REVIEW ARTICLE

Wood nanocelluloses: fundamentals and applications as new bio-based nanomaterials

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Abstract Nanocelluloses, which include nanofibrillated celluloses (NFCs) and cellulose nanocrystals (CNCs) with high and low aspect ratios, respectively, are promising new bio-based nanomaterials, prepared from wood and other plant celluloses by mechanical shearing in water with or without pretreatments. Low degrees of enzymatic hydrolysis, carboxymethylation, acetylation, oxidation, and other position-selective modifications on cellulose microfibril surfaces have been applied as pretreatments to wood celluloses to reduce energy consumption in the mechanical shearing process and to improve the nanofibrillation level of the obtained NFCs. NFCs are convertible to nanocellulose sheets, films, hydrogels, foams, and aerogels with fibril network structures or close-packing structures using coating on base films or filtration process like papermaking, which is advantageous for efficient removal of water predominantly present in the NFC/water dispersions. NFC-containing self-standing films, coated films, and NFC/matrix nanocomposites in most cases show explicitly high mechanical strength and ductility despite being lightweight and having optical transparency, thermal stability, and gas-barrier properties. Because NFCs have aspect ratios and molecular weights higher than those of CNCs, the most promising and challenging end products are NFC-containing nanocomposite materials having higher functionalities than those of the conventional fiber-reinforced composite materials.

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Introduction

A further increase in the utilization amount of plantation wood would contribute to the acceleration of the immobilization of atmospheric carbon dioxide in materials, and to the establishment of a sustainable society based on reproducible biomass recourses. Because the consumption of conventional woody materials such as housing, furniture, paper, and board has been decreasing especially in developed countries, new application fields of wood cellulose have been extensively investigated in both academia and industry in these decades. If wood cellulose produced by cost-effective and environmentally friendly processes could be used as new high-tech and commodity materials with high performance, partly in place of petroleum-based materials, a new material stream of wood cellulose from forestry to industry would be created, which may enhance immobilization of carbon dioxide in materials. One of the promising new material streams is the production and utilization of "nanocelluloses" prepared from wood biomass. Therefore, nanocellulose-related fundamental and application research and development have remarkably started early this century and expanded worldwide up to date.

Higher plants form highly crystalline cellulose microfibrils, each of which consists of 30–40 fully extended and linear cellulose chains and are the elements with the second smallest width (~3 nm) after single cellulose chains. Plant cell walls comprise cellulose microfibrils filled with hemicelluloses and lignin, forming natural nanocomposites that protect their living bodies against biological attack and external stress (Fig. 1). The pulp and paper industries have used such wood fiber microfibril structures to effectively control paper properties by controlling their degrees of fibrillation, generally using disk refiners and other mechanical fibrillation apparatuses in stock preparation
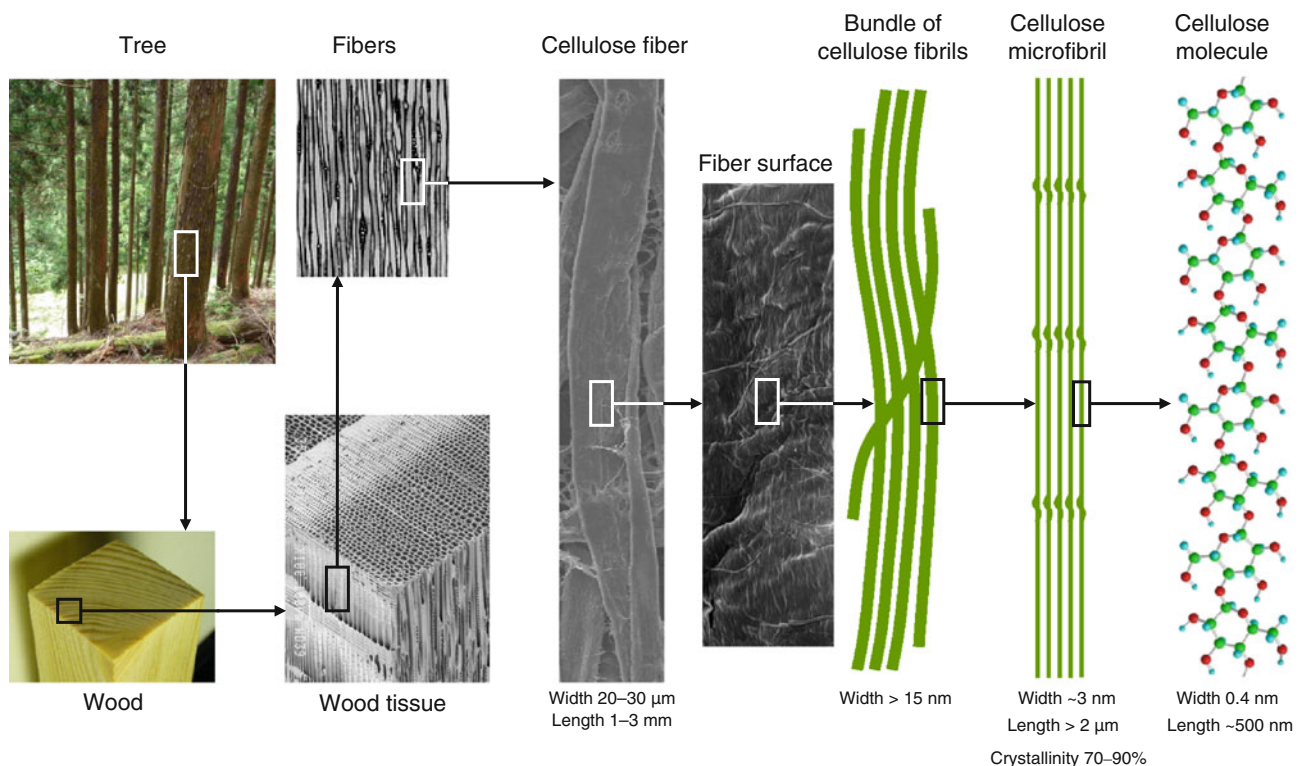
Fig. 1 Hierarchical structure of wood cellulose, forming crystalline cellulose microfibrils. Some photos are used from the Web site of Forestry and Forest Products Research Institute

processes. Because numerous hydrogen bonds are formed and are present between cellulose microfibrils in wood cellulose fibers, it has been difficult to prepare highly fibrillated celluloses from wood cellulose fibers by only mechanical refining in water. In the 1980s, Turbak and his coworkers of ITT Rayonier developed a new method to prepare highly fibrillated celluloses, i.e., microfibrillated celluloses (MFCs), directly from wood cellulose fibers by repeated high-pressure homogenization treatment in water [1]. Daicel Company, Japan, commercialized MFCs suspended in water at ~2 % solid consistency (CELISH®) during the 1980s [2], although the energy required to produce MFCs is large.

There are several reasons for the greatly increased interest in nanocelluloses in these decades: (1) nanocelluloses can be produced from abundant wood biomass partly using conventional and already established pulping/bleaching technologies; (2) recent advances in nanotechnology-related science and engineering such as carbon nanotubes and graphene have opened up new applications in high-tech material fields; (3) nanocelluloses originating from reproducible wood biomass are thought to be much more preferential and beneficial in terms of production process, energy consumption, and environmental and safety issues; (4) pulp and paper industry particularly in developed countries has been looking for new applications

of wood fibers and therefore (5) nanocelluloses have great potential to be used as new bio-based nanomaterials.

In this review paper, wood nanofibrillated cellulose-related topics are summarized and reported primarily based on the results recently published in scientific journals, although it is an impossible task for this author to cover all nanocellulose-related and significant topics reported across the world. Several comprehensive review papers concerning various aspects of nanocelluloses have already been published in scientific journals [3–10].

Preparation and characterization of nanocelluloses

Various pretreatments of wood cellulose fibers have been studied since the early 2000s to reduce the energy consumption of mechanical nanofibrillation processes and to improve the degree of nanofibrillation achievable. When commercially available wood cellulose fibers used as dissolving and paper pulps were subjected to mechanical fibrillation in water, some of the fibers were converted to nanofibrils with 10–20 nm width. On the other hand, when a wood holocellulose was mechanically treated under the same conditions, cellulose nanofibrils with ~3 nm width were obtained (Fig. 2) [11]. Thus, the original wood cellulose microfibrils are likely to have homogeneous widths of ~3 nm, which have been supported also by X-ray
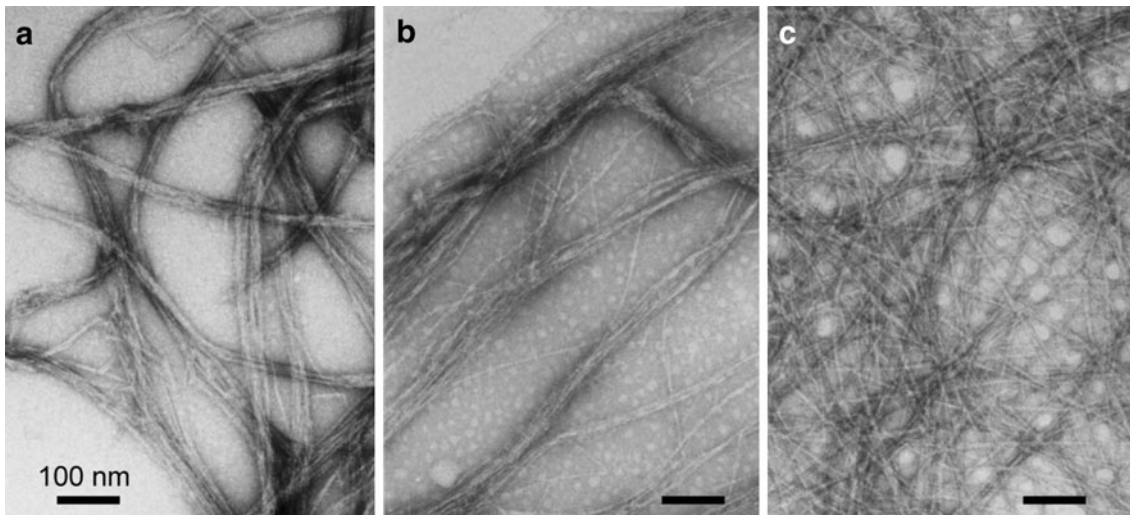
Fig. 2 TEM images of mechanically fibrillated cellulose nanofibrils prepared from **a** kraft pulp, **b** sulfite pulp, and **c** holocellulose. Reproduction of these images from ref. 11 with permission from Springer (© Springer 2003)

diffraction patterns. During the harsh chemical pulping or delignification processes at high temperatures in the presence of water, i.e., under hydrothermal conditions, aggregation of the original cellulose microfibrils may take place between cellulose microfibrils, forming bundles of cellulose microfibrils in commercial chemical pulps. Hence, the width/width distributions and length/length distributions are significantly different between nanocelluloses, depending on the wood celluloses used as starting materials, pretreatments, apparatuses of mechanical fibrillation treatment, and other factors, which have explicit influence on the resultant nanocellulose-containing composite materials.

Preparation of NFCs using new disintegration methods

Yano and his coworkers have found that highly fibrillated NFCs with 10–20 nm average widths can be prepared more efficiently from commercial wood pulps and partially or fully delignified wood holocelluloses using more efficient fibrillation apparatuses, by which wood celluloses undergo much strong share forces in water [12–17]. Here, high-pressure homogenizers, microfluidizers, ultrafine friction grinders (i.e., Super Masscolloiders®), high-speed blenders, aqueous counter-collision [18], and twin screw-type extruders were used for nanofibrillation, in some cases with thermo-plastics used as fibrillation media instead of water. Each apparatus has both advantageous and disadvantageous points in terms of nanofibrillation efficiency, depending on the targeted nanofibrillation level and also the pretreatments applied to the original wood cellulose. Characteristics and potential applications of the NFCs thus obtained were evaluated in terms of mechanical strengths, optical transparency, and thermal stability as composites prepared with acrylic resins and other thermo-plastics [12–17, 19–27]. Not only composites, but also some NFC-based hydrogels prepared by alkali treatment had unique properties [28, 29]. The presence of hemicelluloses in wood pulps and holocelluloses enhances the degree of nanofibrillation of NFCs during the mechanical disintegration treatment in water, primarily because carboxyl groups present in hemicelluloses bring about electrostatic repulsion between cellulose microfibrils in water [11, 15–17]. When the number of grinding treatment of wood cellulose in water was increased, the degrees of both polymerization and cellulose I crystallinity decreased to some extent, resulting in clear decreases in mechanical strength and thermal stability of NFC-containing composite films [14].

Surface treatments of cellulose microfibrils
for preparation of NFCs

A novel route toward exploiting the attractive mechanical properties of cellulose I nanoelements was developed that combines cellulose pretreatment and mechanical shearing. This involved the introduction of mild enzymatic hydrolysis combined with mechanical shearing using a high-pressure homogenizer, which led to a controlled nanofibrillation and a network of long and highly entangled cellulose I elements. Partial cleavage of cellulose glycoside bonds present on the surface layers of wood pulp fibers may improve nanofibrillation efficiency during mechanical treatment in water. The surface-active properties of enzyme molecules seem to synergistically improve nanofibrillation efficiency during mechanical homogenization [30–32]. The strong aqueous NFC network gels thus

obtained exhibited more than five orders of magnitude tunable storage modulus G' upon changing the concentration. Cryo-transmission electron microscopy, atomic force microscopy (AFM), and solid-state ^{13}C NMR suggested that the cellulose I structural elements obtained were dominated by two fractions, one with lateral dimensions of 5–6 nm and the other with lateral dimensions of about 10–20 nm. The thicker diameter regions may have acted as junction zones for the networks.

Minimal carboxymethylation of the hydroxyl groups of wood cellulose with aqueous NaOH and monochloroacetic acid to introduce anionic charges on the surfaces of the cellulose microfibrils was developed in the next stage [33]. Because the carboxymethylation and preparation processes of CMCs from wood cellulose have been established at the industrial level, and because the safety standard issues of CMCs and their production systems have been already satisfied, the conventional industrial-scale carboxymethylation process is applicable to the pretreatment, which is advantageous. However, because carboxymethylation itself is a type of competition reaction between cellulose hydroxyl groups and water molecules always present in the reaction media, the reaction efficiency of introducing carboxymethyl groups only on the crystalline cellulose microfibril surfaces may not be so high. In a contradictory manner, introduction of sufficient amounts of cationic charges to wood cellulose microfibril surfaces originally having anionic charges using cationic polymers via paper chemistry technology has also been exploited as a pretreatment [34]. Partial acetylation of cellulose microfibril surfaces has also been applied to wood cellulose, in which mechanical disintegration of the partially acetylated cellulose fibers was applied to acetone or acrylic resins in the mechanical disintegration stage to reduce energy consumption and achieve homogeneous NFC distribution in the polymer matrix [26, 35]. Each pretreatment resulted in a remarkable reduction of fibrillation energy to lower than 10 % of that without pretreatment.

TEMPO-mediated oxidation as pretreatment for preparation of NFCs

On the other hand, new methods using 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation in water have been developed to selectively introduce abundant sodium carboxylate groups on crystalline wood cellulose microfibril surfaces [8, 10, 36–38]. TEMPO is a water-soluble and stable nitroxyl radical, and its chemical structure changes to N-oxoammonium cation and hydroxylamine structures upon oxidation and reduction, respectively. de Nooy et al. [39] were the first to succeed in the highly position-selective and efficient conversions of C6-primary hydroxyl groups of water-

soluble polysaccharides such as pullulan and amylodextrin to C6-carboxylates by TEMPO/NaBr/NaClO oxidation under aqueous alkaline conditions. When TEMPO-mediated oxidation is applied to bleached wood cellulose fibers, the original fibrous morphologies and the crystal structure, crystallinity, and crystal width of cellulose I are unchanged before and after the oxidation, while significant amounts of sodium carboxylate groups are formed in the oxidized cellulose fibers. Subsequent studies showed that such sodium carboxylate groups are formed selectively on crystalline cellulose microfibril surfaces by TEMPO-mediated oxidation; the C6-primary hydroxyl groups of glucosyl units exposed on the crystalline cellulose microfibril surfaces are selectively oxidized to C6-carboxyl groups of glucuronosyl units [40, 41]. Aqueous slurries of TEMPO-oxidized wood celluloses having sufficient C6-carboxylate content (>1.2 mmol/g) are convertible to highly viscous and transparent gels consisting of mostly individualized TEMPO-oxidized cellulose nanofibrils (TOCNs) by gentle mechanical disintegration treatment (Fig. 3).

For effective preparation of TOCNs with sufficient amounts of carboxylate groups within a shorter reaction time, printing and writing papermaking-grade bleached kraft pulps containing 10–15 % hemicelluloses are preferable. In the case of TEMPO-mediated oxidation, oxidized TEMPO molecules or N-oxoammonium ions should have covalent bonds with C6-primary hydroxyls present on the crystalline cellulose microfibrils. Hemicellulose fractions present between crystalline cellulose microfibrils in such paper-grade kraft pulps behave like sponges, achieving quite smooth movement of the TEMPO molecules between the fibrils [8, 10]. Because completely individualized and long nanofibrils were obtained, the tensile strengths and Young's moduli of individual TOCNs were measured using AFM. TOCN tensile strength was estimated based on a model for the sonication-induced fragmentation of filamentous nanostructures. The resulting strength parameters were then analyzed based on fracture statistics. The thereby obtained mean strength of the wood cellulose nanofibrils ranged from 1.6 to 3 GPa, comparable to those of commercially available multi-walled carbon nanotubes and Kevlar® [42].

Preparation of CNCs

Acid hydrolysis pretreatment of native celluloses with, for example, 64 % H_2SO_4 has been well known to prepare CNCs [or called as nanocrystalline celluloses (NCCs) and cellulose nanowhiskers (CNWs)] with yields of 40–60 %. These have spindle-like morphologies with low aspect ratios [3, 5, 6, 9, 43]. The disordered regions periodically present along the longitudinal direction of wood cellulose
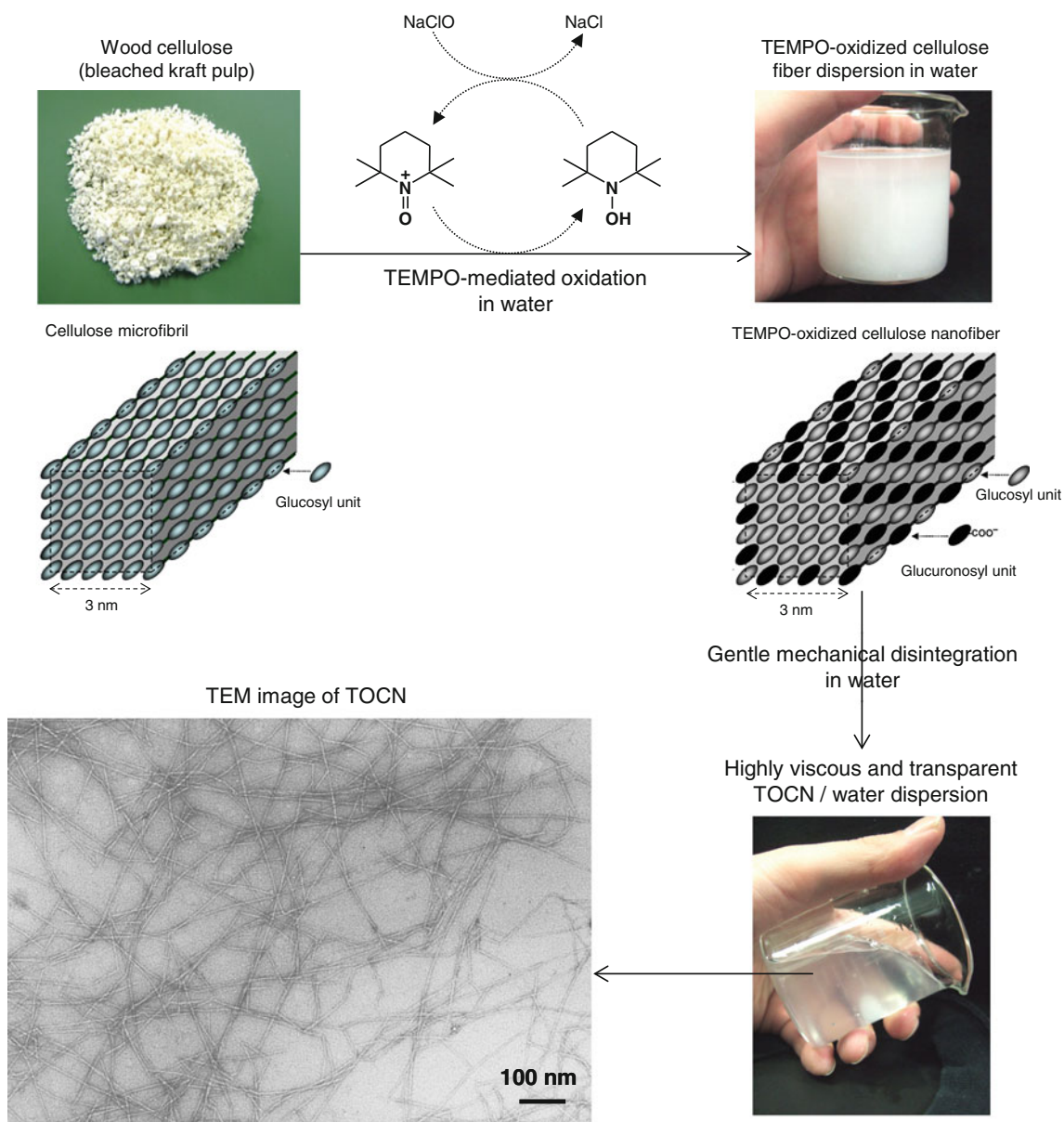
Fig. 3 Preparation of TEMPO-oxidized cellulose nanofibrils (TOCNs) from wood cellulose and the corresponding structural model of TOCN

microfibrils are preferentially hydrolyzed and removed to form CNCs with degrees of polymerization of 100–200. Anionically charged sulfate ester groups of ~ 0.3 mmol/g are introduced on the CNC surfaces simultaneously during the acid hydrolysis, which causes sufficient dispersions at the individual CNC level in water. The average lengths of CNCs are 200 nm or lower, depending on the hydrolysis time [43]. CelluForce, Canada, has begun production of CNCs at 1 ton/day from 2012 for various applications in high-tech fields [44]. In the case of CNCs, fully spray-dried and powder-like samples can be delivered, which is advantageous when compared with aqueous MFC, NFC, and TOCN dispersions containing more than 95 % water.

Processing of NFCs to bulk and composite materials

NFCs with various fibrillation levels, width/width distributions, length/length distributions, and surface structures are obtained, as described above, from wood celluloses with or without subjecting to various pretreatments under different nanofibrillation conditions. The next stage is how to process such new bio-based and water-dispersed nanocelluloses into functional materials, in which the following two key points are required: (1) an efficient way to remove abundant water from the highly swollen and nanodispersed NFC/water dispersions while maintaining the unique properties of NFCs and (2) an effective procedure to add

functionalities to wet or dried bulk materials and composites containing NFCs.

Paper-like NFC films and aerogels

Drying of NFC/water dispersions having low solid consistencies cast on a plate to make films or paper-like materials takes a long time. Filtration is one of the most effective ways to remove water from aqueous NFC dispersions and increase their solid content. Rapid preparation of large and flat nanopaper films of high surface smoothness and optical transparency is, therefore, important to facilitate the development of such new applications. In this context, a procedure which uses a semiautomatic sheet former to make large and smooth nanopaper films of 200 mm diameter and 60 μm thickness from NFC/water dispersions has been developed. Flat nanopaper films can be prepared using this procedure within about 1 h [25, 45]. This procedure is applicable to the preparation of not only cellulose nanopapers, but also NFC/inorganic hybrid films.

The filtration time of the 0.2 wt% NFC dispersion depended on the final thickness of the nanopaper, and was ∼45 min for a 60 μm thick nanopaper film [46]. The strongest nanopaper film prepared above exhibited a strength of above 200 MPa. The film showed yield at a stress level of ∼100 MPa much lower than its ultimate strength, which was followed by a plastic deformation region with considerable strain hardening due to the formation of a nanofibrous network [47]. The obtained results show that the strongest nanopaper films were also the most ductile. Their high degrees of cellulose polymerization (DP) should have a positive effect on tensile strength [48]. The best nanopaper structures also had carboxylate groups on the fibril surfaces, prepared by TEMPO-mediated oxidation [49]. Because the tensile tests were carried out under conditions of 50 % relative humidity (RH), those nanofibrils with carboxylate functionality in aqueous dispersions were surface hydrated in nanopaper form. This could favor plastic deformation since the hydrated region may serve as a lubricant and thus facilitate the sliding of fibrils with respect to each other. The nanopaper films with different pore structures were those prepared with the solvent-exchange and filtration method [50]. Nanopaper films with preferred orientation of TOCNs have been prepared by cold drawing, which can also be applied to TOCN/hydroxyethylcellulose (HEC) nanocomposites [50].

Aqueous NFC and TOCN dispersions can be converted into nanopaper aerogels using new drying methods [28, 29, 49, 51]. Very porous aerogels were prepared by solvent exchange from water to t-butanol followed by drying. This resulted in much higher specific surface areas of the aerogels (150–280 m^2/g) compared with those of freeze-dried aerogels prepared from water. The resulting aerogels showed a fine NFC network structure and much lower modulus and yield strength compared with those of cellular structured freeze-dried foams. Fitting of modulus data to a theoretical fiber network model resulted in estimated NFC segment lengths between fibril–fibril joints of 300–480 nm in agreement with the structures observed in SEM images. Drying from supercritical carbon dioxide resulted in a specific surface area of 480 m^2/g. In the context of a fiber network model, a higher specific surface area of the nanopaper may be related to increased length of fibril segments between fibril–fibril joints, which would explain the lowered modulus and yield strength obtained [49].

Preparation of bulk materials from TOCN/water dispersions

When TEMPO-oxidized wood celluloses have sufficient amounts of carboxylate groups (>1.2 mmol/g), transparent and highly viscous TOCN/water dispersion gels consisting of completely individualized cellulose nanofibrils can be obtained by mild mechanical disintegration treatment in water. For such TOCNs, filtration is not suitable for making dried films, although complete filtration takes a long time due to clogging and some of the TOCNs pass through a fine pore-sized membrane. Thus, casting of the TOCN/water dispersions on a plate and drying are used. The TOCN films thereby obtained are transparent and self-standing with plywood-like nanolayered structures originating from nematic-ordered domains consisting of self-aligned structures of TOCN elements and show good oxygen-barrier properties under dry conditions and high mechanical strengths [8, 10, 52–55].

In addition, careful adjustment of the pH and solvent evaporation in TOCN dispersions produce a wide range of artificial bulk materials with outstanding properties. Examples include unprecedentedly stiff freestanding hydrogels with a water content of 99.9 % and ultralow density and tough aerogels with large surface areas. These materials are expected to be further developed as robust frameworks for polymer nanocomposites or high-capacity supports for catalysts and the other functional materials [53]. On the other hand, porous TOCN networks, similar in appearance to spider webs, have been prepared by direct air drying of TOCN/surfactant dispersions using support materials containing micrometer- or submicrometer-sized pores. These network structures can be categorized as nanoporous materials [56]. The conversion systems used to form bulk materials from TOCN/water dispersions containing self-aligned TOCN elements are summarized in Fig. 4.

NFC-containing composites

Based on the aforementioned preparation techniques of NFC films and aerogels and their specific properties,
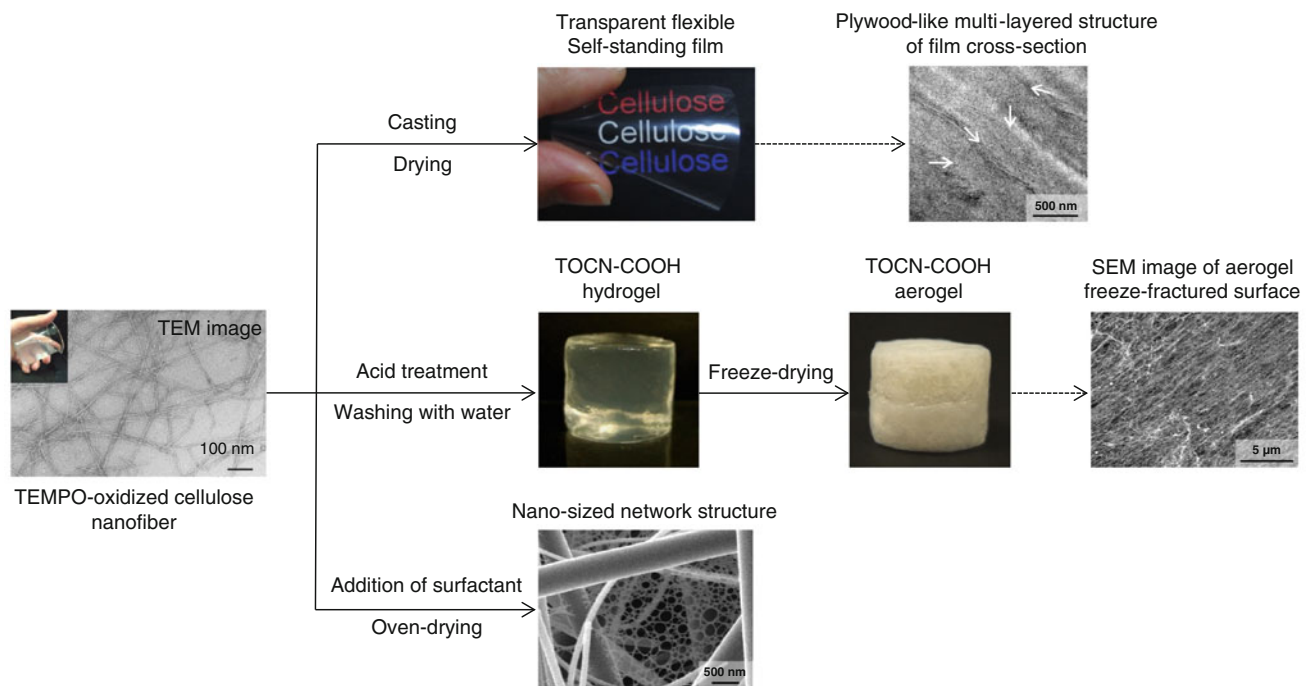
Fig. 4 Conversion from TOCN/water dispersion to diverse bulk materials

various NFC-containing composites have been prepared in the expectation of high mechanical strengths and unique functionalities. Chemically unmodified NFC/polymer nanocomposites were prepared, with the aim of preparing flexible flat panel display devices [12–17], electronic devices with high thermal stability [20–23], and bio-based composites with high mechanical strengths [19, 24, 25, 27].

The grinder treatment in water resulted in the efficient fibrillation of wood pulp fibers into NFCs, which demonstrated promising characteristics as reinforcement material for optically transparent composites. Since the NFCs form aggregates of semi-crystalline extended cellulose chains, NFC/acrylic resin composites showed low thermal expansion coefficients, while maintaining its ease of bending [12]. When a dissolving pulp was subjected to various passes through grinder treatment and the obtained NFCs were used to make NFC/acrylic resin composites, the light transmittances of the composite films increased to 80 % up to five grinder passes. However, because partial depolymerization and a decrease in cellulose I crystallinity took placed on NFCs during the grinder treatment, mechanical strengths and thermal stability of the NFC/acrylate resin composites decreased with increasing grinder pass number [14]. Hemicelluloses as matrix substances in wood pulps showed an important role in nanofibrillation process using grinding treatment. In fact, hemicelluloses provide adhesion between NFCs, contributing to reduction of thermal expansion and enhancement of mechanical properties in NFC/acrylate resin composites [15].

Composite films of poly(L-lactide) (PLLA) and NFC were prepared, and mechanical and thermo-mechanical properties of the films after hot-pressing were studied. When NFC was premixed with PLLA using an organic solvent and the mixture was kneaded after the removal of the solvent, the NFC elements were uniformly dispersed in the PLLA matrix. The NFC addition increased Young's modulus and tensile strength of PLLA by 40 and 25 %, respectively, without a reduction of yield strain at a 10 wt% NFC content [19]. Moreover, NFC-reinforced partially crystallized PLLA composites were prepared, with the goal of reducing the time required to fabricate PLLA parts. A series of NFC/PLLA composites at a 10 wt% NFC content and degrees of crystallinity from 0 to 43 % was prepared by annealing the composites at 80 °C. The results showed that partially crystallized NFC/PLLA composites can replace fully crystallized neat PLLA [27].

Nine types of matrix resin were reinforced with surface-acetylated NFCs prepared from wood cellulose, and light transmittances, tensile moduli, and coefficient of thermal expansion values of the composite films were evaluated to make clear the potential application of the composite films as display substrates, i.e., organic light-emitting diode materials. As a result, flexible, thermally stable, and optically transparent NFC/resin nanocomposites were obtained. At the same NFC content, the nanocomposites using lower Young's modulus matrix resin exhibited higher thermal stability than using higher Young's modulus matrix resins [26].

NFC/amylopectin/glycerol composite films were prepared by casting and drying dispersions of nanostructured cellulose network combined with amylopectin–glycerol blend. High tensile strength was combined with high modulus and very high work of fracture in the nanocomposite with 70 wt% NFC [57, 58]. Clay/NFC hybrid composites consisting of montmorillonite platelets in a continuous NFC matrix have been prepared with the aim of harnessing the intrinsic toughness of fibrillar networks. The continuous NFC matrix is a new concept and provides unusual ductility to the nanocomposite, allowing inorganic contents as high as 90 wt% [57]. Moreover, NFC/HEC biocomposites showed unique nanostructural toughening effects; the strong property improvements were achieved with increasing NFC content due to the load-carrying ability of the fibril network [58]. NFC-reinforced starch-based foams, prepared by the freezing/freeze-drying route, are interesting porous materials due to strong NFC reinforcement of the cell wall itself [59]. This is based on the nanocomposite concept in the form of an NFC network reinforcing the hygroscopic amylopectin starch matrix in the cell wall [60].

Because TOCN elements form dense films with plywood-like nanolayered structures [53], not only TOCN self-standing films but also TOCN-coated PLLA and poly(ethylene terephthalate) films have high oxygen-barrier properties under dry conditions [52, 54, 55]. These close-packed structures of TOCN elements in the layers likely originate from strong electrostatic repulsion between anionically charged TOCN elements, which may work efficiently not only in the aqueous dispersion state but also during the drying process of water evaporation. However, the low oxygen permeabilities of the TOCN-COONa films and layers remarkably increase with RH due to the hydrophilic nature of TOCN-COONa type structures, which is one of the shortcomings of TOCN films and layers used as gas-barrier materials [54].

The following TOCN-containing composite fibers and films were prepared, and their mechanical, optical, thermal, oxygen barrier, and electric properties were characterized: poly(vinyl alcohol)/TOCN composite drawn fibers [61], TOCN/montmorillonite (MTM) composite films [62], TOCN/metal nanoparticle composites [63, 64], TOCN/single walled carbon nanotube composite films [65], TOCN/poly(styrene) (PS) composite films [66], and surface-modified TOCN/PLLA composite films [67]. Dynamic mechanical analysis of TOCN/PS composites showed that the storage modulus of the obtained TOCN/PS films increased significantly with TOCN content above the glass-transition temperature of PS due to the formation of an interfibrillar network structure of TOCNs in the polymer matrix, based on percolation theory [66]. Especially, the tensile strength, Young's modulus, and work of fracture of TOCN/PLLA composite films were remarkably improved,
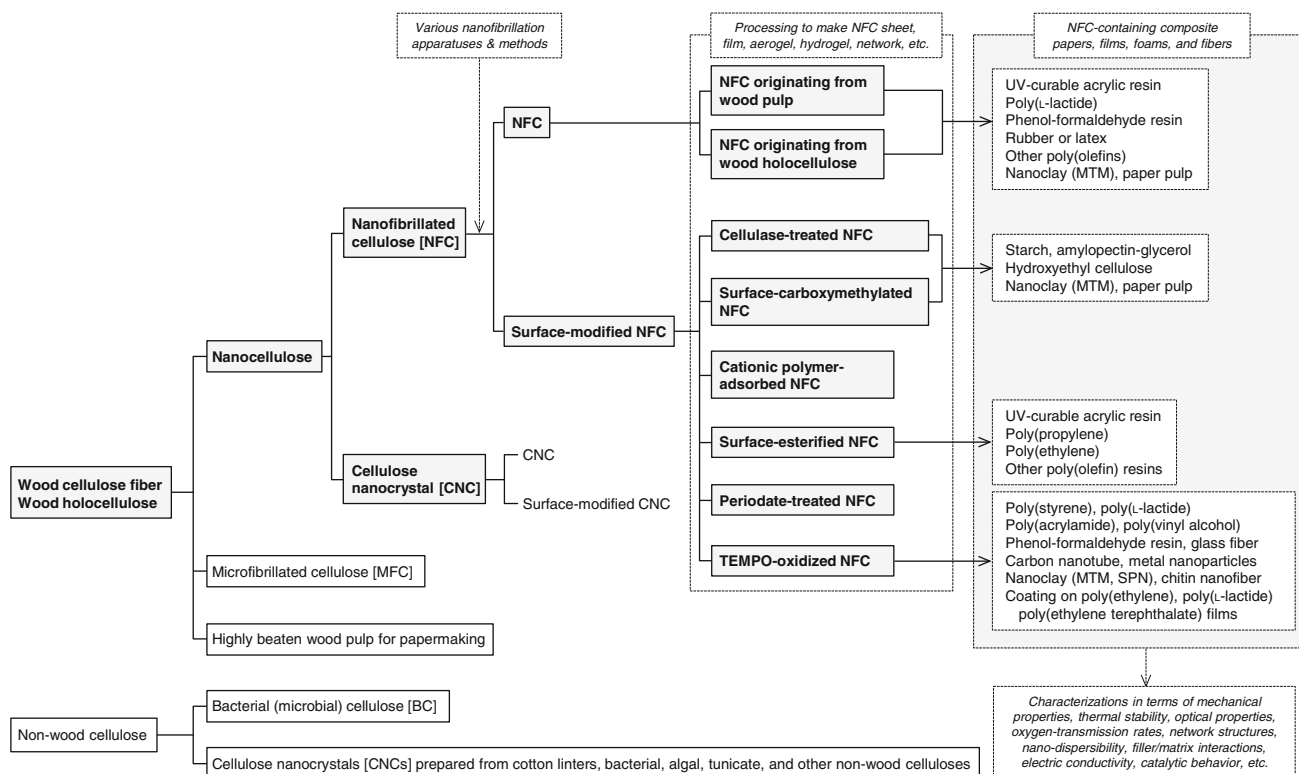

Fig. 5 Categories of nanocelluloses, nanofibrillated cellulose (NFC)-containing composite materials, and related studies reported so far

despite low cellulose addition levels (<1 wt%). This highly efficient nanocomposite effect was explained in terms of high aspect ratio and high crystallinity of TOCNs, and achievement of nanodispersion of the TOCN elements in the polymer matrices [66, 67].

Prospects of nanocelluloses

The NFCs including TOCNs prepared from wood cellulose have unique and promising properties, such as high crystallinities, aspect ratios, Young's moduli, and tensile strengths, which originate from the properties of natural wood cellulose microfibrils. Categories of nanocelluloses prepared with and without pretreatments and their composite materials investigated so far are summarized in Fig. 5. NFCs prepared without chemical pretreatment such as TEMPO-mediated oxidation are less damaged in terms of molecular weight and fibril length, and form nanofibril network structures having fibril–fibril joints in both aqueous dispersion and dried films and aerogels. These are useful in making lightweight NFC/matrix nanocomposite materials with high mechanical strengths including high ductility. NFC films and aerogels can be prepared efficiently from aqueous NFC dispersions using filtration processes like those used during papermaking, which are expected to widen the practical applications of NFCs. One of the characteristics of TONCs, on the other hand, is their nanodispersibility in both water and some organic solvents by modification of the abundant carboxyl groups present on their crystalline surfaces with hydrophobic compounds through ion exchange. If such completely nanodispersed states of TOCNs can also be achieved in hydrophilic and hydrophobic polymer matrices, increased mechanical and thermal properties are expected to be achieved for TOCN-containing composite materials even at low TOCN loading ratios. The oxygen-barrier properties of TOCN films and coating layers are also promising for application in high-performance packaging materials, although the hydrophilic nature of the TOCNs must first be effectively controlled.

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