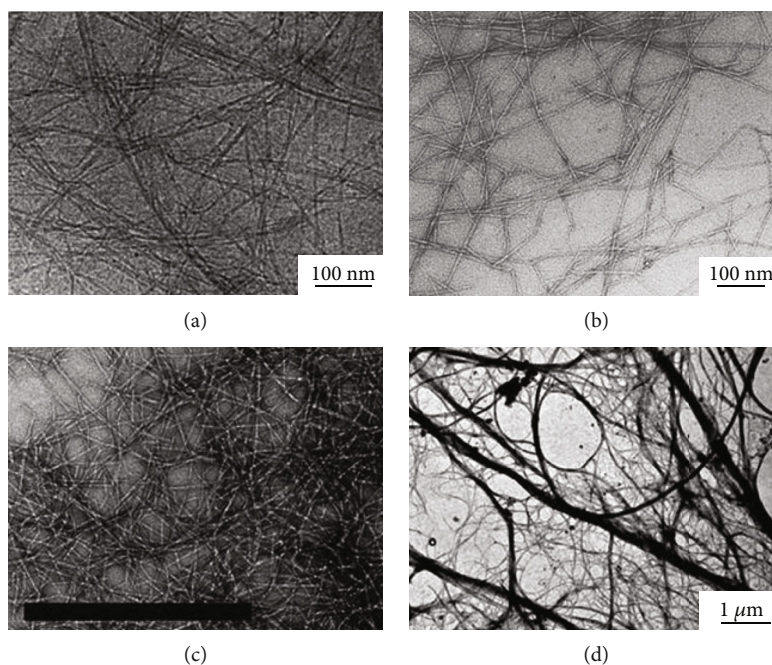


FIGURE 4: TEM of CNCs obtained from wood pulp using different pretreatments, (a) enzymatic, (b) TEMPO-mediated oxidation, and (c) carboxymethylation, and obtained from (d) *Opuntia ficus-indica* [51].

TABLE 1: Comparison of BNC and cellulose II.

Type	Length (μm)	Width (nm)	Height (nm)	Cross-section	Crystallinity ^a (%)	I β (%)
Acetobacter	>1	30-50	6-10	Rectangular	63	3-27
Acetobacter ^b	>1	6-10	6-10	Square	—	53
Cellulose II	Filament	—	—	Cylindrical	27-43	—

Usually, the BNC was extruded through the bacterium cell pores in the form of ribbons. These ribbons started at specific points on the cell surface and became thicker as they built a composite ribbon. Finally, the cellulose nanofibers were with a 2~4 nm diameter and several 100 μm length [51, 56]. However, each bacterium BNC had its own merits according to the difference in the bacterium type as well as its cultured conditions. For instance, the *Acetobacter* BNC was with an α -crystalline structure and its fiber showed a rectangular section with a parameter in (6~10) nm \times (30~50) μm . A list of CNC with different characterizations is shown in Table 1 [57].

Although the characterizations of the component ratio of amorphous and crystalline regions and size of the microcellulose are according to the kinds of bacteria, the ways of dividing them from each other by removing the amorphous zones are common, and the cellulase acts as a pair of scissors to do it. Usually, the scissors consisted of several cellulases, 1,4- β -D-glucan glucanohydrolase, 1,4- β -D-glucan cellobiohydrolase, β -1,4-glucosidase, etc. [58]. Because of the heterogeneous catalytic reaction of the cellulase, no cellulase possessed the ability to efficiently catalyze the BC hydrolysis individually, and the biological process was always focused on increasing the hydrolyzed efficiency with the combined actions of kinds of cellulases.

BNCs obtained by catalyzing the pulp with *Trichoderma viride* G were with great globular characterizations (2.5~10 nm) with optimum conditions of pH 4.8 and temperature of 45°C for 2 h [59]. It was indicated that the BNC produced by *Acetobacter xylinum* was with a great thermostability ($\leq 330^\circ\text{C}$) and swelling resistance, while the producing efficiency raised by controlling the fermentation temperature and rotation speeds [60]. On the other hand, researches on the BNC production by sugar derivatives were also focused on long ago, with results showing that the productivity obtained from arabitol and mannitol was 6.2 and 3.8 times, respectively, more than that from the glucose [61]. The MCC obtained from the *Cladophora* showed an average length of 350 nm with a degree of polymerization of 690 for β -glucan chain [59]. More and more attentions were drawn for its economic efficiency and irreplaceable sustainability.

2.4. Preparation via the Combined Method. In general, all the above solutions could be applied for CNC preparation, but there exists lots of problems that limit the development of those technologies, such as the energy-extensive consumption of the mechanical process, the heavy pollution of the chemical process, and the underactivity of the biological process on raw plant fibers. Therefore, the combination of several methods is an irresistible trend of the CNC preparation. And the normal

combinations are between the process of machinery and chemistry or biology.

By combining chemical pretreatment and mechanical methods, Alemdar and Sain obtained the MFC with a 10~80 nm in diameter and several microns in length [62]. Meanwhile, the MFC from the preoxidized pulp were with average diameters of 5.51 nm by rotation and 4.7 nm by ultrasound [63].

3. Applications of CNC

Owing to lots of perfect properties of strength, light transmission, gas barrier, et al., the applications of the CNC were focused on the optical film, electronics, composite materials, and other fields [64–68].

3.1. CNC Reinforcement Composites. As a preprocessing field, the development of nanocomposites was drawing more and more attentions since the properties of CNC included high strength, low density, great biodegradation, green renewability, crystallinity, porosity, and interphase effects [69].

As a nanofiber from the natural resources, the CNC possessed a mean strength within the ranges of 1.6~3 GPa, which was comparable with those of commercially available multiwalled carbon nanotubes [70]. Therefore, it was available for the reinforcement of the composites with CNC.

It was shown that the CNC-reinforced Polyvinyl Alcohol (PVA) fibrils possessed a tensile modulus of 57 GPa far greater than those of PVA fibrils as well as its storage modulus [71], which was because of uniform dispersion of CNC in the PVA and their hydrogen bonding. Another research employed the use of CNC to modify polyethylene oxide (PEO) and showed that E and S_t of the 20%-CNC/PEO composites improved 2 and 2.5 times comparing to the pure PEO, respectively, [72].

Li et al. [73] obtained the nanocomposites by combining the CNC with the polymerization of phenol, and their thermal stability was much better than the polyphenols. Wang et al. [74] prepared a CNC/soy protein thermoplastics and found that E and S_t of the composite changed from 0.53 to 1.02 GPa and from 16.7 to 31.2 MPa, respectively, by adding 20% CNC. However, it changed from 0.60 to 1.82 GPa and from 20.2 to 59.3 MPa, respectively, with 30% CNC [75].

3.2. Barrier Films. Because of its waterproof and barrier functions, the CNC-modified composites have attracted interest in the applications of barrier films with potential utilizations in filtration and packaging [76]. The investigations were mainly focused on how to prevent water vapor and oxygen from permeation into the envelope.

It was shown that the water vapor permeability decreased with the CNC addition in the envelope. Choi and Simonsen [77] indicated that the CNC composite film possessed great water vapor preventions with a permeability decrease to 11% in thermal treatments. Chinga-Carrasco and Syverud [78] proved that the oxygen permeating speed was $3.0 \text{ cm}^3 \cdot (\text{m}^2 \cdot 24 \text{ h} \cdot 0.1 \text{ MPa})^{-1}$ with a 50% relative humidity level by testing the CNC film. The great barrier property was proven by Fukuzumi et al. [79] that the average pore size

of CNC film was about 0.47 nm close to the kinetic diameter of oxygen, and this structure would prevent oxygen from approaching into the envelope.

Meanwhile, applications of CNC in the oxygen permeability of composite film were also investigated. Petersson and Oksman [80] found that the oxygen permeability of the polylactic acid (PLA) was increased by over 3 times compared to pure PLA with 5 wt% MCC addition. In contrast, other researches showed that the oxygen permeability of CNC/PLA film was significantly lowered to $1 \text{ mL} \cdot \text{m}^{-2} \cdot \text{day}^{-1} \cdot \text{Pa}^{-1}$ with a film structure of a 0.4 mm TEMPO-NFC film on top of a 25 mm thick PLA film ($746 \text{ mL} \cdot \text{m}^{-2} \cdot \text{day}^{-1} \cdot \text{Pa}^{-1}$) [81]. It was interesting that the properties went in the opposite directions with different film structures. Because the barrier properties of envelopes were connected to factors that influence the tortuous path of the diffusion species through the film, the difference between the two studies mentioned above might be affected by several factors, such as orientation, concentration, reinforcement shape, crystallinity, porosity, and interphase effects.

Similarly, it was demonstrated that neat CNC films possessed a relatively low oxygen permeability of $17 \text{ mL} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$ with a thickness of 20~30 mm [82]. However, it was below $10 \sim 20 \text{ mL} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$ of the oxygen transmission rate of the atmosphere packaging with this CNC modification [83]. This property demonstrated the potential of neat and/or modified CNC films for oxygen barrier applications.

3.3. Biomaterials. CNC has been widely used in biomedical scaffolds, strain sensor, oil/water separation, drug excipient, wound dressings, and other biological materials for its biodegradability, high biocompatibility, and nontoxicity [84, 85].

Zhang et al. [86] developed an optical probe for the selective and quantitative detection of Cu^{2+} using surface-modified fluorescent CNC. The external surface of fluorescent CNC was modified by the mild EDTAD esterification and amidation with 7-amino-4-methylcoumarin, which caused the topological distribution of fluorescent moieties and other functional groups. It is possible that the fluorescent CNC can be widely used for bioimaging and metal ion detection in the coming years. Recently, the CNC-based composite using 3D printing technology has attracted extensive attention in the medical field. Sultan and Mathew [87] prepared porous and 3D printable scaffolds from the hydrogel ink of sodium alginate and gelatin reinforced with CNC. CNC provided nice structural orientation, rheological properties, and mechanical properties during the 3D printing process. The biobased scaffolds with pore size from 80 to $2125 \mu\text{m}$ and nanoscale pore wall roughness were considered suitable for cell interactions and guided cell growth during tissue regeneration. Though many researches about biocompatibility, long-term toxicology, and security between CNC-based composite and human bodies remain in the exploration stage, lots of results indicate a promising future.

3.4. Other Applications. As a promising material for energy application, the flexible energy storage device was made by using the MWNT nanowire arrays of CNC [88]. The typical structure was based on a single sheet of conductive cellulose

paper (separator) made from room temperature ionic liquid and CNC (electrode). Zhu et al. [89] proved that the CNC nanopapers could be applied as the matrix for light-emitting diode (LED) and also found that LED with CNC matrix are highly transparent in the visible and near-infrared wavelength regions. Meanwhile, the CNC matrix was all flexible enough to be compatible with roll-to-roll processing.

Niu et al. [90] employed the CNC for preparation of the multilayer membrane electrode for the supercapacitor. It indicated that the prepared composite film exhibited great flexibility and elastic resilience for the application prospect. Gao et al. [91] manufactured a conductive paper with a self-assembly of the CNC and reduced graphene oxide (RGO). It indicated that the composite paper possessed an excellent mechanical property, and its transmittance and sheet surface resistance could be designed by controlling the number of layer-by-layer (LbL) assembly. For example, the paper with a 20 LbL shows a sheet resistance of $\sim 2.5 \text{ k}\Omega$ and a transmittance of 76% (at 550 nm). It revealed a greater prospect in the field of information-transfer than conventional paper.

4. Conclusions

The preparation methods and applications of the CNC were summarized in this paper, and the scarcity of resources urged us to find some renewable resources to effectively contrast this phenomenon. CNC in the form of microfiber or nanofiber had unique properties including high elastic modulus, dimensional stability, outstanding reinforcement potential, and transparency. As a natural resource, efficient obtainment and smart application were still drawing the attentions on environmentally friendly utilization all the time. Since CNC research is still at its booming stage, industrial commercialization has not been arrived at yet. There exists a huge market of CNC, and indications show that the world market of CNC would be 60 billion dollars in 2020. Therefore, a great prospect is displayed for its development. With proof-based investigations, there would be a real improvement in this field to reply all circumstances.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

Acknowledgments

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