1

Introduction to Nanocellulose

Jin Huang[1]*, Xiaozhou Ma*[1]*, Guang Yang*[2]*, and Dufresne Alain*[3]

[1] *Southwest University, Chongqing Key Laboratory of Soft-Matter Material Chemistry and Function Manufacturing, School of Chemistry and Chemical Engineering, Tiansheng Road 2, Chongqing, 400715, China*
[2] *Huazhong University of Science and Technology, College of Life Science and Technology, Luoyu Road 1037, Wuhan 430074, China*
[3] *University Grenoble Alpes, CNRS, LGP2, Grenoble INP, 38000 Grenoble, France*

1.1 Introduction

Cellulose is the most abundant polymer on earth produced by plants, microorganisms, and cell-free systems. Chemically, it is composed of repeated β-ᴅ-glucose monomers linked together through β-(1,4) glycoside linkage. The morphology of natural cellulose is usually fibrous with intermittent crystalline and amorphous sections [1]. Separation of fibers results in nanoscale cellulose substances known as nanocellulose, which exists in different morphologies such as cellulose nanocrystals (CNCs) or cellulose nanowhiskers (CNWs) as another name, and cellulose nanofibers (CNFs) (Figure 1.1). Compared to the plant cellulose containing lignin and hemicelluloses, microbial cellulose, termed as bacterial nanocellulose (BNC) and cell-free cellulose, represents the purest form of cellulose. Nanocellulose exhibits distinctive structural and physicochemical, mechanical, and biological characteristics, including reticulate fibrous three-dimensional web-shaped structure, high crystallinity, good mechanical strength, biocompatibility, biodegradability, optical transparency, high specific surface area, polyfunctionality, hydrophilicity, and moldability into 3D structures [2–4]. As a sustainable material, nanocellulose could be extracted from the disintegration of plant and animal cellulose [5], synthesized by different microbial strains [6], and cell-free systems [7]. As a tunable material, nanocellulose both alone and in composite form with other materials is immensely used in various fields such as wound dressing, textiles and clothing, food, cosmetics, regenerative medicines, tissue engineering, energy, optoelectronics, bioprinting, environmental remediation, and so on [2, 8–13].

Nanocellulose exhibits superior structural characteristics than microcrystalline cellulose (MCC), and possesses high mechanical strength and can be facilely surface-modified via different strategies. For example, the longitudinal modulus of CNC extracted from tunicate can reach as high as 151 GPa, while the Young's modulus of CNF varies between 58 and 180 GPa and its tensile

Nanocellulose: From Fundamentals to Advanced Materials, First Edition.
Edited by Jin Huang, Alain Dufresne, and Ning Lin.

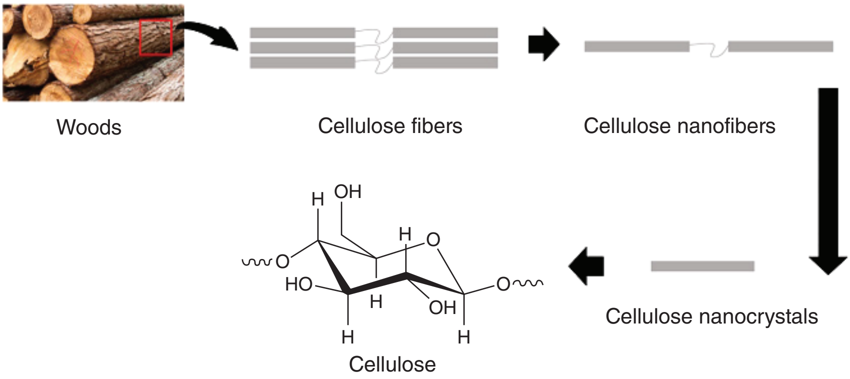

Figure 1.1 Schematic illustration for the preparation of cellulose nanofibers and cellulose nanocrystals using the wood resource.

strength can reach up to 22 GPa according to the type of raw material and the preparation method [14, 15]. Nanocellulose contains greater number of hydroxyl (OH) groups, which make it highly hydrophilic and can be modified via different chemical and physical strategies [16]. Thus, considering its high biocompatibility, high mechanical strength, renewability, and low cost, nanocellulose has received immense consideration as an ideal nanostructure to make new high-value nanomaterials.

1.2 Preparation of Nanocellulose

Depending on the type of nanocellulose and its source, different strategies are employed for its production. For example, destructuring strategies involving high-pressure homogenization, grinding, and chemical or enzymatic treatments, are used for the isolation of nanocrystalline cellulose (NCC). In contrast, BNC is naturally produced by different microorganisms. The following section briefly overviews different preparation methods of nanocellulose (see Chapters 2, 3 and 4 for details).

1.2.1 Cellulose Nanocrystals

Cellulose nanocrystals (CNCs) are the mostly commonly used nanocellulose, which are mainly produced through hydrolysis of the amorphous section of cellulose fibers [17]. This process consists of two steps: the pretreatment of the raw material followed by its hydrolysis into CNCs. The raw material contains different impurities in the form of esters, wax, hemicelluloses, and lignin, which are removed by treating with alkaline (NaOH) solution or applying a bleaching method before hydrolysis. Thereafter, the purified raw material is heat-treated in the acidic environment for around 45 min in general or longer time up to several hours to hydrolyze the amorphous section of cellulose fibers. The obtained suspension is then centrifuged and dialyzed to achieve the purified CNCs. The CNCs produced through this strategy commonly show a rod-like morphology when observed under transmission electron microscopy (TEM)

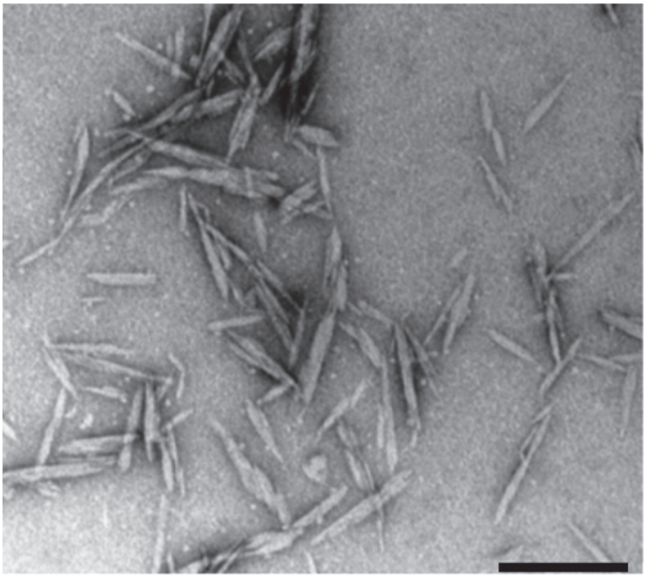

Figure 1.2 TEM micrograph of cotton linter-derivate CNC obtained through acid hydrolysis (scale bar = 200 nm).

(Figure 1.2). The diameter and length of CNCs obtained through acid hydrolysis vary depending on raw material type, acid type, and hydrolysis temperature and time. For example, CNCs with diameter of 10–30 nm and length 200–300 nm were obtained through acid hydrolysis of cotton fibers at 65 °C using H_2SO_4. In contrast, CNCs with the length more than 1 μm were obtained from ascidian under the same experimental conditions [18, 19]. Similarly, CNCs with length 100–200 nm and diameter 10 nm were obtained through acid hydrolysis using HCl under the analogous experimental conditions [20]. Besides acid hydrolysis, other reactants including oxidants such as tetramethyl-piperidin-1-oxyl (TEMPO) or ammonium persulfate (APS), and some bio-enzymes, are also used for the production of CNCs. For instance, TEMPO, NaBr, and NaClO could be together used to directly produce TEMPO-oxidized CNC (TOCNC) from cellulose fibers [21]. During the preparation process, the reaction is carried out in an alkaline environment by constantly adding NaOH solution to the reaction mixture until a constant pH is kept. The TOCNC in the mixture could be purified by centrifugation and dialysis. Similarly, Satyamurthy et al. used the cellulolytic fungus to hydrolyze MCC. The yield of this strategy could be as high as 20%; however, its high cost strongly limits its large-scale application [22].

1.2.2 Cellulose Nanofibers

Compared to CNCs, the preparation of cellulose nanofibers (CNFs) is much simpler as it does not require severe chemical cleavage in the molecular structure of the cellulose chain. Generally, CNFs are prepared by the physical separation of cellulose fibers, such as grinding, homogenization, and ultrasonication [23–26].

Besides the strategies of mechanical peeling and dissection, CNFs can also be prepared by chemical methods. For example, oxidation of wood raw material by TEMPO under gentle stirring results in fine individual CNFs [27]. Sometimes, both mechanical and chemical strategies could be employed together to produce individual CNFs. For example, carboxymethylation and high-pressure homogenization can be applied simultaneously to prepare uniformly distributed CNFs [28]. For the preparation of CNFs, the most commonly used raw materials are wood, however, cotton fibers, tunicate, and other raw materials are also attempted to be used. Depending on the type of raw materials, the diameter of CNFs usually varies from 2 to 50 nm [29] (Figure 1.3). CNF usually has a high aspect ratio, which makes it an ideal positive ingredient for the enhancement of polymer materials (see Chapter 3, 6 and 8 for details).

1.2.3 Bacterial Nanocellulose

Bacterial nanocellulose (BNC) is naturally produced by several bacterial genera including *Acetobacter*, *Rhizobium*, *Agrobacterium*, *Aerobacter*, *Achromobacter*, *Azotobacter*, *Salmonella*, *Escherichia*, and *Sarcina* [30] and cell-free systems [7]. It is produced in the form of a hydrogel at the air–medium interface. During the synthesis, β-1,4-glucan chains are produced in the interior of the bacterial cell, which is then excreted across the cell membrane as protofibrils that crystallize to form ribbon-shaped microfibrils followed by formation of pellicle [31] (Figure 1.4). The structural characteristics such as diameter (20–100 nm), arrangement of fibers, and physico-mechanical properties of BNC strictly depend on the microbial strain type, the synthesis method (cell and cell-free systems), and the culture conditions including carbon and nitrogen source [33, 34]. BNC has been largely used for various biomedical applications such as tissue engineering, regenerative medicines, enzyme immobilization, drug delivery, and 3D printing biomaterials [2, 35–37]. However, the large-scale applications of BNC are hampered by its high production cost [38]. Different strategies have been developed for high-yield and cost-effective production of BNC with superior structural and physico-mechanical features. These include the advanced fermentation approaches, genetic engineering strategies, and strain improvement for high-yield BNC production, and use of different industrial wastes such as fruit juices, sugarcane molasses and agricultural wastes for low-cost production [39–43] (see Chapter 4 for details).

1.3 Surface Modification of Nanocellulose

The hydroxyl groups present on the surface of nanocellulose make it highly hydrophilic and favorable for surface chemical modification or physical interaction [16]. The chemical and physical properties of nanocellulose can be easily controlled by different strategies (see Chapter 5 for details), and some chemical methods are summarized in Figure 1.5 [44]. In order to guarantee the quality and efficiency of surface modification of nanocellulose, the uniform dispersibility of nanocellulose in the suspension medium is the principle factor to reactive

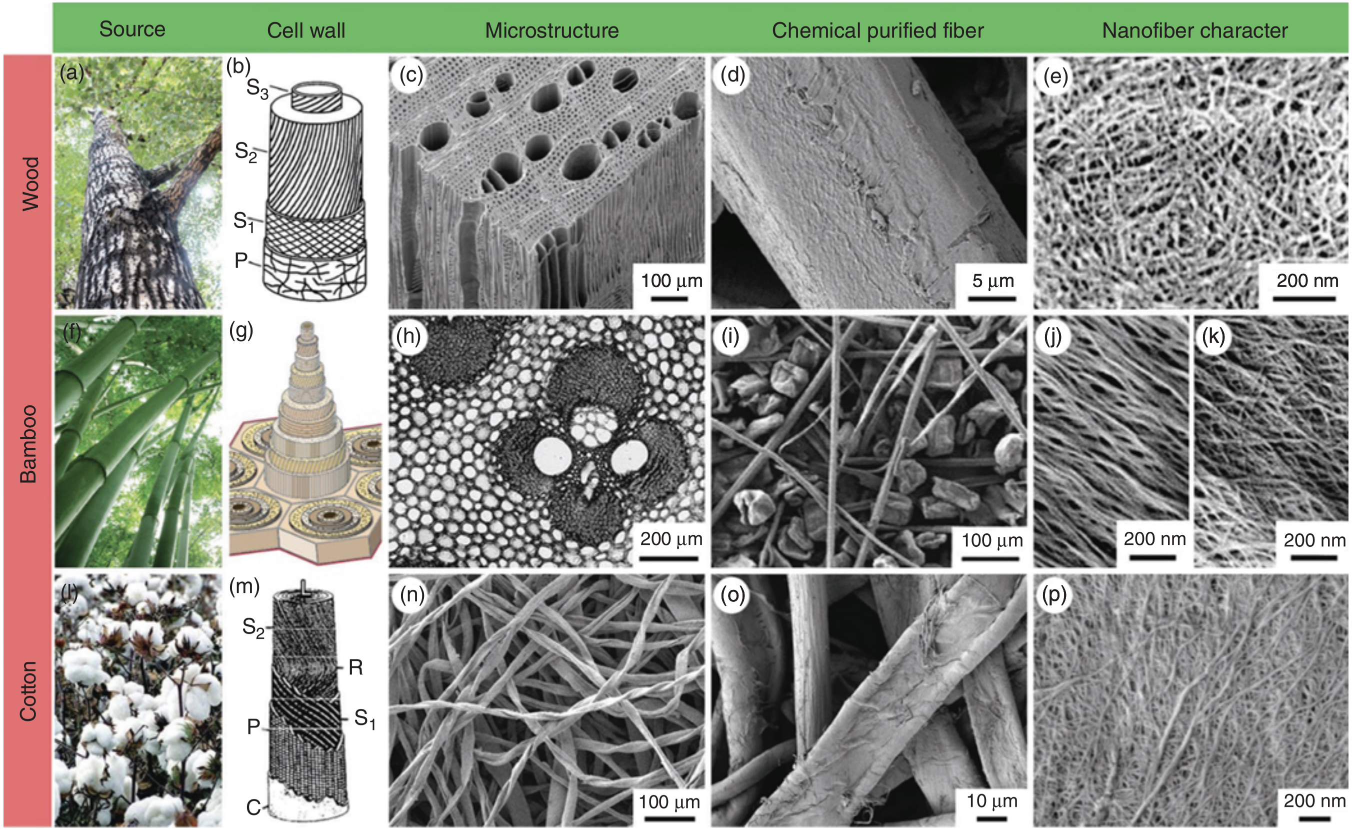

Figure 1.3 Preparation of cellulose nanofibers from different raw materials. Source: Chen et al. 2018 [29]. Reproduced with permission of RSC.

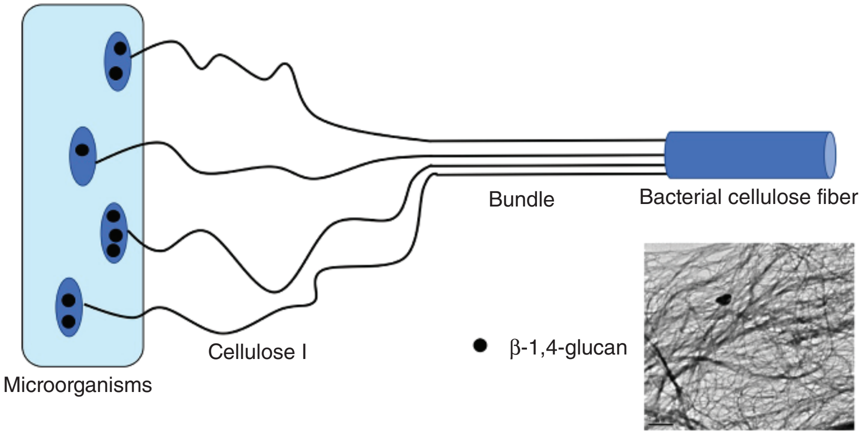

Figure 1.4 Preparation of bacterial cellulose. Source: Lai et al. 2013 [32]. Reproduced with permission of Springer Nature.

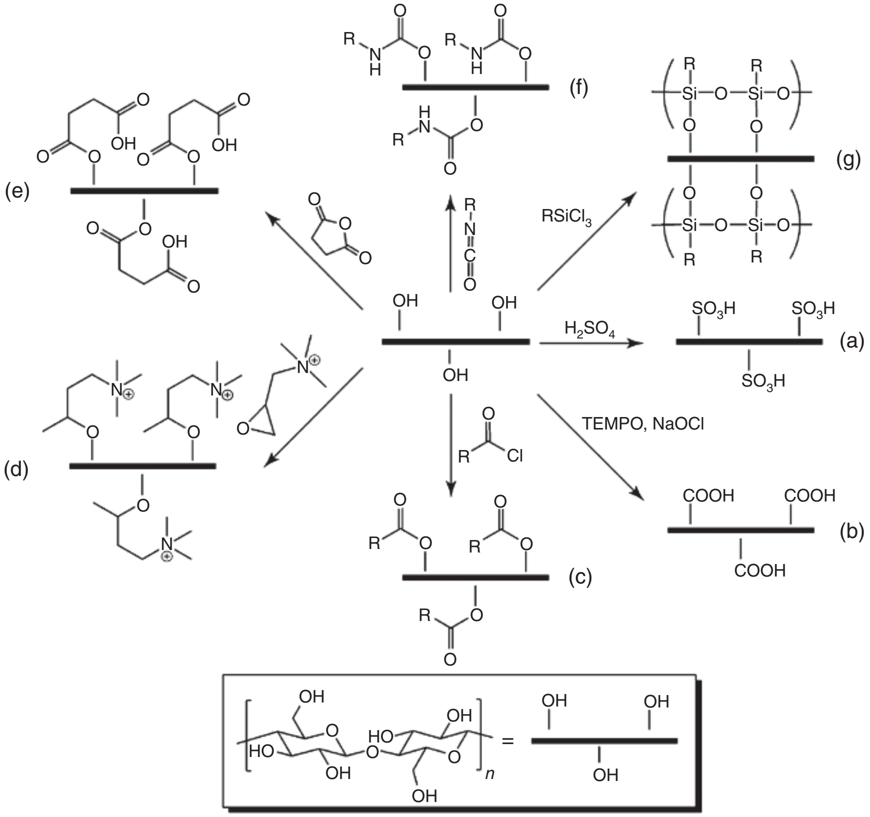

Figure 1.5 Schematic illustration for surface chemical modification of CNCs by various methods including sulfonation (a), oxidation (b), nucleophilic substitution (c), etherification (d), esterification (e), carbamation (f), and silylation (g).

conjugation and physical attachment of the nanocellulose surface. Especially when using an organic solvent as the suspension medium, due to the hydrophilicity of the nanocellulose surface, the solvent replacement from aqueous medium to organic solvent is employed as an effective way while the intensified dispersion techniques, such as ultrasonication, high-speed shear and so on, are essential to homogenize the nanocellulose suspension.

1.3.1 Esterification

The most common strategy used to modify nanocellulose is by esterification, which offers a high substitution ratio of OH groups on nanocellulose surface [45–47]. According to the chemical structure of cellulose, there are three OH groups on each glucoside unit, which are C2-OH, C3-OH, and C6-OH. In general, the order of activity of these OH groups is C6-OH > C3-OH > C2-OH (Figure 1.5). During the chemical reaction, only one moiety for C3-OH and C2-OH might be modified due to the steric hindrance effect of nanoscale CNC surface. Another advantage of this esterification method is that the reaction conditions are mild; thus, a high substitution ratio can be achieved without compromising the crystalline structure of nanocellulose [48–50]. Researchers have successfully used this method to make hydrophobic nanocellulose, which can be easily used to enhance the mechanical properties of hydrophobic polymer matrix. In addition, when using ethylenediaminetetraacetic dianhydride (EDTAD) to decorate carboxyl groups onto the CNC surface, high carboxylation degree of the CNC surface was achieved. Furthermore, in comparison with the TEMPO-oxided CNC with an equivalent carboxylation degree, the surface integrality of EDTAD-esterified CNC was kept [51].

1.3.2 Oxidation

Oxidation is the most commonly used method for making carboxylated nanocellulose because the C6-OH on nanocellulose surface can be easily oxidized into a carboxyl group. This oxidation reaction usually takes place in the presence of TEMPO [27, 32, 52]. Additionally, TEMPO can selectively oxidize C6-OH to a carboxyl group in the presence of NaClO and NaBr under alkaline environment. However, high TEMPO concentration and long oxidation time may break the chemical bonds between glucoside units, and thus compromise the crystalline structure and surface integrality of nanocellulose [21]. It was also reported that such phenomenon could be used in making carboxylated CNC directly from the cellulose-containing raw materials. Another oxidant that can be used in nanocellulose oxidation is APS. However, due to its high oxidation potential, APS seriously damages the crystalline structure of cellulose; thus the morphology of the CNC produced is obviously shorter and thinner than the one produced through traditional acid hydrolysis [53]. By using oxidation strategy, aldehyde groups can also be formed onto the nanocellulose surface. Usually, sodium periodate ($NaIO_4$) is used to oxidize the 2,3-diol structure of the glucoside, and thus can make two aldehyde groups, which can be widely used in Schiff base reaction-based further modification [54]. Besides, a study has also reported that some of the glucoside units on CNC innately present aldehyde groups, and thus the amino- or diamine-containing fluorescent molecules could be directly conjugated on the CNC surface without any additional pretreatment [55].

1.3.3 Etherification

Etherification is a highly efficient modification method for cellulose, which usually uses an epoxylated molecule as the modification agent together with organic solvent-containing heating system [56–58]. The efficiency of this process is largely compromised by the polymerization; nevertheless, it offers a high substitution ratio. As well-known, the epoxy group reacts with the OH group of the nanocellulose surface and forms ether bonds and an OH at its β position. The OH group formed further reacts with the epoxy groups; hence, polymerization takes place on the nanocellulose surface. This issue can be partially resolved by controlling the reaction conditions; however, polymerization cannot be completely avoided.

1.3.4 Amidation

As most biomolecules possess amine groups, amidation is considered as a mild and efficient way to modify the nanocellulose surface with these biomolecules. The amidation reaction can take place both in organic solvents (e.g. dimethylformamide, abbreviated as DMF) and aqueous solutions to conjugate two molecules that have carboxyl groups and amine groups, respectively. Since nanocellulose generally has no carboxyl groups or amine groups on its surface, the carboxyl groups or amine groups should be decorated on the nanocellulose surface before the amidation, for example using TEMPO oxidation. In the aqueous reaction system, the carboxylated nanocellulose is thereafter reacted with *N*-hydroxylsuccinimide (NHS), which can improve the reactivity of carboxyl groups on nanocellulose surface with the amide groups. The final step of amidation modification is to mix the NHS-activated carboxylated nanocellulose with the amide-containing molecules. The amine groups of the molecules can directly react with NHS-activated carboxylated nanocellulose, and conjugate the molecules onto the nanocellulose surface with the linkage of amide bonds [59, 60]. However, if organic solvent (e.g. DMF) is used instead of aqueous medium, the amine-containing molecules can be directly conjugated onto the carboxylated surface of nanocellulose.

1.3.5 Other Chemical Methods

Other chemical methods, such as nucleophilic substitution, carbamation and so on, have also been reported to modify the nanocellulose surface, especially in making hydrophobic nanocellulose for nanocomposite enhancement or fluorescent nanocellulose for biomedical applications [61, 62]. In addition, long chain molecules and polymers have been attempted to be grafted on the nanocellulose surface. In this case, the "graft onto" strategy has been employed via the above-mentioned chemical methods to covalently linked long chains on the nanocellulose surface, but is obviously subject to the steric hindrance of nanoscale surface;

meanwhile, the “graft from” strategy could produce higher grafting density and longer polymer chains using various polymerization methods, which are initiated by hydroxyl groups and newly formed corresponding functional groups on the nanocellulose surface (see Chapter 5 for details). All these methods mentioned above generally require organic solvents and heating condition during the reaction. As a result, such chemical modification methods are quite suitable to hydrophobic surface modification of nanocellulose; however, these methods are limited for the modification of many hydrophilic molecules on the nanocellulose surface due to the mismatching of solvent in the reaction system.

1.3.6 Physical Interaction

Physical interaction is another way to modify the nanocellulose surface; however, the physical interactions are commonly relatively weaker than the covalent bonds. Generally, physical interactions include hydrogen bonding, electrostatic interaction, hydrophilic/hydrophobic interaction, and π–π stacking. The rich OH groups on nanocellulose surface can directly interact with the electron-rich groups containing oxygen or nitrogen atom, other hydroxyl groups, and carboxyl groups to form hydrogen bonds. The hydrogen bonding potential of nanocellulose might improve the association with the pre-designated modifiers; and then the hydrophobized nanocellulose after physical modification has been frequently used to enhance its dispersibility in nonpolar polymer matrix of composites. For example, a simple method that can improve the dispersion of nanocellulose in nonpolar matrix is to introduce surfactants or amphiphilic polymers containing both polar and nonpolar moieties, which can interact with both hydrophilic nanocellulose surface in physical pre-modification stage and the nonpolar matrix in material compounding process, and can act as a bridge to improve the compatibility between nanocellulose and the matrix [63, 64]. Also, the carboxylated surface enables nanocellulose to strongly interact with the molecules containing positive charges (e.g. ammonium-containing molecules). Such interaction can also be used in the surface modification of nanocellulose and thus allows compounding with nonpolar polymers or hydrogels to produce nanocellulose-based composites with excellent properties. The surface modification strategy based on physical interaction of nanocellulose with other substances offers several advantages, including the protection of nanocellulose crystalline structure, facile and cost-effective preparation process, and so on. However, it is also noteworthy that the physical interaction between the components in most cases is not as strong as covalent bonds, and the integrity preservation of nanocellulose and modifiers in applications is a key issue (see Chapter 5 and 6 for details).

1.4 Nanocellulose-Based Materials and Applications

Based on the chemical and physical properties of nanocellulose and its surface modification strategies related with various methods, varieties of nanocellulose-based composite materials have been developed and widely applied in electronic and energy devices, biomedical diagnosis and treatment, and other high-value fields. Nanocellulose generally possesses high mechanical properties; and, for example, the longitudinal modulus of CNC extracted from tunicate can reach as high as about 151 GPa, which is equivalent to that of steel as about 200 GPa. Such high mechanical strength with highly reactive surface, renewability and degradability, makes nanocellulose an ideal sustainable candidate for material enhancement. Similarly, when cellulose raw material is hydrolyzed into CNC, the resultant suspension can perform some interesting optical properties. The as-prepared CNC in the suspension can form a chiral nematic liquid crystal phase. The pitch and twist angle of this liquid crystal structure strongly depend upon the cellulose resources and the concentration of CNC in suspension, and also are affected by some environmental conditions, such as salt concentration, temperature, pH and so on. Furthermore, this kind of chiral nematic CNC arrangement could be transplated into the solid-state materials, and even the matrix exhibit stimuli-response characteristics and contribute to produce thermo-, pH-, and other stimuli-sensitive composite materials (see Chapter 9 for details). In addition, without any material as matrix, the CNC could arrange vertically to the suspension plane by a facile evaporation-induced method, and produce the film-form materials with a structural color of monochromatic light as specifically limited in the ultraviolet region, which is attributed to scattering enhancement of uniaxial periodical CNC arrays. It is worthy of note that this assembly strategy removes the usual chirality and iridescence of the traditional optical materials derived from the free assembly of CNC mentioned above, and prevents the iridescence-based information from being misread and shows an application potential as information-hiding and anti-counterfeiting materials [65]. The following section overviews various preparation strategies, performances and potential applications of nanocellulose-based materials (detailed in Chapter 6-13 of this book).

Firstly, the major issue associated with the fabrication of nanocellulose-based composite material is the compatibility and dispersion of the nanofiller in the matrix. Generally, the nanocellulose reinforcer is blended with the hydrophobic polymer matrix, such as polypropylene (PP) or poly(butylene succinate) (PBS). However, its hydrophilic nature makes it hard to uniformly disperse into the hydrophobic material, thus seriously affecting the performance of as-prepared composite material. As described earlier, the hydrophobic moieties can be conjugated to the nanocellulose surface to turn the particles or fibers hydrophobic together with polarity matching. An effective way is to conjugate the acetyl groups onto the nanocellulose surface via different chemical reactions. A study has shown that modifying the acetyl groups onto CNC surface via esterification of acetic anhydride improved the dispersibility of CNC in organic solvents as a blending medium, which ultimately enhanced the performance of the composite material [49, 66]. On the other hand, various processing technologies and compatibilizers (via in situ chemical reactions or physical interaction) can also be used to improve the compatibility of nanocellulose with nonpolar and hydrophobic matrix [50, 67]. For example, CNFs can be blended into polypropylene and polyethylene by twin-screw extrusion with maleic anhydride as compatibilizer. Maleic anhydride forms hydrogen bonds or esterifies the hydroxyl groups of CNF during the blending process and thus can adjust the hydrophobicity and polarity of the nanocellulose surface; it facilitates the uniform dispersion of CNF in the matrix. The results showed that the Young's modulus of polyolefin-based composites was improved about six times after blending with 50 wt% CNF. The situation becomes more complex when BNC is used to blend with nonpolar substances [68]. As BNC is synthesized by microorganisms in the culture medium, the achieved BNC usually presents in gel state, [69] while all the fibers are entangled with each other and hard to be separated. Thus, blending BNC with nonpolar polymers requires surface pre-modification towards BNC as that of CNF (see Chapter 4, 5 and 8 for details). In contrast, it is relatively easier to enhance the polar polymers such as poly(lactic acid) (PLA) using nanocellulose as filler due to its innate polarity nature mainly ascribed to surface OH groups. The nanocellulose or modified nanocellulose has been directly blended with various types of matrix by different processing technologies, and showed excellent dispersion, mainly attributed to the matching surface characteristics of nanocellulose.

Another important application of nanocellulose in material field is the unique self-assembling behavior of CNCs. The CNCs self-assemble into cholesteric liquid crystal under higher concentration in aqueous media and demonstrate interesting optical phenomenon [70], which is utilized in the preparation of optical materials and devices (see Chapter 9 for details). According to previous report [71], the morphology of the films made by the CNC self-assembly is intimately related to the ionic strength and evaporation speed of the system. The ionic strength in CNC suspension affects the pitch of the liquid crystal structure formed by CNC, while the evaporation speed also exerts some effect on the integrity and pitch of the CNC film. High ionic strength and fast evaporation are unfavorable to the pitch of ordered structure and make a disordered CNC film, while low ionic strength and slow evaporation make the CNC film more uniform with good optical properties. It is believed that the ions in the system and evaporation speed affect the formation of hydrogen bonds and the electrostatic interaction between the CNCs [71]. Based on these basic principles, the composite materials, which inherited optical properties of CNC assembly, can be prepared. For example, by in situ polymerization of the suspension containing monomers and 3% CNCs, the ordered spacial arrangement of CNC could be kept in the newly formed polymer matrix, and the as-prepared composite inherited the optical properties of the CNC-based liquid crystal structure [72]. Furthermore, the CNC also enhanced the mechanical strength of the polymer materials [72]. In another work, the CNC with a higher loading-level was used to prepare tough composite film with high mechanical strength. The mass fraction of CNC in the composite material could reach 50–90%, while the mechanical strength of the composite material could be as high as about 12 GPa [73]. Currently, various kinds of monomers, such as organosilica monomer of tetramethoxysilane, have been attempted to fabricate the supporting matrix of chiral nematic-arranged CNCs [74]. Moreover, the silicon oxide-based mesoporous chiral materials were derived by removing the chiral nematic phase of CNC, which inherited the unique optical properties [74], and further acted as a removable hard-template to produce the mesoporous titanium oxide-based replica films as the candidates of energy and sensor materials [75]. In addition, one more facile method has been carried out to controllably prepare the chiral plasmonic films via simple mixing and subsequent evaporation of the gold rod and CNC suspension, and showed a potential of the scalable and cost-effective manufacturing [76]. (see Chapter 9 for details).

Nanocellulose-based materials and composites possess high biocompatibility, improved mechanical properties, good degradability, and special optical properties. These materials and composites have found potential applications in various fields. For example, fluorescent cellulose nanocrystal (fCNC) can be used in in vivo bioimaging. Studies have shown that the Alexa Fluor 633-decorated fCNC can be injected into living mice, where the fluorescence can be held in the body for more than seven days and the fCNC can be selectively enriched at the limb bones of mice; furthermore, these fCNCs can also be potentially used as a biocompatible luminous reporter of bone disease [55]. As described earlier, the CNF can also be used as filler in food packaging materials where it is blended with polypropylene and polyethylene after being modified. The addition of CNF can improve both the mechanical strength and oxygen barrier properties while maintaining good optical transparency. The high mechanical strength and biocompatibility of nanocellulose make it can be used in the fabrication of transparent wound dressing in various forms such as hydrogel. The material was produced by polymerization of 2-hydroxyethyl methacrylate and in situ nanoparticlation of silver nitrate reduction with the incorporation of bacterial cellulose nanocrystals (BCNCs). The presence of BCNC improved the flexibility and water absorption of the material while silver nanoparticle could provide good antibacterial activity. The high optical transmittance could facilitate the observation of the wound healing while antibacterial activity makes it become a promising wound coverage material. [77]. In addition, BNC aerogels are used to separate oil/water mixture [78]. The hydrophilic surface of BNC enables these aerogels to show a high affinity for water. With rational modification, BNC aerogels could be used to selectively absorb water molecules in oil, and thus showed an application potential in the petrochemical industry. Chapters 10–13 provide a detailed description of the application of nanocellulose-based materials and composites in biomedicine, energy, and other high-value fields, respectively.

Interestedly, it was found that highly crystalline CNC could be carbonized into well-shaped carbon nanorod under high temperature. This kind of one-dimensional carbon nanorods was more uniform with less structural deficiencies, and was believed to fabricate carbon-based energy materials with high specific-surface-area and porosity. For example, along with the chiral self-assembling behavior of CNC, the as-prepared silicon-based materials containing chiral nematic CNC phase were treated at 900 °C under nitrogen atmosphere, and the CNC was converted into carbon nanorods with a chiral nematic arrangement in the silicon-based matrix. Such derived mesoporous carbon materials exhibited high conductivity of 1.3×10^{-2} S/cm and the specific capacitance as high as ca. 170 F/g, which was mainly ascribed to their high porosity (0.3 - 1.22 cm^3/g) [79]. If doping nitrogen atoms into the CNC-derived carbon, the capacitance could be further improved. After coating the CNC with melamine formaldehyde, the N-doping carbon nanorod prepared under

800-1000 °C for 5 min showed the capacitance up to 352 F/g [80]. Depending upon high capacitance and conductivity, this kind of CNC-derived carbon materials could have a great potential as a high-performance electrode of batteries. Besides the direct carbonization of CNC for energy application, high mechanical performances of nanocellulose also contribute to develop conductive films by compounding carbon nanoparticles [81–83] or conductive polymers [84] with nanocellulose (especially for the CNF and BNC with an entanglement network structure). The mechanical properties of conductive films are extremely critical to the wearable devices, which can improve the durability of the devices and make it suitable for sensing and monitoring during vigorous sport exercise. In this case, nanocellulose was usually mixed with carbon nanomaterials such as carbon nanotube (CNT) [81] or graphene oxide (GO) [82], and then processed into fibers (via electrospinning or wet-spinning) and films (via casting/evaporation method). In addition, by mechanical compressing CNF and graphene nanosheets (GN), high-mechanical strength conductive film could be produced [83]. When the GN content was 30%, the Young's modulus and tensile strength could be as high as about 7.5 GPa and about 140 MPa, respectively. Moreover, the conductance of the CNF/GN film could be 1×10^{-1} S/cm [83]. These nanocellulose-derived materials and nanocellulose-based composites are promising in energy and electronics applications, which will be discussed in detail in Chapter 12.

1.5 Conclusions and Prospects

Nanocellulose is an interesting material that has received immense consideration in various academic and application fields owing to its unique structural, physicochemical, mechanical and biological properties, and availability to being modified by various methods. However, its wide applications have been overshadowed by high production cost and a few limitations associated with tuning of its structural features through surface modification. The high production cost of nanocellulose is mainly attributed to cost of energy consumption and generated waste post-treatment during the preparation process [85]. Extensive efforts have been devoted to the cost-effective production of nanocellulose from many low-cost raw materials; nevertheless, the structural parameters and mechanical properties of nanocellulose produced from those low-cost raw materials need to be further improved. Similarly, several physical approaches have been developed for the preparation of nanocellulose to circumvent the energy consumption issue; however, these approaches compromise its crystalline structure and other physical properties. To address the issues of low-cost and energy-saving, cell-free enzyme strategies are also used; however, these are also compromised by extended production time to be applicable at an industrial scale.

The good mechanical properties of nanocellulose make it possible to enhance polymer materials. However, the hydrophilic surface of nanocellulose results in a poor dispersion in most of non-polar polymer matrices. As a result, in order to improve the compatibility and dispersibility of nanocellulose in the composite system, the principal issues involve the approaching of hydrophilicity/hydrophobicity and the matching of interaction groups between nanocellulose and matrix. In this case, surface modification towards nanocellulose is the common strategy. Many chemical and physical methods have been developed, and especially the chemical methods abide by the concepts of small-molecules conjugation, and polymer "graft onto" and "graft from". Further, it has also been found that the addition of nanocellulose may improve the crystallinity of the polymer matrix, which may ultimately increase the rigidity of composite materials. Furthermore, nanocellulose fillers with an optimal loading-level could form a network associated with hydrogen bonds, which can significantly improve the final mechanical performances (especially for strength and modulus) of the composite material. These findings indicate that in order to continuously improve the performance of the composite material, the regulation mechanism of interaction between the nanocellulose and the matrix should be further explored. Some recent reports indicate that the mode of association between nanocellulose and modifiers could also affect the performance of the composite materials filled with modified nanocellulose. For instance, studies have compared the differences of the composite materials when CNCs interacted with two kinds of modifiers via either hydrogen bonding or electrostatic interaction. The results showed that strong interaction might lead to a tougher composite material [86]. However, to answer how the surface modification strategy affects the mechanical properties, extensive research is still required. On the whole, the authors believe that the composite material is always the field in the most extensive application and the most consumption of nanocellulose. As the reinforcing fillers for composite materials, three main types of nanocellulose, i.e. CNC, CNF and BNC, provide abundant options of short/rigidity and corresponding long/flexibility, adjacention and homologous entanglement percolation, and so on. It is critical to select the proper type of nanocellulose for the given polymer materials and match the appropriate processing techniques. Furthermore, in order to improve the compatibility and dispersibility of nanocellulose in the matrix together with achieving the optimal mechanical performances, the key issue is to balance the interaction intensities between two of at least three components (i.e. nanocellulose and its modifier, and matrix) and self-agglomeration force of each component. Herein, the employed association modes of nanocellulose/modifier and modified-nanocellulose/matrix are very important, and the related theoretical prediction should be established.

Although nanocomposites are commonly believed to be the most popular field in terms of the demanded quantity and application range of nanocellulose, it is currently constrained by high production cost mentioned above. Therefore, how to use nanocellulose to develop high-value functional materials has attracted much attention, and is greatly expected to impulse the current application of nanocellulose. To date, several nanocellulose-based functional materials have also been developed. Studies have shown that one-dimension rigid structure of CNC can prevent the fluorescent molecules from self-quenching and produced a solid-state luminescent material of fluorescent molecules-modified CNC [51]. In this case, the controlled chemical reaction together with steric effect of rigid CNC support is the key. In addition, CNC could assemble to give the ordered structures of 2D uniaxial orientational alignment and 3D chiral nematic arrangement, which have been developed as advanced optical materials and hence derived mesoporous functional materials. Moreover, CNC can be directly 3D-printed into a specific controlled structure with special optical properties [87]. As a result, how to more effectively and programmatically control CNC to orderly arrangement is full of practical significance, and might become the major way to develop advanced nanocellulose materials. Nanocellulose-based aerogels could selectively separate oil from water, thus finding potential application in petrochemical industry. So more applications of lightweight porous aerogels based on nanocellulose are expected, and the chemical modification might contribute or intensify the functionality of materials. Besides, nanocellulose-based composite materials can be used to prepare transparent wound dressing materials and double-network hydrogels for potential biomedical applications [77, 88]. In view of good biocompatibility of nanocellulose (especially for BNC), more biomedical applications are worthy to be explored. In short, this book provides a comprehensive overview of the fundamentals of nanocellulose research and the latest developments in nanocellulose-based materials, and proposes future prospects toward the development of advanced applications.

References

1 Klemm, D., Kramer, F., Moritz, S. et al. (2011). Nanocelluloses: a new family of nature-based materials. *Angewandte Chemie International Edition* 50 (24): 5438–5466.

2 Czaja, W., Krystynowicz, A., Bielecki, S., and Brown, R.M. (2006). Microbial cellulose – the natural power to heal wounds. *Biomaterials* 27 (2): 145–151.

3 Moon, R.J., Martini, A., Nairn, J. et al. (2011). Cellulose nanomaterials review: structure, properties and nanocomposites. *Chemical Society Reviews* 40 (7): 3941–3994.

4 Shah, N., Ul-Islam, M., Khattak, W.A., and Park, J.K. (2013). Overview of bacterial cellulose composites: a multipurpose advanced material. *Carbohydrate Polymers* 98 (2): 1585–1598.

5 Dufresne, A. (2013). Nanocellulose: a new ageless bionanomaterial. *Materials Today* 16 (6): 220–227.

6 Ullah, M.W., Ul Islam, M., Khan, S. et al. (2017). Recent advancements in bioreactions of cellular and cell-free systems: a study of bacterial cellulose as a model. *Korean Journal of Chemical Engineering* 34 (6): 1591–1599.

7 Ullah, M.W., Ul-Islam, M., Khana, S. et al. (2015). Innovative production of bio-cellulose using a cell-free system derived from a single cell line. *Carbohydrate Polymers* 132: 286–294.

8 Jasim, A., Ullah, M.W., Shi, Z. et al. (2017). Fabrication of bacterial cellulose/polyaniline/single-walled carbon nanotubes membrane for potential application as biosensor. *Carbohydrate Polymers* 163: 62–69.

9 Klemm, D., Heublein, B., Fink, H.P., and Bohn, A. (2005). Cellulose: fascinating biopolymer and sustainable raw material. *Angewandte Chemie International Edition* 44 (22): 3358–3393.

10 Lin, N. and Dufresne, A. (2014). Nanocellulose in biomedicine: current status and future prospect. *European Polymer Journal* 59: 302–325.

11 Shi, Z., Gao, X., Ullah, M.W. et al. (2016). Electroconductive natural polymer-based hydrogels. *Biomaterials* 111: 40–54.

12 Ul-Islam, M., Ullah, M.W., Khan, S. et al. (2016). Recent advancement in cellulose based nanocomposite for addressing environmental challenges. *Recent Patents on Nanotechnology* 10 (3): 169–180.

13 Yan, C., Wang, J., Kang, W. et al. (2014). Highly stretchable piezoresistive graphene-nanocellulose nanopaper for strain sensors. *Advanced Materials* 26 (13): 2022–2027.

14 Iwamoto, S., Kai, W., Isogai, A., and Iwata, T. (2009). Elastic modulus of single cellulose microfibrils from tunicate measured by atomic force microscopy. *Biomacromolecules* 10 (9): 2571–2576.

15 Sturcova, A., Davies, G.R., and Eichhorn, S.J. (2005). Elastic modulus and stress-transfer properties of tunicate cellulose whiskers. *Biomacromolecules* 6 (2): 1055–1061.

16 Eyley, S. and Thielemans, W. (2014). Surface modification of cellulose nanocrystals. *Nanoscale* 6 (14): 7764–7779.

17 Trache, D., Hussin, M.H., Haafiz, M.K.M., and Thakur, V.K. (2017). Recent progress in cellulose nanocrystals: sources and production. *Nanoscale* 9 (5): 1763–1786.

18 Heux, L., Chauve, G., and Bonini, C. (2000). Nonflocculating and chiral-nematic self-ordering of cellulose microcrystals suspensions in non-polar solvents. *Langmuir* 16 (21): 8210–8212.

19 Pakzad, A., Simonsen, J., and Yassar, R.S. (2012). Gradient of nanomechanical properties in the interphase of cellulose nanocrystal composites. *Composites Science and Technology* 72 (2): 314–319.

20 Araki, J., Wada, M., and Kuga, S. (2001). Steric stabilization of a cellulose microcrystal suspension by poly(ethylene glycol) grafting. *Langmuir* 17 (1): 21–27.

21 Perez, D.D., Montanari, S., and Vignon, M.R. (2003). TEMPO-mediated oxidation of cellulose III. *Biomacromolecules* 4 (5): 1417–1425.

22 Satyamurthy, P., Jain, P., Balasubramanya, R.H., and Vigneshwaran, N. (2011). Preparation and characterization of cellulose nanowhiskers from cotton fibres by controlled microbial hydrolysis. *Carbohydrate Polymers* 83 (1): 122–129.

23 Uetani, K. and Yano, H. (2011). Nanofibrillation of wood pulp using a high-speed blender. *Biomacromolecules* 12 (2): 348–353.

24 Abe, K., Iwamoto, S., and Yano, H. (2007). Obtaining cellulose nanofibers with a uniform width of 15 nm from wood. *Biomacromolecules* 8 (10): 3276–3278.

25 Chen, W., Li, Q., Wang, Y. et al. (2014). Comparative study of aerogels obtained from differently prepared nanocellulose fibers. *ChemSusChem* 7 (1): 154–161.

26 Paakko, M., Ankerfors, M., Kosonen, H. et al. (2007). Enzymatic hydrolysis combined with mechanical shearing and high-pressure homogenization for nanoscale cellulose fibrils and strong gels. *Biomacromolecules* 8 (6): 1934–1941.

27 Saito, T., Kimura, S., Nishiyama, Y., and Isogai, A. (2007). Cellulose nanofibers prepared by TEMPO-mediated oxidation of native cellulose. *Biomacromolecules* 8 (8): 2485–2491.

28 Wagberg, L., Decher, G., Norgren, M. et al. (2008). The build-up of polyelectrolyte multilayers of microfibrillated cellulose and cationic polyelectrolytes. *Langmuir* 24 (3): 784–795.

29 Chen, W., Yu, H., Lee, S.-Y. et al. (2018). Nanocellulose: a promising nanomaterial for advanced electrochemical energy storage. *Chemical Society Reviews* 47 (8): 2837–2872.

30 Ullaha, W., Ul-Islam, M., Khana, S. et al. (2016). Structural and physico-mechanical characterization of bio-cellulose produced by a cell-free system. *Carbohydrate Polymers* 136: 908–916.

31 Iguchi, M., Yamanaka, S., and Budhiono, A. (2000). Bacterial cellulose – a masterpiece of nature's arts. *Journal of Materials Science* 35 (2): 261–270.

32 Lai, C., Zhang, S., Sheng, L. et al. (2013). TEMPO-mediated oxidation of bacterial cellulose in a bromide-free system. *Colloid and Polymer Science* 291 (12): 2985–2992.

33 Ul-Islam, M., Khan, T., and Park, J.K. (2012). Nanoreinforced bacterial cellulose-montmorillonite composites for biomedical applications. *Carbohydrate Polymers* 89 (4): 1189–1197.

34 Castro, C., Zuluaga, R., Alvarez, C. et al. (2012). Bacterial cellulose produced by a new acid-resistant strain of Gluconacetobacter genus. *Carbohydrate Polymers* 89 (4): 1033–1037.

35 Aljohani, W., Ullah, M.W., Zhang, X., and Yang, G. (2018). Bioprinting and its applications in tissue engineering and regenerative medicine. *International Journal of Biological Macromolecules* 107: 261–275.

36 Khan, S., Ul-Islam, M., Ikram, M. et al. (2018). Preparation and structural characterization of surface modified microporous bacterial cellulose scaffolds: a potential material for skin regeneration applications in vitro and in vivo. *International Journal of Biological Macromolecules* 117: 1200–1210.

37 Mahmoudi, K., Hosni, K., Hamdi, N., and Srasra, E. (2015). Kinetics and equilibrium studies on removal of methylene blue and methyl orange by adsorption onto activated carbon prepared from date pits. A comparative study. *Korean Journal of Chemical Engineering* 32 (2): 274–283.

38 Ul Islam, M., Ullah, M.W., Khan, S. et al. (2017). Strategies for cost-effective and enhanced production of bacterial cellulose. *International Journal of Biological Macromolecules* 102: 1166–1173.

39 Kurosumi, A., Sasaki, C., Yamashita, Y., and Nakamura, Y. (2009). Utilization of various fruit juices as carbon source for production of bacterial cellulose by *Acetobacter xylinum* NBRC 13693. *Carbohydrate Polymers* 76 (2): 333–335.

40 Cakar, F., Kati, A., Ozer, I. et al. (2014). Newly developed medium and strategy for bacterial cellulose production. *Biochemical Engineering Journal* 92: 35–40.

41 Tsouko, E., Kourmentza, C., Ladakis, D. et al. (2015). Bacterial cellulose production from industrial waste and by-product streams. *International Journal of Molecular Sciences* 16 (7): 14832–14849.

42 Kumbhar, J.V., Rajwade, J.M., and Paknikar, K.M. (2015). Fruit peels support higher yield and superior quality bacterial cellulose production. *Applied Microbiology and Biotechnology* 99 (16): 6677–6691.

43 Khattak, W.A., Khan, T., Ul-Islam, M. et al. (2015). Production, characterization and biological features of bacterial cellulose from scum obtained during preparation of sugarcane jaggery (gur). *Journal of Food Science and Technology-Mysore* 52 (12): 8343–8349.

44 Ma, X., Zhang, Y., and Huang, J. (2017). Surface chemical modification of cellulose nanocrystals and its application in biomaterials. *Paper and Biomaterials* 2 (4): 34–57.

45 Sirbu, E., Eyley, S., and Thielemans, W. (2016). Coumarin and carbazole fluorescently modified cellulose nanocrystals using a one-step esterification procedure. *Canadian Journal of Chemical Engineering* 94 (11): 2186–2194.

46 Spinella, S., Maiorana, A., Qian, Q. et al. (2016). Concurrent cellulose hydrolysis and esterification to prepare a surface-modified cellulose nanocrystal decorated with carboxylic acid moieties. *ACS Sustainable Chemistry and Engineering* 4 (3): 1538–1550.

47 Fumagalli, M., Sanchez, F., Molina-Boisseau, S., and Heux, L. (2015). Surface-restricted modification of nanocellulose aerogels in gas-phase esterification by di-functional fatty acid reagents. *Cellulose* 22 (3): 1451–1457.

48 Chen, G., Dufresne, A., Huang, J., and Chang, P.R. (2009). A novel thermoformable bionanocomposite based on cellulose nanocrystal-graft-poly(epsilon-caprolactone). *Macromolecular Materials and Engineering* 294 (1): 59–67.

49 Gan, L., Liao, J., Lin, N. et al. (2017). Focus on gradientwise control of the surface acetylation of cellulose nanocrystals to optimize mechanical reinforcement for hydrophobic polyester-based nanocomposites. *ACS Omega* 2 (8): 4725–4736.

50 Lin, N., Chen, G., Huang, J. et al. (2009). Effects of polymer-grafted natural nanocrystals on the structure and mechanical properties of poly(lactic acid): a case of cellulose Whisker-graft-polycaprolactone. *Journal of Applied Polymer Science* 113 (5): 3417–3425.

51 Zhang, Y.-J.; Ma, X.-Z.; Gan, L. et al. (2018) Fabrication of fluorescent cellulose nanocrystal via controllable chemical modification towards selective and quantitative detection of Cu(II) ion. *Cellulose* 25 (10): 5831–5842.

52 Mondal, S. (2017). Preparation, properties and applications of nanocellulosic materials. *Carbohydrate Polymers* 163: 301–316.

53 Leung, A.C.W., Hrapovic, S., Lam, E. et al. (2011). Characteristics and properties of carboxylated cellulose nanocrystals prepared from a novel one-step procedure. *Small* 7 (3): 302–305.

54 Bansal, M., Chauhan, G.S., Kaushik, A., and Sharma, A. (2016). Extraction and functionalization of bagasse cellulose nanofibres to Schiff-base based antimicrobial membranes. *International Journal of Biological Macromolecules* 91: 887–894.

55 Colombo, L., Zoia, L., Violatto, M.B. et al. (2015). Organ distribution and bone tropism of cellulose nanocrystals in living mice. *Biomacromolecules* 16 (9): 2862–2871.

56 Hasani, M., Cranston, E.D., Westman, G., and Gray, D.G. (2008). Cationic surface functionalization of cellulose nanocrystals. *Soft Matter* 4 (11): 2238–2244.

57 Zaman, M., Xiao, H., Chibante, F., and Ni, Y. (2012). Synthesis and characterization of cationically modified nanocrystalline cellulose. *Carbohydrate Polymers* 89 (1): 163–170.

58 de la Motte, H., Hasani, M., Brelid, H., and Westman, G. (2011). Molecular characterization of hydrolyzed cationized nanocrystalline cellulose, cotton cellulose and softwood kraft pulp using high resolution 1D and 2D NMR. *Carbohydrate Polymers* 85 (4): 738–746.

59 Cao, S.-L., Li, X.-H., Lou, W.-Y., and Zong, M.-H. (2014). Preparation of a novel magnetic cellulose nanocrystal and its efficient use for enzyme immobilization. *Journal of Materials Chemistry B* 2 (34): 5522–5530.

60 Kim, H.J., Park, S., Kim, S.H. et al. (2015). Biocompatible cellulose nanocrystals as supports to immobilize lipase. *Journal of Molecular Catalysis B-Enzymatic* 122: 170–178.

61 Dong, S. and Roman, M. (2007). Fluorescently labeled cellulose nanocrystals for bioimaging applications. *Journal of the American Chemical Society* 129 (45): 13810–13811.

62 Shang, W., Huang, J., Luo, H. et al. (2013). Hydrophobic modification of cellulose nanocrystal via covalently grafting of castor oil. *Cellulose* 20: 179–190.

63 Passantino, J.M., Haywood, A.D., Goswami, J., and Davis, V.A. (2017). Effects of polymer additives and dispersion state on the mechanical properties of cellulose nanocrystal films. *Macromolecular Materials and Engineering* 302 (4): 1600351.

64 Muiruri, J.K., Liu, S., Teo, W.S. et al. (2017). Highly biodegradable and tough polylactic acid-cellulose nanocrystal composite. *ACS Sustainable Chemistry and Engineering* 5 (5): 3929–3937.

65 Gan, L., Feng, N., Liu, S. et al. (2019) Assembly-induced emission of cellulose nanocrystals for hiding information. *Particle & Particle Systems Characterization* Doi:10.1002/ppsc.201800412.

66 Hu, F., Lin, N., Chang, P.R., and Huang, J. (2015). Reinforcement and nucleation of acetylated cellulose nanocrystals in foamed polyester composites. *Carbohydrate Polymers* 129: 208–215.

67 Lin, N., Huang, J., and Dufresne, A. (2012). Preparation, properties and applications of polysaccharide nanocrystals in advanced functional nanomaterials: a review. *Nanoscale* 4 (11): 3274–3294.

68 Abeer, M.M., Amin, M.C.I.M., and Martin, C. (2014). A review of bacterial cellulose-based drug delivery systems: their biochemistry, current approaches and future prospects. *Journal of Pharmacy and Pharmacology* 66 (8): 1047–1061.

69 Ullah, M.W., Ul-Islam, M., Khan, S. et al. (2016). In situ synthesis of a bio-cellulose/titanium dioxide nanocomposite by using a cell-free system. *RSC Advances* 6 (27): 22424–22435.

70 Lagerwall, J.P.F., Schutz, C., Salajkova, M. et al. (2014). Cellulose nanocrystal-based materials: from liquid crystal self-assembly and glass formation to multifunctional thin films. *NPG Asia Materials* 6: e80.

71 Pan, J., Hamad, W., and Straus, S.K. (2010). Parameters affecting the chiral nematic phase of nanocrystalline cellulose films. *Macromolecules* 43 (8): 3851–3858.

72 Giese, M., Blusch, L.K., Khan, M.K. et al. (2014). Responsive mesoporous photonic cellulose films by supramolecular cotemplating. *Angewandte Chemie International Edition* 53 (34): 8880–8884.

73 Wang, B. and Walther, A. (2015). Self-assembled, iridescent, crustacean-mimetic nanocomposites with tailored periodicity and layered cuticular structure. *ACS Nano* 9 (11): 10637–10646.

74 Shopsowitz, K.E., Hamad, W.Y., and MacLachlan, M.J. (2012). Flexible and iridescent chiral nematic mesoporous organosilica films. *Journal of the American Chemical Society* 134 (2): 867–870.

75 Shopsowitz, K. E., Stahl, A., Hamad, W. Y., and MacLachlan, M. J. (2012) Hard Templating of Nanocrystalline Titanium Dioxide with Chiral Nematic Ordering. *Angewandte Chemie-International Edition* 51 (28): 6886–6890.

76 Querejeta-Fernandez, A., Chauve, G., Methot, M .et al. (2014) Chiral Plasmonic Films Formed by Gold Nanorods and Cellulose Nanocrystals. *Journal of the American Chemical Society* 136 (12): 4788–4793.

77 Di, Z., Shi, Z., Ullah, M.W. et al. (2017). A transparent wound dressing based on bacterial cellulose whisker and poly(2-hydroxyethyl methacrylate). *International Journal of Biological Macromolecules* 105: 638–644.

78 Sai, H., Fu, R., Xing, L. et al. (2015). Surface modification of bacterial cellulose aerogels' web-like skeleton for oil/water separation. *ACS Applied Materials and Interfaces* 7 (13): 7373–7381.

79 Shopsowitz, K.E., Hamad, W.Y., MacLachlan, M.J. (2011) Chiral Nematic Mesoporous Carbon Derived From Nanocrystalline Cellulose. *Angewandte Chemie International Edition* 50: 10991–10995.

80 Wu, X.Y., Shi, Z.Q., Tjandra, R., et al. (2015) Nitrogen-enriched porous carbon nanorods templated by cellulose nanocrystals as high performance supercapacitor electrodes. *Journal of Materials Chemistry A* 3: 23768–23777.

81 Niu, Q., Gao, K., Shao, Z. (2014) Cellulose nanofiber/single-walled carbon nanotube hybrid non-woven macrofiber mats as novel wearable supercapacitors with excellent stability, tailorability and reliability. *Nanoscale* 6(8): 4083–4088.

82 Liu, Y., Zhou, J., Zhu, E., et al. Facile synthesis of bacterial cellulose fibres covalently intercalated with graphene oxide by one-step cross-linking for robust supercapacitors. *Journal of Materials Chemistry C* 3(5): 1011–1017.

83 Yang, W. X., Zhang, Y., Liu, T. Y., et al. (2017) Completely green approach for the preparation of strong and highly conductive graphene composite film by using nanocellulose as dispersing agent and mechanical compression. *ACS Sustainable Chemistry & Engineering* 5(10): 9102–9113.

84 Wang, Z., Carlsson, D. O., Tammela, P., et al. (2015) Surface modified nanocellulose fibers yield conducting polymer-based flexible supercapacitors with enhanced capacitances. *ACS Nano* 9(7): 7563–7571.

85 Thomas, B., Raj, M. C., Athira, K. B., et al. (2018) Nanocellulose, a Versatile Green Platform: From Biosources to Materials and Their Applications. *Chem. Rev.* 118 (24): 11575–11625.

86 Mariano, M., Pilate, F., de Oliveira, F. B., et al. (2017) Preparation of cellulose nanocrystal-reinforced poly(lactic acid) nanocomposites through noncovalent modification with PLLA-based surfactants. *ACS Omega* 2(6): 2678–2688.

87 Hausmann, M. K., Ruhs, P. A., Siqueira, G., et al. (2018) Dynamics of cellulose nanocrystal alignment during 3D Printing. *ACS Nano* 12(7): 6926–6937.

88 Hagiwara, Y., Putra, A., Kakugo, A., et al. (2010) Ligament-like tough double-network hydrogel based on bacterial cellulose. *Cellulose* 17(1): 93–101.