

UC Davis

UC Davis Previously Published Works

Title

Cellulose Nanofibers: Electrospinning and Nanocellulose Self-Assemblies

Permalink

<https://escholarship.org/uc/item/4rq8b8t1>

ISBN

9781119323266

Author

Hsieh, You-Lo

Publication Date

2018-10-01

DOI

10.1002/9781119323327.ch4

Peer reviewed

Cellulose Nanofibers: Electrospinning and Nanocellulose Self-assemblies

You-Lo Hsieh

University of California, Davis

Abstract

This chapter highlights top-down and bottom-up approaches to generate ultra-fine cellulose fibers of nano-scale dimensions, micro-porous, meso-porous and sheath-core hybrid structures as well as surface functionalized fibrous materials. Versatile solvent systems have been established to efficiently dissolve cellulose acetate to enable robust electrospinning into homogeneous 1D nanofibers and submicron size fibers that could be easily converted from amorphous to moderately crystalline cellulose II via alkaline hydrolysis. By pairing with either compatible or incompatible polymers, hybrid and nanocomposite fibers as well as porous fibers may be engineered. Surface reactions, grafting and electrostatic deposition can further offer surface functionalization for controlled hydrophobicity, stimuli-responsive behaviors and bound enzyme catalyses. Highly crystalline I β nanocelluloses with varied geometries and surface chemistries have been efficiently derived via chemical means and/or shear forces in nanorod and nanofibril forms that have been shown to exhibit unique dispersing and emulsifying properties for oil-water emulsions, coagulants for microbes as well as templates for nanoparticles and nanoprisms. These nanocelluloses can be facilely assembled into new fibrous structures, super-absorbent hydrogels, films and amphiphilic to hydrophobic aerogels for applications, such as oil recovery and separation, water purification, etc. While ultra-fine fibers from these two approaches share some common fibrous morphologies, their crystalline structures, thermal behaviors, surface chemistries, reactivity and chemical functionalities are distinctively different, offering a wide range of strategies for fabricating cellulose nanofibers with tunable functional characteristics for novel materials and advanced composites.

Keywords: Electrospinning, nanocellulose, self-assembly, morphology, surface

*Corresponding author: ylhsieh@ucdavis.edu

4.1 Introduction

Nanoscale materials are of great interest for their novel structural properties and their high specific surface, i.e., surface area per volume or mass, among others. Nanoparticles or zero dimensional (0 D) nanomaterials of inorganic origins have been most widely studied for their ease of synthesis and unique surface characteristics as nanometer scales approaching molecular scales. However, their particulate sizes also attribute to their easy dissemination into the environment and biological systems such as human and marine lives, raising serious concerns. One dimensional (1 D) nanomaterials, such as nanorods and, in particular, nanofibers with higher aspect ratios, can be more easily integrated into larger and well inter-connected structures, thus more easily handled or potentially less likely to migrate into the surrounding environment and biological systems.

Strictly speaking, nanomaterials refer to those materials with dimensions less than 100 nm. Nanofibers are 1 D nanomaterials with their lateral dimensions less than 100 nm. However, the term “nanofibers” have been commonly used for those with lateral dimensions, i.e., widths, thickness or diameters, in the hundreds nm. Nanofibers that are tens of nanometer wide are three orders of magnitude narrower than the conventional fibers with typically tens of micrometer widths; therefore their specific surfaces are three orders of magnitude higher. Such ultra-high specific surface fibrous materials are highly desirable for applications that rely on surface properties, such as controlled release and delivery, separation and filtration of chemicals, biological and pharmacologically active agents and molecules, etc. At these nanometer scale sizes, new properties and unexpected behaviors may also surface, offering potentially new functions for applications.

Cellulose, nature's most abundant polymer, is among the most renewable materials to be targeted for nanomaterials. Native cellulose found in a wide range of origins is highly fibrillated and semi-crystalline, which makes it difficult to dissolve and recalcitrant to be refined and converted into biofuels and small molecules.

Cellulose is a long chain polysaccharide, poly(1,4 β -anhydroglucopyranose), that consists of D(+)-glucopyranose building blocks linked by β (1 $\rightarrow$ 4)-glucosidic bonds (Figure 4.1a). The β -1,4 link between C1 and C4 of the adjacent D-glucose units resembles the stereo-regularity of a syndiotactic polymer, as opposed to the isotactic form of starch amylose with α -1,4 link. The cellobiose structural repeating units provide the steric effects to limit free rotation of the C-O-C link, adding stiffness to the already bulky glucose structure. The three hydroxyl groups on each anhydroglucose unit, i.e., one primary C6 and two secondary C2 and C3, along with the chain

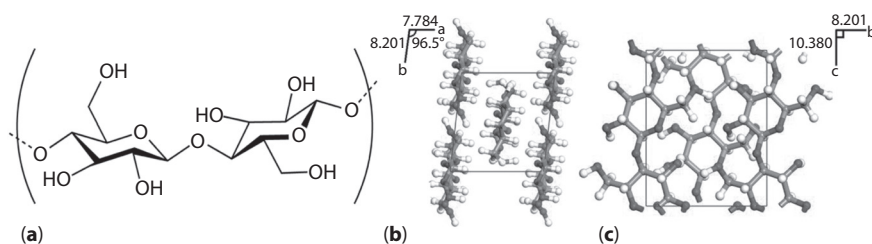


Figure 4.1 Cellulose: (a) cellulose repeating unit; cellulose I β unit cell (b) top view along C axis; (c) along A axis [1] (Reprinted with permission from Industrial & Engineering Chemistry Research. Copyright 2015 American Chemical Society).

conformation allow optimal inter-molecular and intra-molecular hydrogen bonding to further enhance the rigidity of the cellulose chain and crystalline structure. In fact, the highly hydrogen bonded crystalline structure of cellulose is the main impediment to hydrolysis to fermentable sugars for biofuel generation. Native cellulose from higher plants consists of crystalline domains in cellulose I β form (Figure 4.1b) [1] (two chain monoclinic unit cell: $a = 7.784 \text{ \AA}$, $b = 8.201 \text{ \AA}$, $c = 10.380 \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 96.5^\circ$) [2] whereas that from bacteria is in cellulose I α form.

While early effort in utilizing cellulose focused on dissolution of cellulose for regenerated cellulose fibers or cellulose derivatives for fibers and films, more recent interest has been on separating and using the crystalline domains or the so-called nanocelluloses. The interest in nanocelluloses has increased tremendously and especially over the past decade as evident by not only the increased numbers of papers but also reviews on the subject. The most studied source of cellulose to date is wood pulp whereas efforts related to other plant sources, especially agriculture crop residues and food processing by-products, are much less. This chapter presents some current perspectives and summarizes some of the recent developments related to nanocelluloses from non-wood sources without duplicating the reviews already available in the literature. Furthermore, the attention is drawn to the processes by which nanocelluloses are assembled into nanofibers.

To date, nanofibers have been most commonly fabricated by electrospinning in which either polymer solutions or melts are ejected by high voltages, after overcoming their surface tensions, into unstable jets that further reduce in sizes to generate nanoscale fibers with extremely long lengths. Fabricating nanofibers by electrospinning has been attractive because of easy fiber formation from a wide range of organic polymers including those that cannot be spun into fibers by conventional solution

or melt spinning processes due to lacking of specific viscoelastic properties and/or chain length requirements. However, electrospinning tends to produce fibers in heterogeneous widths that are, more often than not, in the hundreds of nm to a few micrometers. Electrospinning is generally lower in productivity than conventional fiber spinning processes, but is often offset by the unique advantages in fiber qualities it offers and/or by applications as a minor component with other bulk materials such as in the case of coating or laminating on other fibrous or porous substrates for filtration applications.

4.2 Electrospinning of Cellulose Solutions

As cellulose does not melt and is difficult to dissolve into homogeneous solutions, electrospinning of cellulose is challenging and has been met with limited success. While wet spinning of cellulose has been commercialized for over a century and continuing research in cellulose dissolution has advanced and reviewed recently [3], wet processing remains to be the key approach.

While cellulose can be dissolved in *N*-methyl-morpholine *N*-oxide (NMMO), lithium chloride/dimethyl acetamide (LiCl/DMAc) and ionic liquids, electrospinning cellulose from these solvents into fibers have been met with various dielectric and solvent removal constraints, among others. Electrospinning of cellulose from NMMO can produce 3–10 mm wide fibers [4] but requires elevated temperatures (70–110 °C) to lower viscosity [5] or smaller 200–700 nm wide fibers by using water as a coagulant to diffuse the solvent [6, 7]. While LiCl/DMAc dissolves cellulose well and charge carrying LiCl salt facilitates electrospinning into fibers, the volatile DMAc and the salt must be removed in subsequent steps [8, 9]. Ionic liquid, such as 1-butyl-3-methylimidazolium chloride, also dissolves and enables electrospinning of cellulose, but the solvent must be removed by coagulation in ethanol [10]. In all cases of electrospinning cellulose from these solvents, neither the feasibility of continuous fiber production nor the productivities of electrospinning from these solvent systems were reported.

4.3 Cellulose Nanofibers via Electrospinning and Hydrolysis of Cellulose Acetate

A facile approach to cellulose dissolution and fiber spinning is to work with cellulose derivatives, in particular cellulose esters that are mass produced

as commodity polymers and are commercially available. By replacing the pendant hydroxyls with ester groups, inter-molecular hydrogen bonding capability is essentially eliminated while interaction with organic solvents is significantly enabled. Significant lowering of chain lengths to 300–500 units of glucose repeating units or degree of polymerization that are about one order of magnitude lower than the cellulose precursor further enhance the solubility. In the case of cellulose acetates (CAs), solubility in a range of organic liquids becomes possible. CA with a molecular weight of 30 *kDa* and a degree of substitution (DS) of 2.45, i.e., an average of 2.45 of 3 hydroxyls being replaced with esters, is soluble in solvents with Hildebrand solubility parameters (δ) between 9.5 and 12.5 (cal/cm³)^{1/2} such as acetone, acetic acid and N,N-dimethylacetamide (DMAc) and dimethylformamide (DMF). However, electrospinning CA (30 *kDa*) in any of these liquids does not produce uniform fibers [11, 12]. Mixing DMAc with either acetone or acetic acid, both having lowered surface tensions and boiling points, enables efficient electrospinning of CA [9]. For instance, 15% CA in acetone/DMAc mixtures in mass ratios between 2:1 and 10:1 could be continuously electrospun into fibrous membranes. The 2:1 acetone/DMAc mixture has shown to be the most versatile, permitting 12.5–20% CA solutions to be continuously electrospun into highly uniform fibers with smooth surfaces deposited in thousands of layers across the thickness of the fibrous mat (Figure 4.2) and in increasing widths from about 100 nm to 2 μ m with increasing CA concentrations. These concentrations of CA in 2:1 acetone/DMAc correspond to η between 1.2 and 10.2 poise and γ around 26 dyne/cm. Solutions with viscosities lower than this lead to extensive bead formation whereas those with higher viscosities result in instability in electrospinning.

The fiber packing may also be regulated by collecting fibers on different materials, e.g., more densely packed fibers on conductive aluminum foil or

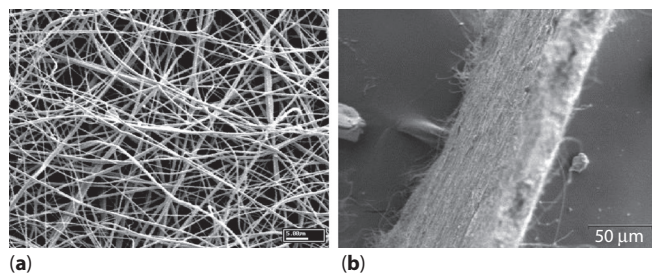


Figure 4.2 Electrospun CA (DS=2.45, 30 *kDa*, 20 w%) in 2:1 acetone/DMAc: (a) top and planar view, (b) cross-sectional view.

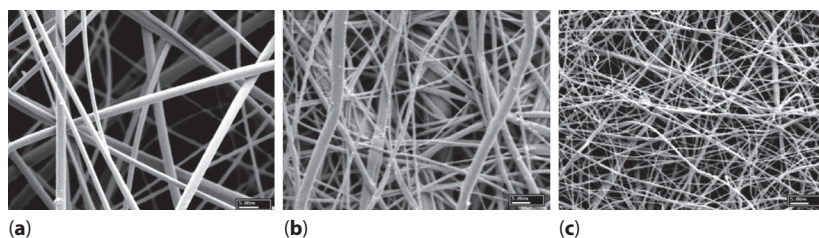


Figure 4.3 Electrospun cellulose acetate (CA, DS=2.45, 30 kDa) from 2:1 acetone/DMAc: (a) 20% CA collected on paper; (b) 20% CA collected on water; (c) 15 % CA collected on water, showing fiber packing as affected by collecting materials (a & b) and fiber size as affected by solution concentrations (b & c) [11] (Reprinted with permission from Journal of Polymer Science Part B: Polymer Physics. Copyright © 2002 Wiley Periodicals, Inc.).

water and less packed fibers on non-conductive cellulose paper (Figure 4.3). In all cases, these CA fibers may be deacetylated in mild (0.05 M) aq. or ethanolic NaOH, to DS 1.14 in 140 min or DS 0.15 in 60 min, respectively, with the latter more efficient and complete.

This approach of productive electrospinning CA in versatile solvent mixtures and efficient hydrolysis is significant and has been followed by others in the following years [13–16]. Other cellulose derivatives, such as hydroxypropyl cellulose, hydroxypropyl methyl cellulose, and ethyl-cyanoethyl cellulose, can also be dissolved in solvents suitable for electrospinning but are not reverted back to cellulose to be included in this discussion. In addition, fibrous membranes for many novel functional properties and broad applications are discussed in the following section.

4.3 Bicomponent Hybrid and Porous Cellulose Nanofibers

With similar physical constants, such as a high dielectric constant desirable for electrospinning as DMAc, DMF also dissolves CA. CAs of higher molecular weights of 50 and 60 kDa can be electrospun from DMF alone into uniform fibers whereas the lower 30 kDa CA requires the addition of dioxane to be electrospun into nanofibers in 1:1 DMF/dioxane mixture [17]. It should be noted that CA cannot be electrospun in dioxane alone either, similar to acetone, acetic acid and DMAc. In DMF, the semidilute entangled concentration (C_e) that is commonly used to determine the onset concentration for fiber spinning begins at 19.6% for 30 kDa CA and 16.5% for 50 kDa CA. The fact that fiber formation from 50 kDa CA in

DMF is more efficient at 20% concentration, significantly higher than the 16.5% C_e , suggests that other solution behaviors also contribute to electrospinning. Never-the-less, fibers electrospun from 20% CA (30 kDa) in 1:1 DMF/dioxane mixture were 50 to 200 nm wide, much smaller than those from the 2:1 acetone/DMAc mixture (0.83 to 2.5 μ m). This is attributed to the low dielectric constant and higher compatibility of dioxane with CA than acetone. This significant reduction in fiber sizes demonstrates the critical role of solvents in not only regulating electrospinning but also the fiber structure.

DMF is also a common solvent for many synthetic polymers, thus amenable to incorporate other polymers, such as poly(vinyl pyrrolidone) (PVP) [17], β -cyclodextrin (β -CD) [17] and poly(ethylene oxide) (PEO) [18], with CA. In the cases of PVP and β -CD, their additions greatly facilitate electrospinning of CA. The charge-holding ability of PVP enables electrospinning of CA/PVP mixtures in DMF alone into uniform hybrid nanofibers containing up to 70% CA (30 kDa) that by itself cannot be electrospun from DMF. In fact, PVP is not only electrospun into fibers from DMF alone, but its addition to CA increases the electrospinning rate of CA/PVP mixtures to approach that of PVP alone. CA/PVP bicomponent hybrid nanofibers consist of phase-separated PVP domains in a continuous CA matrix in increasing widths from 20 to 650 nm, with either higher PVP molecular weights (55 to 360 kDa) or quantities (up to 70 %) [15]. Upon dissolving PVP in water, mesoporous CA nanofibers with rough surfaces can be fabricated from CA/PVP hybrids with as high as up to 50% PVP.

With 50 kDa CA, a 12.5 wt% solution in DMF is not as electrospinnable because it is below the minimum concentration necessary for chain entanglement (C_e), but can be efficiently electrospun into nanofibers when equal amount of β -CD was added [17]. β -CD is 7-membered truncated cyclic oligosaccharide with all hydroxyls pointing outwards from the truncated ring: C6 primary hydroxyls along the smaller rim and C2 and C3 secondary hydroxyls along the larger rim. The fact that β -CD enables fiber formation of CA below its C_e concentration indicates that β -CD molecules are well dispersed among CA chains as individual molecules to enhance CA chain entanglement via hydrogen bonding interactions between remaining hydroxyls of CA and β -CD hydroxyls as confirmed by Fourier transform infrared (FTIR) spectroscopy. Up to 50 wt% of β -CD can be well distributed in the CA matrix as individual inclusive complexes with 2-nm mesopores, exactly internal cavity dimension of β -CD. As β -CD has a hydrophobic cavity, non-polar compounds of similar or smaller dimensions may be encapsulated within cellulose nanofibers in significant proportion for robust controlled release applications.

While both CA and PEO are easily soluble in DMF, the DMF-dioxane binary solvent system supports efficient electrospinning of all combinations of CA (30–50 kDa) and PEO (10–600 kDa) into CA/PEO bicomponent hybrid nanofibers [18]. Generally, a higher molecular weight of either CA or PEO lowers the threshold concentration necessary to achieve sufficient viscosities for fiber formation by electrospinning and results in generating wider fibers. Increasing total CA/PEO concentrations (5–20%) improves fiber formation by electrospinning, but also leads to wider fibers. In most cases, PEO phase separated into sheath with CA continuous matrix core structures.

Another advantage of these versatile solvent systems is the ability to incorporate nanomaterials with CA. Multi-walled carbon nanotubes (MWCNTs) can be well dispersed with CA in 2:1 wt:wt acetone/DMAc to be electrospun, then alkaline hydrolyzed into MWCNTs-filled cellulose nanofibers [19]. Both the addition of MWCNTs and hydrolysis reduce fiber widths, by up to ca. 50 and 100 nm, respectively. While, not surprisingly, only about a third of the fibers appear to contain MWCNTs at very low loadings of 0.11 and 0.55 wt%, all MWCNTs are well aligned along the fiber direction, showing shear force during electrospinning to be sufficient to orient MWCNT nanofibers within CA matrix. In fact, the addition of 0.55 wt% MWCNTs also reduced CA fiber widths from 321 to 228 nm.

All as-spun CA fibrous membranes, with or without MWCNT, are amorphous whereas the hydrolyzed cellulose nanofibers show two crystalline peaks, one at 20.2° peak, close to the typical 101 reflection of cellulose II ($2\theta = 19.8^\circ$) another at 22.0°, close to the 002 reflection of cellulose I ($2\theta = 22.5^\circ$) [19]. However, both are far weaker than the cellulose I observed in cotton [20] and cellulose II in regenerated cellulose [21]. These XRD patterns suggest that low quantities of cellulose I and II crystalline allomorphs are present in the fully hydrolyzed cellulose nanofibers and the presence of MWCNTs appears to slightly enhance their crystallinity. Intriguingly, both strength and wetting properties of cellulose nanofibers were significantly improved even at such low MWCNT loadings.

4.4 Wholly Polysaccharide Cellulose/Chitin/Chitosan Hybrid Nanofibers

Chitin is the second most abundant polysaccharide in nature. Like cellulose, chitin and chitosan have been widely studied as platforms for advanced materials. Together, cellulose, chitin and chitosan have been combined to take the advantage of their collective desirable properties.

Chitin has the same β -1,4-D(+)-anhydroglucosidic main chain with two hydroxyls (C-6 primary and C-3 secondary) as cellulose but differs only on the C-2 pendant group, i.e., an acetyl amine as opposed to a hydroxyl for cellulose. Hydrolyzing the acetyl amine to amine converts chitin to chitosan, which is the most significant cationic polysaccharide with many desirable properties. Also, like cellulose, the rigid main chain structure and the extensive inter- and intra-molecular hydrogen bonded structure of chitin and chitosan give them their non-thermoplastic characteristics and insolubility in most common solvents, significant barriers to their processing and conversion to materials. Thus, processing chitin or chitosan into fibers is also challenging. For instance, chitosan is soluble in 1:1 acetone/acetic acid at up to 3%, but none of these solutions with chitosan alone can be electrospun into fibers.

Water-soluble chitosan derivatives have been synthesized but could not be electrospun from aqueous solutions alone. Carboxymethyl chitosan (CMCS) in varied molecular weights ($M_v = 40$ to 405 kDa) and degrees of substitution (DS = 0.25 to 1.19) has been synthesized by alkalization of chitosan, followed by carboxymethylation with monochloroacetic acid to show excellent water solubility, however, electrospinning aq. CMCS requires the addition of another fiber-forming water-soluble polymers, such as PEO, PAA, PAAm and PVA [22]. Other water-soluble chitosan derivatives, poly (ethylene glycol) (PEG, $M_n = 500$ Da to 2 kDa) grafted chitosan ($M_v = 137$ to 400 kDa), i.e., PEG-*N*-chitosan and PEG-*N,O*-chitosan, have been synthesized via reductive amination and acylation, respectively. However, none of these aqueous solutions on their own could be electrospun into fibers [23]. PEG-*N,O*-chitosan is, however, soluble in organic solvents, including CHCl_3 , DMF, DMSO and THF, and can be electrospun by using a cosolvent to increase solution viscosity or adding a non-ionic surfactant to reduce solution surface tensions. For instance, fibers with diameters ranging from 40 to 360 nm with average diameter of 162 nm have been electrospun from 15% PEG-*N,O*-chitosan in 75/25 (v/v) THF/DMF cosolvents with 0.5% Triton X-100TM [23].

An elegant approach to generate chitin or chitosan nanofibers is by electrospinning a chitin derivative and then reverting back to chitin or further hydrolyzing chitin to chitosan. A simple and robust acylation reaction can render chitin derivative soluble in most common solvents that are also conducive to processing into fibers, films and coatings. The C3 and C6 hydroxyls on chitin can be acetylated with butyric anhydride to convert chitin to dibutyryl chitin (DBC) [24]. The newly formed butyl groups on C3 and C6 not only disrupt the inter-molecular hydrogen bonds, but also confer non-polar characteristics, offering DBC robust solubility (13–19 wt%) in

acetone, DMAc, DMF, ethanol and acetic acid, all appropriate for electrospinning. As all these, except ethanol, are also solvents for CA, DBC and CA, allowing their dissolution and mixing at any ratios. The optimal solvent system for electrospinning either DBC or CA alone as well as their mixtures at all ratios is 1:1 acetone/acetic acid, resulting in fully integrated CA/DBC hybrid fibers with 30–350 nm widths with no phase separation of the two polymers. Alkaline hydrolysis of CA/DBC nanofibers in any proportion proceeds easily to first regenerate CA back to cellulose then DBC to chitin, further hydrolysis at higher alkaline concentrations and/or temperatures deacetylates chitin to chitosan from 80 to 90%, depending on conditions. Therefore, this derivatization strategy of chitin not only improves its solubility in organic liquids, but also enables its electrospinning alone and/or with CA in any proportion into homogeneous fibers of cellulose/chitin derivatives that can be easily hydrolyzed to cellulose/chitin and cellulose/chitosan hybrid nanofibers, presenting promising holistic polysaccharide functional materials.

4.5 Surface-Active Cellulose Nanofibers

In addition to homogeneous hybrid cellulose nanofibers, other materials can also be integrated into the cellulose nanofiber structure as surface layers or sheath-core structures. For example, polysaccharide nano-films could be assembled on cellulose nanofibers via electrostatic forces [25]. By alternating polymers with opposing charges, cationic chitosan and anionic dextran sulfate can be deposited to cellulose nanofiber surface in a layer-by-layer (LbL) fashion, forming multiple bilayer nanofilms, each of 6.4 to 9.0 nm thickness. This LbL approach can also be applied to construct surface bound lipase hydrolase enzymes as single outer layer [26] or alternating bilayers with Cibacron blue reactive dye ligand [27]. Such surface bound approach enhances enzyme loadings on cellulose nanofibers, extends their activities as well as enables retrieval and repetitive use in biocatalysis.

The highly reactive surfaces of electrospun and hydrolyzed cellulose nanofibers are also evident by easy reactions to introduce hydrophobic grafts [28], hydrophilic PVA [29] and thermally responsive poly (N-isopropylacrylamide) [30] hydrogels as well as super-hydrophilic polyacrylic acid hydrogels for enzyme encapsulation [31] and amphiphilic polyethylene glycol (PEG) tethered lipase enzymes [32] to enhance enzyme activities and repetitive catalysis. Recycled CA from cigarette filter has also been co-axially electrospun as core and fluoropolymer as shell fibrous membranes as separators for lithium-ion battery [33].

In summary, cellulose nanofibers can be robustly fabricated from electrospinning of CAs in a diverse array of binary solvent systems to allow addition of other biopolymers, synthetic polymers or nanomaterials to form either fully integrated or phase-separated hybrid, sheath-core and porous structures. Solvent selection is critical as demonstrated by the examples discussed. In electrospinning of either single component or bicomponent polymer systems, longer polymer chains, higher polymer concentration and lower proportion of short polymer chains all contribute to necessary polymer-polymer entanglement to support continuous polymer jets and improved fibers formation. This enhanced polymer chain interaction also increases resistance to the stretching force, leading to larger fibers. These cellulose nanofibers from electrospinning and hydrolysis of cellulose derivatives are regenerated and highly reactive for introducing new surface functionalities by chemical reactions and grafting. The pathways presented offer ways to fabricate ultra-high specific surface cellulose nanofibrous substrates and enabled more recent inquiries, ours as well as many others, into functional nanomaterials based on polysaccharides such as cellulose, chitin, chitosan, etc.

4.6 Nanocelluloses

'Nanocelluloses' have been used to describe the nano-scale fibrillar crystalline domains separated or derived from various native cellulose sources. Nanocelluloses vary in their dimensions depending on their origins and the processes by which they are derived. The rod-like nanocelluloses have been referred as cellulose nanowhiskers (CNWs), nanocrystalline cellulose (NCC) or cellulose nanocrystals (CNCs) whereas the longer fibrils of varied lateral dimensions are termed microfibrillated cellulose (MFCs), cellulose microfibrils, nanofibrillated cellulose (NFCs) or cellulose nanofibrils (CNFs).

Small organisms such as bacteria [34], algae [35] and marine animal tunicates [36] synthesize fibrillar nanocelluloses. Among these, bacterial cellulose (BC), also referred as bacterial nanocellulose or microbial cellulose, is extensively studied. BC is synthesized by a gram-negative strain of acetic-acid-producing bacteria, the acetic bacterium *Acetobacter xylinum* (or *Gluconacetobacter xylinus*) in a fermentation process [37]. BC is extracellular gel-like product excreted into the culture medium in the form of pellicles in a web-like network of continuous ca. 10 to 100 nm wide nanofibers. In plants, fibrillar bundles of cellulose are synthesized by a hexagonal array called rosette in the presence of hemicellulose and lignin.

By separating and/or removing the amorphous or less ordered cellulose chains, the crystalline domains can be extracted from a broad range of natural sources. Both rod-like and fibrillar nanocelluloses are mostly produced by top-down approaches from higher plants.

Nanocelluloses may be in either cellulose Ia or Ib crystalline forms, depending on their origins. Native cellulose is synthesized in two allomorphs or crystalline forms, i.e., cellulose Ia from algal and Ib from higher plants, as confirmed by high resolution, solid state ^{13}C NMR spectroscopy [38].

Relatively uniformly sized CNCs can be produced from a single source under a fixed condition. However, widely varied dimensions (3–70 nm widths and 35–3,000 nm lengths) have been reported from different cellulose sources and hydrolysis conditions [39–41]. By hydrolyzing and removing cellulose chains in the less ordered regions, CNCs generated are more crystalline than the original sources but usually at less than 30% yields [40, 41]. Hydrochloric acid, hydrobromic acid as well as mixed acetic and nitric acids are also capable of hydrolyzing cellulose into CNCs, but without esterifying the surfaces as in the case with sulfuric acid, while in higher yields [44, 45]. The dimensions of CNCs have shown to be mostly 5 to 20 nm wide and 100 nm or longer, dependent on the sources of cellulose as well as the hydrolysis conditions, including temperature, time and agitation [41].

Longer CNFs can ~~also~~ be produced by shear, high-energy forces or chemical means. Shear force processing involves repetitive processing aqueous wood cellulose suspensions or pastes using mechanical homogenizers [46], cryogenic grinders or microfluidizers, high-pressure homogenizers and ultrasonic homogenizers [47] or steam explosion [48]. Further details about mechanical processes in deriving NFC can be found in a recent review [49]. The most reported chemical method for CNF derivation involves 2,2,6,6-tetramethylpyperidine-1-oxyl (TEMPO)-mediated oxidation of C6 primary hydroxyl using nitroxyl radicals in the presence of sodium hypochlorite and sodium bromide at pH around 10 and ambient temperature [50–52] and can reach a 90% yield when aided with mechanical means [53]. Due to oxidative effect, CNFs tend to be less crystalline than the sources from which they are derived.

In addition to their nanoscale lateral dimensions, nanocelluloses are generally recognized as among the strongest materials, far exceeding any of high strength synthetic polymers. The uniquely high moduli were first reported on fibrillar nanocelluloses synthesized by small organisms, such as tunicate. The elastic modulus of tunicate CNWs has been reported to be ca. 143 GPa using the Raman spectroscopic technique [54] and the elastic moduli of single microfibrils from TEMPO-oxidation and acid hydrolysis

from tunicate were measured by AFM to be ca.145 and 150 GPa, respectively [36].

Early reviews of nanocelluloses have focused mostly on those derived from bacteria and wood cellulose [55, 56]. The tremendous interest in nanocelluloses is evident from the increasing numbers of publications. As the interest in nanocelluloses has escalated over the past decade, further advancement on nanocelluloses and their applications have been extensively reviewed [57–62]. Hence, the following discussions focus on aspects of nanocelluloses from the much less studied agricultural biomass, in particular rice straw, to offer current insight on the origin- and process-linked aspects.

4.7 Nanocelluloses from Agricultural By-Products

As cellulose is the nature's most abundant polymer, it is found in a wide range of origins. From the source perspective, major plant fibers whose features, strength and most significant constituent that are attributed to cellulose have been classified into bast fibers (flax, jute, hemp, ramie, kenaf, etc.), leaf fibers (abaca, sisal, pineapple, etc.), seed fibers (cotton, coir, kapok, etc.), core fibers (kenaf, hemp, jute, etc.), grass and reed fibers (wheat, corn, rice, etc.) and others (wood, roots, etc.) [63]. From the perspective of human activities, cellulose may be classified as primary sources for textiles, paper and wood and biofuel [63, 64], secondary non-processed residues from agricultural/forestry activities and by-products of food industry, such as: bark, straw, leaves, husks as well as tertiary wastes from the use, transformation and conversion of cellulosic biomass [65]. Therefore, nanocelluloses may be viewed from a much wider perspective in terms of both origins and processes, thus the focus of the following.

There has been an increasing interest in deriving nanocelluloses from more diverse, non-wood and already existing sources, such as agricultural and industrial lignocellulosic residues and byproducts. Current uses of these lignocellulosics are mainly for low value-added practices, such as feed and bedding for livestock, composting, soil fertilization or combustion for energy recovery. With the advent of biofuel production from lignocellulosic biomass, generating green chemicals and materials from these sources have also become logical solutions to save not only our limited fossil fuel resources but also to reduce the environmental impact.

While biomass possesses diverse chemical compositions, structures, and properties depending on their origins, one major distinction of non-woody biomass is their lower content or absence of lignin, making it less recalcitrant

to chemical, microbial and enzymatic digestion than woody biomass. With the exception of the fibrous crops such as cotton and flax that contain significantly higher cellulose contents, the cellulose contents in most agricultural biomass vary between one third to two thirds [66], thus are close to or higher than that in woody biomass, making them viable sources for cellulose. Furthermore, cellulose in these agricultural and industrial by-products may be less integrated in their matrixes to be potentially more easily extracted.

The top-down approaches to produce nanocelluloses involve either removing amorphous cellulose chains by chemical hydrolysis or separating the crystalline domains apart from each other via chemical reactions and/or mechanical forces using cellulose isolated from various sources of higher plants. With a recent review on nanocelluloses from various agricultural crop residues and industrial wastes [65], these following analyses specifically detail the origin and process-linked effects.

4.8 Source Effects – CNCs from Grape Skin, Tomato Peel, Rice Straw, Cotton Linter

Rod-like CNCs are typically derived by hydrolysis and removal of amorphous cellulose using various acids, most commonly sulfuric acid. Cellulose in the more accessible amorphous domains is hydrolyzed by sulfuric acid via rapid protonation of glucosidic oxygen (1) or cyclic oxygen (2) by protons from the acid followed by scission of the glucosidic bonds (Figure 4.4a) [18], fragmenting into small sugars. In due process, CNC surface hydroxyls are esterified to sulfate groups that introduce negative charges to their surfaces (Figure 4.4b), thus preventing aggregation and keep CNCs well dispersed in a stable aqueous suspension.

CNCs derived from different sources under the same sulfuric acid hydrolysis (64–65% H_2SO_4 , 45 °C) have shown very different nano-scale dimensions, reflecting the structural distinctions that stem from their origins. From the same 30 min reaction, grape skin CNCs consist of mainly nanoparticles less than 5 nm in diameters among a few <10 nm wide nanorods [67] whereas both tomato peel [68] and rice straw [69] CNCs are flat spindle or ribbon like rods with asymmetric cross-sectional shapes, i.e., larger width (W) than thickness (T) as measured by transmission electron microscopy and atomic force microscopy, respectively (Table 4.1). The same hydrolysis reaction produces over four times wider and slightly longer rice straw CNCs with a 5:1 W:T ratio and 270 nm length whereas tomato peel CNCs have 2:1 W:T ratio and are less than 200 nm long. Hydrolyzed for a longer, 45 min period reduces the width and length of rice straw CNCs to

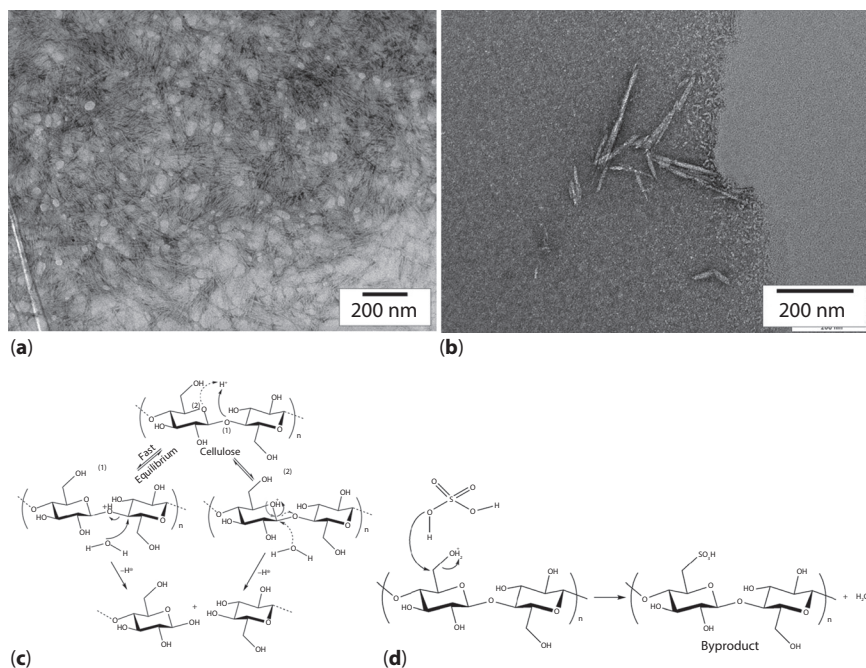


Figure 4.4 Cellulose nanocrystals (CNCs) by sulfuric acid hydrolysis (64–65% H_2SO_4 , 45 °C, 60 min): (a) AMF of CNCs from cotton linter; (b) protonation and scission of cellulose chains in amorphous domains; (c) esterification of surface hydroxyl to sulfate [20] (Reprinted with permission from Carbohydr. Polym. Copyright © 2010 Elsevier Ltd).

less than half, but only slightly lowers the thickness, giving a 2:1 W:T ratio, similar to tomato CNCs hydrolyzed for 30 min. Cotton linter CNCs, on the other hand, are less than 10 nm wide, similar in widths as others, but longest at up to 40 L:W aspect ratios, from longest hydrolysis time of one hr [20]. These results show that CNCs generated from cotton linters have the highest L:T aspect ratio, rice straw CNC has the highest W:T ratio and grape skin CNCs are the smallest and mostly nanoparticles.

Upon freezing (−196 °C) and lyophilization (−50 °C) dilute aqueous suspensions, these geometrically distinct CNCs self-assemble into different morphologies. The largest cotton CNCs self-assemble in various forms of nanorods, hollow nanospheres or porous network [20] whereas the smallest grape skin CNCs agglomerate mainly into clusters with 5 nm nanoparticles surrounding nanorod cores, interestingly, resembling grape bundles [65]! Both flat ribbon like tomato peel [68] and rice straw [69] CNCs assembled anisotropically into ultra-fine fibers with diameters depending on the lateral dimensions of the original CNCs. The smaller tomato CNC (7.2 nm W,

Table 4.1 CNCs from sulfuric acid hydrolysis (64–65% H₂SO₄, 45 °C) of cellulose of different origins.

Source	Time (min)	Shape/ W/T ratio	Width (W, nm) or thickness (T, nm)	Length (L, nm)	L:W Ratio
Grape Skin	30	Nanorods Nanoparticles	W < 10 W < 5	50–100 NA	5–10 NA
Tomato Peel	30	Flat ribbon/ 2.2	W = 7.2 ± 1.0 T = 3.3 ± 1.2	100–200	20
Rice Straw	30	Flat ribbon/ 5.2	W = 30.7 T = 5.95	270	8.8
Rice Straw	45	Flat ribbon/ 2.2	W = 11.2 T = 5.06	117	10
Cotton liter	60	Nanorods	W < 10	200–400	20–40

3.3 nm T) self-assembled into mostly sub-micron wide fibers (ϕ = 260 nm) interconnected with few nanofibers (ϕ = 38 nm). The smaller rice straw CNCs (11.2 nm W, 5.06 nm T), ca. 1.5 times wider and thicker than tomato CNC, self-assemble into proportionally larger sub-micron (ϕ = 386 nm) fibers that are about 1.5 larger than those from tomato CNCs. The larger rice straw CNC (30.7 nm W, 5.95 nm T), i.e., those from 30 m hydrolysis time, assemble into 1–2 mm wide fibers. For CNCs with asymmetric cross-sections, i.e., tomato peels and rice straw, the self-assembled fiber widths appear to be proportional to the widths of the original CNCs. All self-assembled fibers are more crystalline than their cellulose precursors as expected from the more crystalline CNCs. These source-linked unique CNC geometries and the ability of CNCs to self-assemble both laterally and longitudinally into longer and even more crystalline nanofibers and microfibers and possibly other porous morphologies to present interesting prospect of creating stronger and higher specific surface cellulose nanomaterials.

4.9 Process Effect – Nanocelluloses from Single Source (Corn Cob, Rice Straw)

Nanocelluloses derived by different processes from a single source have also shown to have different geometries and surface chemistries. CNCs fabricated

from bleached corn cob cellulose by sulfuric and formic acid hydrolysis and CNFs obtained by TEMPO-mediated oxidation and pulp refining had 2.1 to 43 nm widths and 198 nm to over one micrometer lengths [70]. Among the chemical processes, CNFs from TEMPO oxidation were the finest with highest aspect ratio and relatively high yield (78%) whereas sulfuric acid hydrolysis yielded the least CNCs with lowest aspect ratio. Formic acid hydrolysis produces more (66.3% yield) and longer CNFs (nearly as long as TEMPO) than that by sulfuric acid, but least negatively charged.

Rice straw CNFs have been derived by means of TEMPO mediated oxidation [71], grinding [72], blending [73] mechanical defibrillation [74], coupled TEMPO and blending [75], aqueous counter collision (ACC) [76] and solid acid catalyst [77] in addition to CNCs obtained from sulfuric acid hydrolysis [67, 71]. The effects of the top-down processes on nanocellulose structures and properties and their assembled structure from rice straw conducted in our laboratory to date are summarized in Table 4.2. In contrast to the very strong mineral acids such as sulfuric acid, TEMPO mediated oxidation is a milder reaction that oxidizes only the C6 primary hydroxyls of the cellulose in the less ordered regions, i.e., amorphous and crystalline surfaces and inter-fibril cellulose segments, to carboxylate groups [78]. Under optimal conditions, TEMPO oxidation (5 mmol/g NaClO/cellulose) followed by mechanical blending (37,000 rpm, 30 min) converts 96.8% of rice straw cellulose into the finest and most uniform (1.5 nm thick, 2.1 nm wide, and up to 1 μ m long) CNFs [75]. A shear-force intensive and scalable ACC process that utilizes high-speed collision of two aqueous jets of cellulose suspensions and reported on microbial cellulose [79] and microcrystalline cellulose [80] can fully defibrillate rice straw cellulose into varying sizes of CNFs in 30 passes under 180 MPa pressure (15 kWh/kg) [76]. ACC defibrillated rice straw CNFs varied widely in widths are fragmented via differential centrifugation into width groups of 58.4% less than 5 nm, 20.3% 5–20 nm, 14.4% 20–80 nm and 6.9% 80–200 nm. Furthermore, rice straw cellulose has been fully hydrolyzed using a solid acid catalyst synthesized by lignin-based activated carbon fibers into CNFs and glucose [77]. Under hydrothermal condition (150 °C, 5 atm), this recyclable carbon nanofiber acid catalyst produces 2.1 nm thick, 3.1 nm wide and up to 1 μ m long CNFs in 8.1% yield from rice straw cellulose and the remaining to glucose with an excellent 90% selectivity. The porous carbon nanofiber bound sulfuric acid is thought to hydrolyze cellulose via hydronium ion diffusion to amorphous chains that is facilitated under the hydrothermal conditions. The CNFs produced by this novel solid acid catalyst are nearly as thin as CNFs (1.5 nm T and 2.0 nm W) by the coupled TEMPO oxidation and mechanical blending. Most intriguingly, CNFs by

Table 4.2 Nanocelluloses from rice straw derived by different processes and their self-assembled fibers.

Process	Nanocellulose					Self-Assembled				
	Yield (%)	Thickness (nm)	Length (nm)	Zeta-potential (mV)	Surface charge (mmol/g)	Fiber width (nm)	Crl (%)	T _{max} (°C)	Char at 500 °C (%)	
H ₂ SO ₄ hydrolysis 64%, 45 °C, 45 min [67,69]	6.8	4.72 ± 1.25	143.3 ± 30.9	-57.3 ± 2.7	0.24	440 ± 127	90.7	234	23.9	
TEMPO 5 mmol/gNaClO Blending 30 min [73]	96.8	1.52 ± 0.54	10 ² –10 ³	-97.6 ± 1.5	1.29	497 ± 161	64.4	269	19.0	
Blending 120 min [71]	12.0	2.70 ± 1.22 8.46 ± 4.14	100–200 >10 ³	n.a.	n.a.	153 ± 60	81.5	320	20.3	
ACC 30 passes [74]	58.4–20.3 14.1–6.9	< 5 5–20 20–80 80–200	>10 ³	n.a.	n.a.	136	77.9	345	10.2	
Carbon nanofiber acid catalyst [75]	8.1*	2.1	>10 ³	–	–	–	–	–	–	

* out of 69.8% cellulose hydrolyzed with glucose as remaining product at 92% selectivity.

this porous carbon nanofiber bound sulfuric acid catalyst are less than half as wide or thick as the rigid rod-like CNCs (4.7 nm thick, 6.4 nm wide and 143 nm long) produced by sulfuric acid. Not only this solid acid catalyst is biobased, easily separated from both CNF and glucose products, but also can be used repetitively making the process 'green'.

These processes, i.e., sulfuric acid, coupled TEMPO and blending, blending, ACC and solid acid catalyst, not only produce nanocelluloses of different geometries, but also surface chemistries and charges. While the strong sulfuric acid hydrolysis disintegrates and breaks the less ordered cellulose chemically to release the shorter flat rod-like CNCs, the others can be optimized to defibrillate cellulose into longer CNFs and in higher yields to approach 100% with the exception of the solid acid catalyst that, in fact, generates glucose as the dominant co-product, thus also highly efficient. These geometric and surface chemical characteristics of nanocelluloses also cause them to self-assemble into distinctively different sizes and structures exhibiting amphiphilic behaviors. For instance, the extents of surface carboxylation on CNFs may be increased by increasing the levels of oxidant in the TEMPO-mediated oxidation reaction. CNFs with increasing surface carboxylate densities of 0.59, 0.92, and 1.29 mmol/g assembled into increasingly larger fibers with respective diameters of 125, 327, and 497 nm [75]. Alternatively, the surface carboxylates on CNFs derived from the same coupled TEMPO oxidation and blending may be protonated to different levels from nearly 90% charged sodium salt form to completely uncharged carboxylic acid form to exhibit different behaviors [81]. The mostly charged CNFs assembled into finest and most uniform fibers ($\phi = 137$ nm) that are more hydrophobic than hydrophilic whereas the fully protonated and uncharged CNFs assembled extensively into porous and mostly ultra-thin film-like structures. Therefore, CNFs could be tuned by varying the degree of surface carboxylation as well as protonation to desired hydrophobic-hydrophilic characteristic along the amphiphilic scale, liquid behaviors and self-assembled fiber morphologies. With the exception of CNFs from coupled TEMPO and blending, CNFs self-assemble into more crystalline fibers than the original rice straw cellulose (CrI = 72.2 %), with that of CNC being most as expected.

4.10 Ultra-Fine Cellulose Fibers from Electrospinning and Self-Assembled Nanocellulose

Nanofibers and ultrafine submicrometer wide fibers can be fabricated either with electrospinning of cellulose esters, such as CAs, then

hydrolyzed back to cellulose or via self-assembling of nanocelluloses from either the rod-like CNCs or nanofibrillar CNFs. The electrospun cellulose fibers vary in sizes, appearing similar to and in comparable sizes as the microfibrils observed on cotton fiber cell walls (Figure 4.5), but are in cellulose II crystalline structure as opposed to the highly crystalline cellulose I β in cotton fibers. Both approaches are preceded by top-down processes, i.e., cellulose dissolution for electrospinning and defibrillation for nanocelluloses, that affects down to the molecular level in the former, but only separating the crystalline domains for the latter. Dissolution not only breaks all inter-molecular hydrogen bonds but destroys the crystalline structure. However, neither approach is as far top-down as that in bio-refining that breaks down lignocellulosics to the much smaller molecular biofuels and chemicals.

Due to their different extents of top-down processes, the crystalline structures of cellulose nanofibers from electrospinning of CA and hydrolysis back to cellulose and those from self-assembling of nanocelluloses are cellulose II and I, respectively. As cellulose I and II have distinctively different Young's moduli of 138 GPa and 88 GPa, respectively [82], the nanofibers self-assembled from nanocellulose are expected to be far stronger and stiffer than those by electrospinning. The electrospinning approach tends to generate larger sub-micron sized fibers with smooth surfaces whereas fibers self-assembled from nanocelluloses tend to be smaller and whose sizes are highly dependent on liquid media and drying conditions. Under certain conditions, these two approaches produce similar size fibers (Figure 4.6), but with drastically different chemical and physical attributes.

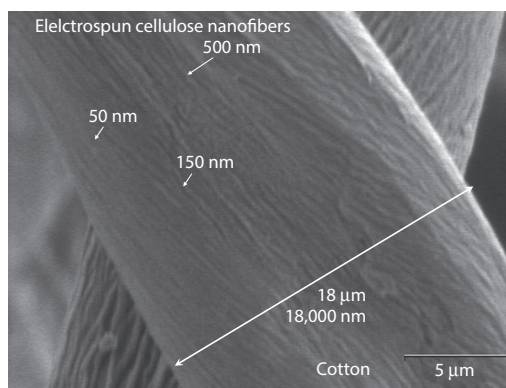


Figure 4.5 Electrospun cellulose nanofibers (inset) and cotton fibers (background).

Fibers formed by electrospinning are generally packed in very thin fibrous sheet or mat whereas those from nanocelluloses may be in any forms determined by the size and shape of containers in which they are dried. Depending on the types of nanocelluloses, the self-assembled fibers are uniquely amphiphilic, and can be tuned to be more hydrophobic by way of media in which they are dispersed and dried from. Electrospun CA fibers are hydrophobic, and become hydrophilic once the surfaces are hydrolyzed while the unhydrolyzed cores may retain some level of hydrophobicity and their thermoplastic nature and completely hydrophilic when fully hydrolyzed into cellulose II. Stemmed from their crystalline structural differences, electrospun cellulose fibers are more accessible to reagents and more chemically reactive than those assembled from nanocelluloses, lending them to be amenable for chemical modification and for chemical, biochemical and biological applications.

In both approaches of electrospun and self-assembled nanofibers, the nanometer to submicron lateral dimensions contribute to their high specific surface characteristics, whereas the much higher aspect ratios offer unique oriented fibrous and porous structures with many potential applications, such as nanocomposites, reactive nanomaterials for separation membranes, medical, pharmaceutical, hygiene, absorbent and cosmetic products, energy devices and beyond.

4.11 Further Notes on Nanocellulose Applications and Nanocomposites

As the emerging nanomaterial, nanocelluloses' unique attributes have drawn and will continue to attract significant interest in many potential

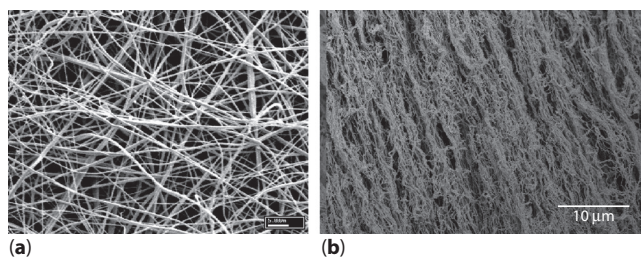


Figure 4.6 Cellulose nanofibers from: (a) electrospinning of CA and alkaline hydrolysis; (b) self-assembling from freezing (-196°C) and lyophilization (-50°C) of CNFs from coupled TEMPO mediated oxidation and blending of rice straw cellulose.

applications. For instance, rice straw nanocelluloses have been shown to exhibit unique dispersing and emulsifying properties for oil-water emulsions [83, 84], coagulants for microbes [85] as well as templates for nanoparticles and nanoprisms [86]. These nanocelluloses can also be electrospun into new nanofibrous structures [87] or assembled into super-absorbent hydrogels and amphiphilic aerogels [88] for applications such as oil recovery and separation, water purification, etc. Others have reviewed nanocellulose colloids assembled at liquid-liquid and air-liquid interfaces [89] and other related applications [90]. Related to food, nanocelluloses have been studied as stabilizing agent, food additive [91] and functional food ingredient [92] as well as additives in plastics for food packaging [93]. Nanocelluloses as part of nanocomposites is perhaps the most studied area since CNWs were first reported as reinforcement for composites [94] and has been extensively reviewed as well [95–101].

Acknowledgement

The author greatly appreciates the contribution of all co-authors on their own work cited and the support for research from the National Textile Center, USDA/NIFA, NSF, NIH, California Rice Research Board and the AgTech Innovation Center at the University of California, Davis.

References

1. C. Meng, H. Lu, G. Cao, C. Yao, Y. Liu, Qi. Zhang, Y. Bai, and H. Wang, Activation of cellulose by supercritical tetrafluoroethane and its application in synthesis of cellulose acetate, *Ind. Eng. Chem. Res.* 54, 12204–12213, 2015.
2. Y. Nishiyama, P. Langan, and H. Chanzy, Crystal structure and hydrogen-bonding system in cellulose I β from synchrotron X-ray and neutron fiber diffraction, *J. Am. Chem. Soc.* 124, 9074–9082, 2002.
3. S. Wang, A. Lu and L. Zhang, Recent advances in regenerated cellulose materials, *Prog. Polym. Sci.* 53, 169–206, 2016.
4. Z. H. Huang, F. Y. Kang, Y. P. Zheng, J. B. Yang, and K. M. Liang, Adsorption of trace polar methy-ethyl-ketone and non-polar benzene vapors on viscose rayon-based activated carbon fibers, *Carbon* 40, 1363–1367, 2002.
5. C.-W. Kim, D.-S. Kim, S.-Y. Kang, M. Marquez, and Y. L. Joo, Structural studies of electrospun cellulose nanofibers, *Polymer* 47, 5097–5107, 2006.
6. P. Kulpinski, Cellulose nanofibers prepared by the N-methylmorpholine-N-oxide method, *J Appl. Polym. Sci.* 98, 1855–1859, 2005.

7. M. S. Khil, H. Y. Kim, Y. S. Kang, H. J. Bang, D. R. Lee, and J. K. Doo, Preparation of electrospun oxidized cellulose mats and their *in vitro* degradation behavior, *Macromolecular Res.* 13, 62–67, 2005.
8. A. Frenot, M. W. Henriksson, and P. Walkenstrom, Electrospinning of cellulose-based nanofibers, *J. Appl. Polym. Sci.* 103, 1473–1482, 2007.
9. C. W. Kim, M. W. Frey, M. Marquez, and Y. L. Joo, Preparation of submicron-scale, electrospun cellulose fibers via direct dissolution, *J. Polym. Sci. Polym. Phys.* 43, 1673–1683, 2005.
10. G. Viswanathan, S. Murugesan, V. Pushparaj, O. Nalamasu, P. M. Ajayan, and R. J. Linhardt, Preparation of biopolymer fibers by electrospinning from room temperature ionic liquids, *Biomacromolecules* 7, 415–418, 2006.
11. H. Liu and Y. -L. Hsieh, Ultra-fine fibrous cellulose membranes from electrospinning of cellulose acetate, *J. Polym. Sci. Polym. Phys.* 40, 2119–2129, 2002.
12. G. Callegari, I. Tyomkin, K. G. Kornev, A. V. Neimark, and Y. -L. Hsieh, Absorption and transport properties of ultra-fine cellulose webs, *J. Colloid Interf. Sci.* 353, 290–293, 2010.
13. W. K. Son, J. H. Youk, T. S. Lee, and W. H. Park, Electrospinning of ultra-fine cellulose acetate fibers: Studies of a new solvent system and deacetylation of ultrafine cellulose acetate fibers, *J. Polym. Sci. Polym. Phys.* 42, 5–11, 2004.
14. W. K. Son, J. H. Youk, and W. H. Park, Preparation of ultrafine oxidized cellulose mats via electrospinning, *Biomacromolecules* 5, 197–201, 2004.
15. Z. W. Ma, M. Kotaki, and S. Ramakrishna, Electrospun cellulose nanofiber as affinity membrane, *J. Memb. Sci.* 265, 115–123, 2005.
16. C. Xiang, M. W. Frey, A. G. Taylor, and M. Rebovich, Selective chemical absorbance in electrospun nonwovens, *J. Appl. Polym. Sci.* 106, 2363–2370, 2007.
17. L. Zhang and Y. -L. Hsieh, Cellulose acetate based ultrafine bicomponent fibers with nanoscale structural features, *Nanosci. Nanotechnol.* 8, 4461–4469, 2008.
18. L. Zhang and Y. -L. Hsieh, Ultra-fine cellulose acetate/poly(ethylene oxide) bicomponent fibers, *Carbohydr. Polym.* 71, 196–207, 2007.
19. P. Lu and Y. -L. Hsieh, Multi-walled carbon nanotube (MWCNT) reinforced cellulose fibers by electrospinning, *ACS Appl. Mater. Inter.* 2, 2413–2420, 2010.
20. P. Lu and Y. -L. Hsieh, Preparation and properties of cellulose nanocrystals: Rods, spheres, and network, *Carbohydr. Polym.* 82, 329–336, 2010.
21. E. Dinand, M. Vignon, H. Chanzy, and L. Heux, Mercerization of primary wall cellulose and its implication for the conversion of cellulose I→cellulose II, *Cellulose* 9, 7–18, 2002.
22. J. Du and Y. -L. Hsieh, Nanofibrous membranes from aqueous electrospinning of carboxymethyl chitosan, *Nanotechnology* 19, 571–579, 2008.
23. J. Du and Y. -L. Hsieh, PEGylation of chitosan for improved solubility and fiber formation via electrospinning, *Cellulose* 14, 543–552, 2007.

24. J. Du and Y. -L. Hsieh, Cellulose-chitosan nanofibers from electrospinning of their ester derivatives, *Cellulose* 16, 247–260, 2009.
25. B. Ding, J. Du, and Y. -L. Hsieh, Layer-by-layer self-assembled polysaccharide electrolytes on cellulose nanofiber, *J. Appl. Polym. Sci.* 121, 2526–2534, 2011.
26. P. Lu and Y.-L. Hsieh, Lipase bound cellulose nanofibrous membrane via Cibacron Blue F3GA affinity ligand, *J. Memb. Sci.* 330, 288–296, 2009.
27. P. Lu and Y.-L. Hsieh, Layer-by-layer self assembly of Cibacron Blue F3GA and lipase on ultra-fine cellulose fibrous membrane, *J. Memb. Sci.* 348, 21–27, 2010.
28. H. Liu and Y.-L. Hsieh, Surface methacrylation and graft-co-polymerization of ultra-Fine cellulose fibers, *J. Polym. Sci. Polym. Phys.* (41), 953–964, 2003.
29. Y. Wang and Y.-L. Hsieh, Aldehyde functionalized cellulose support for hydrogels, *J. Appl. Polym. Sci.* 118, 2489–2495, 2010.
30. J. Xie and Y.-L. Hsieh, Bonded thermosensitive poly(N-isopropylacrylamide) hydrogels on cellulose supports, *J. Appl. Polym. Sci.* 89, 999–1006, 2003.
31. H. Chen and Y.-L. Hsieh, Enzyme immobilization on ultra-fine cellulose fibers via poly(acrylic acid) electrolyte grafts, *Biotechnol. Bioeng.* 90, 405–413, 2005.
32. Y. Wang and Y.-L. Hsieh, Enzyme immobilization to ultra-fine cellulose Fibers via amphiphilic polyethylene glycol (PEG) spacers, *J. Polym. Sci., Polym. Chem.* 42, 4289–4299, 2004.
33. F. Huang, Y. Xu, B. Peng, Y. Su, F. Jiang, Y.-L. Hsieh, and Q. Wei, Co-axial electrospun cellulose-core fluoropolymer-shell fibrous membrane from recycled cigarette filter as separator of high performance lithium-ion battery, *ACS Sustainable Chem. Eng.* 3, 932–940, 2015.
34. C. Castro, R. Zuluaga, J.-L. Putaux, G. Caro, I. Mondragon, and P. Gañán, Structural characterization of bacterial cellulose produced by *Gluconacetobacter swingsii* sp. from Colombian agroindustrial wastes, *Carbohydr. Polym.* 84, 96–102, 2011.
35. Y. Horikawa and J. Sugiyama, Localization of crystalline allomorphs in cellulose microfibril, *Biomacromolecules* 10, 2235–2239, 2009.
36. S. Iwamoto, W. Kai, A. Isogai, and T. Iwata, Elastic modulus of single cellulose microfibrils from tunicate measured by atomic force microscopy, *Biomacromolecules* 10, 2571–2576, 2009.
37. M. Iguchi, S. Yamanaka, and A. Budhiono, Bacterial cellulose—a masterpiece of nature's arts, *J. Materials Sci.* 35, 261–270, 2000.
38. R. H. Atalla and D. L. Vanderhart, Studies on the structure of cellulose using Raman spectroscopy and solid state ^{13}C NMR, C. Schuerch (Ed.), *Cellulose and wood: Chemistry and technology proceedings of the tenth cellulose conference*, pp. 169–187, John Wiley and Sons, New York, 1989.
39. S. Beck-Candanedo, M. Roman, and D. G. Gray, Effect of reaction conditions on the properties and behavior of wood cellulose nanocrystal suspensions, *Biomacromolecules* 6, 1048–1054, 2005.

40. S. Elazzouzi-Hafraoui, Y. Nishiyama, J. L. Putaux, L. Heux, F. Dubreuil, and C. Rochas, The shape and size distribution of crystalline nanoparticles prepared by acid hydrolysis of native cellulose, *Biomacromolecules* 9, 57–65, 2008.
41. Y. Habibi, L. A. Lucia, and O. J. Rojas, Cellulose nanocrystals: Chemistry, self-assembly, and applications, *Chemical Reviews* 110, 3479–3500, 2010.
42. D. Bondeson, A. Mathew, and K. Oksman, Optimization of the isolation of nanocrystals from microcrystalline cellulose by acid hydrolysis, *Cellulose* 13, 171–180, 2006.
43. Lu, P. and Y.-L. Hsieh, Preparation and properties of cellulose nanocrystals: Rods, spheres, and network, *Carbohydr. Polym.* 82, 329–336, 2010.
44. F. Jiang, A. R. Esker, and M. Roman, Acid-catalyzed and solvolytic desulfation of H₂SO₄-hydrolyzed cellulose nanocrystals, *Langmuir* 26, 17919–17925, 2010.
45. H. Sadeghifar, I. Filpponen, S. P. Clarke, D. F. Brougham, and D. S. Argyropoulos, Production of cellulose nanocrystals using hydrobromic acid and click reactions on their surface, *J. Materials Sci.* 46, 7344–7355, 2011.
46. A. F. Turbak, F. W. Snyder and K. R. Sandberg, Microfibrillated cellulose, a new cellulose product: Properties, uses, and commercial potential, *J. Applied Polymer Science*. Applied Polymer Symposium 37, 1983.
47. H. Yano, N. Seki, and T. Ishida, Manufacture of nanofibers and nanofibers manufactured thereby. JP 2007–2229, 17, 2008.
48. B. M. Cherian, A. L. Leão, S. F. de Souza, L. M. M. Costa, G. M. de Olyveira, M. Kottaisamy, E. R. Nagarajan, and S. Thomas, Cellulose nanocomposites with nanofibres isolated from pineapple leaf fibers for medical applications, *Carbohydr. Polym.* 86, 2011, pp. 1790–1798.
49. H. P. S. Abdul Khalil, Y. Davoudpour, Md. Nazrul Islam, Asniza Mustapha, K. Sudesh, Rudi Dungani, and M. Jawaid, Production and modification of nanofibrillated cellulose using various mechanical processes: A review, *Carbohydr. Polym.* 99, 649–665, 2014.
50. P. S. Chang and J. F. Robyt, Oxidation of primary alcohol groups of naturally occurring polysaccharides with 2,2,6,6-tetramethyl-1-piperidine oxoammonium ion, *J. Carbohydrate Chemistry* 15, 819–830, 1996.
51. T. Saito, Y. Nishiyama, J. L. Putaux, M. Vignon, and A. Isogai, Homogeneous suspensions of individualized microfibrils from TEMPO-catalyzed oxidation of native cellulose, *Biomacromolecules* 7, 1687–1691, 2006.
52. T. Saito, S. Kimura, Y. Nishiyama, and A. Isogai, Cellulose nanofibers prepared by TEMPO-mediated oxidation of native cellulose, *Biomacromolecules* 8, 2485–2491, 2007.
53. A. Isogai, T. Saito, and H. Fukuzumi, TEMPO-oxidized cellulose nanofibers, *Nanoscale* 3, 71–85, 2011.
54. Šturcová, G. R. Davies, and S. J. Eichhorn, Elastic modulus and stress-transfer properties of tunicate cellulose whiskers, *Biomacromolecules* 6, 1055–1061, 2005.

55. D. Klemm, D. Schumann, U. Udhardt, and S. Marsch, Bacterial synthesized cellulose – artificial blood vessels for microsurgery, *Progress Polym. Sci.* 26, 1561–1603, 2001.
56. D. Klemm, D. Schumann, F. Kramer, N. Heßler, M. Hornung, H. P. Schmauder, and S. Marsch, Nanocelluloses as innovative polymers in research and application polysaccharides II, *Advances in Polymer Science* 205, 49–96, 2006.
57. D. Klemm, D. Schumann, F. Kramer, N. Hessler, D. Koth, and B. Sultanova, Nanocellulose materials – different cellulose, different functionality, *Macromolecular Research* 280, 60–71, 2009.
58. S. J. Eichhorn, A. Dufresne, M. Aranguren, N. E. Marcovich, J. R. Capadona, S. J. Rowan, C. Weder, W. Thielemans, M. Roman, S. Renneckar, W. Gindl, S. Veigel, J. Keckes, H. Yano, K. Abe, M. Nogi, A. N. Nakagaito, A. Mangalam, J. Simonsen, A. S. Benight, B. Bismarck, L. A. Berglund, and T. Peijs, Review: Current international research into cellulose nanofibres and nanocomposites, *J. Materials Sci.* 45, 1–33, 2010.
59. S. J. Eichhorn, Cellulose nanowhiskers: Promising materials for advanced applications, *Soft Matter* 7, 303–315, 2011.
60. D. Klemm, F. Kramer, S. Moritz, T. Lindström, M. Ankerfors, D. Gray, and A. Dorris, Nanocelluloses: A new family of nature-based materials, *Angewandte Chemie International Edition* 50, 5438–5466, 2011.
61. A. Dufresne, Nanocellulose: From Nature to High Performance Tailored Materials, Walter de Gruyter GmbH, Berlin/Boston, 2012.
62. N. Lavoine, I. Desloges, A. Dufresne, and J. Bras, Microfibrillated cellulose—its barrier properties and applications in cellulosic materials: A review, *Carbohydr. Polym.* 90, 735–764, 2012.
63. O. Faruk, A. K. Bledzki, H.-P. Finkand, and M. Sain, Biocomposites reinforced with natural fibers: 2000–2010. *Topical Issue on Biomaterials, Progress Polym. Sci.* 37, 1552–1596, 2012.
64. E. R. P. Keijsers, G. Yilmaz, and J. E. G. van Dam, The cellulose resource matrix, *Carbohydr. Polym.* 93, 9–21 2013.
65. A. García, A. Gandini, J. Labidi, N. Belgacem, and J. Bras, Industrial and crop wastes: A new source for nanocellulose biorefinery. *Ind. Crop. Prod.* 93, 26–38, 2016.
66. V. Menon and M. Rao, Trends in bioconversion of lignocellulose: Biofuels, platform chemicals & biorefinery concept, *Prog. Energ. Combust.* 38, 522–550, 2012.
67. P. Lu and Y.-L. Hsieh, Cellulose isolation and core-shell nanostructures of cellulose nanocrystals from chardonnay grape skins, *Carbohydr. Polym.* 87, 2546–2553, 2012.
68. F. Jiang and Y.-L. Hsieh, Cellulose nanocrystal isolation from tomato peels and assembled nanofibers, *Carbohydr. Polym.* 122, 60–68, 2015.

69. P. Lu and Y.-L. Hsieh, Preparation and characterization of cellulose nano-crystals from rice straw., *Carbohydr. Polym.* 87, 564–573, 2012.
70. C. Liu, B. Li, H. Du, D. Lv, Y. Zhang, G. Yu, X. Mu, and H. Peng, Properties of nanocellulose isolated from corncob residue using sulfuric acid, formic acid, oxidative and mechanical methods, *Carbohydr. Polym.* 151, 716–724, 2016.
71. F. Jiang and Y.-L. Hsieh, Chemically and mechanically isolated nanocellulose and their self-assembled structures, *Carbohydr. Polym.* 95, 32–40, 2013.
72. K. Abe and H. Yano, Comparison of the characteristics of cellulose microfibril aggregates of wood, rice straw and potato tuber, *Cellulose* 16, 1017–1023, 2009.
73. F. Jiang, T. Kondo, and Y.-L. Hsieh, Rice straw cellulose nanofibrils via aqueous counter collision and differential centrifugation and their self-assembled structures, *ACS Sustainable Chem. Eng.* 4, 1697–1706, 2016.
74. W. S. Chen, Q. Li, J. Cao, Y. X. Liu, J. Li, J. S. Zhang, S. Y. Luo, and H. P. Yu, Revealing the structures of cellulose nanofiber bundles obtained by mechanical nanofibrillation via TEM observation, *Carbohydr. Polym.* 117, 950–956, 2015.
75. F. Jiang, S. Han, and Y.-L. Hsieh, Controlled defibrillation of rice straw cellulose and self-assembly of cellulose nanofibrils into highly crystalline fibrous materials, *RSC Advances* 3, 12366–12375, 2013.
76. F. Jiang, T. Kondo, and Y.-L. Hsieh, Rice straw cellulose nanofibrils via aqueous counter collision and differential centrifugation and their self-assembled structures, *ACS Sustainable Chem. Eng.* 4, 1697–1706, 2016.
77. S. Hu, F. Jiang, and Y.-L. Hsieh, 1D lignin based solid acid catalysts for direct hydrolysis of crystalline cellulose, *ACS Sustainable Chem. Eng.* 3, 2566–2574, 2015.
78. Y. Okita, S. Fujisawa, T. Saito, and A. Isogai, TEMPO-oxidized cellulose Nanofibrils dispersed in organic solvents, *Biomacromolecules* 12, 518–522, 2011.
79. R. Kose, I. Mitani, W. Kasai, and T. Kondo, “Nanocellulose” As a Single Nanofiber Prepared from Pellicle Secreted by *Gluconacetobacter xylinus* using aqueous counter collision, *Biomacromolecules* 12, 716–720, 2011.
80. T. Kondo, R. Kose, H. Naito, and W. Kasai, Aqueous counter collision using paired water jets as a novel means of preparing bio-nanofibers, *Carbohydr. Polym.* 112, 284–290, 2014.
81. F. Jiang and Y.-L. Hsieh, Self-assembling of TEMPO Oxidized cellulose nanofibrils as affected by protonation of surface carboxyls and drying methods, *ACS Sustainable Chem. Eng.* 4, 1041–1049, 2016.
82. T. Nishino, K. Takano, and K. Nakamae, Elastic modulus of the crystalline regions of cellulose polymorphs, *J. Polym. Sci., Part B: Polym. Phys.* 33, 1647–1651, 1995.

83. F. Jiang and Y.-L. Hsieh, Novel holocellulose nanocrystals: Amphiphilicity, O/W emulsion and self-assembly, *Biomacromolecules* 16, 1422–1441, 2015.
84. J. Gu and Y.-L. Hsieh, Surface and structure characteristics, self-assembling and solvent compatibility of holo-cellulose nanofibrils, *ACS Appl. Mater. Inter.* 7, 4192–4201, 2015.
85. M. S. Wang, F. Jiang, Y.-L. Hsieh, and N. Nitin, Cellulose nanofibrils improve dispersibility and stability of silver nanoparticles and induce production of bacterial extracellular polysaccharides, *J. Mat. Chem. B*, 2, 6226–6235, 2014.
86. F. Jiang and Y.-L. Hsieh, Synthesis of cellulose nanofibril bound silver nanoprism for surface enhanced Raman scattering, *Biomacromolecules* 15, 3608–3616, 2014.
87. P. Lu and Y.-L. Hsieh, Cellulose nanocrystal filled poly(acrylic acid) nanocomposite fibrous membranes, *Nanotechnology* 20, 415604–415612, 2009.
88. F. Jiang and Y.-L. Hsieh, Amphiphilic superabsorbent cellulose nanofibril aerogels, *J. Mater. Chem. A*, 2, 6337–6342, 2014.
89. C. Salas, T. Nypelö, C. Rodriguez-Abreu, C. Carrillo, and O. J. Rojas, Nanocellulose properties and applications in colloids and interfaces. *Curr. Opin. Coll. Interf. Sci.* 19, 383–396, 2014.
90. S. J. Eichhorn, A. Dufresne, M. Aranguren, N. E. Marcovich, J. R. Capadona, S. J. Y. Habibi, L. A. Lucia, and O. J. Rojas, Cellulose nanocrystals: Chemistry, self-assembly, and applications. *Chemical Reviews* 110, 3479–3500, 2010.
91. Z. Shi, Y. Zhang, G. O. Phillips, G. Yang, Utilization of bacterial cellulose in food, *Food Hydrocolloids* 35, 539–545, 2014.
92. Gómez H., A. Serpa, J. Velásquez-Cock, P. Gañán, C. Castro, L. Vélez, and R. Zuluaga, Vegetable nanocellulose in food science: A review, *Food Hydrocolloids* 57, 178–186d, 2016.
93. F. Li, E. Mascheroni, and L. Piergiovanni, The potential of nanocellulose in the packaging field: A review, *Packaging Techn. Sci.* 28, 475–508, 2015.
94. V. Favier, G. Canova, J. Cavaillé, H. Chanzy, A. Dufresne, and C. Gauthier, Nanocomposite materials from latex and cellulose whiskers, *Polym. Advanced Techn.* 6, 351–355, 1995.
95. M. A. Hubbe, O. J. Rojas, L. A. Lucia, and M. Sain, Cellulosic nanocomposites: A review, *Bioresources* 3, 929–980, 2008.
96. I. Siró and D. Plackett, Microfibrillated cellulose and new nanocomposite materials: A review, *Cellulose* 17, 459–494, 2010.
97. S. Kalia, A. Dufresne, B. M. Cherian, B. S. Kaith, L. Avérous, J. Njuguna, and E. Nassiopoulou, Cellulose-based bio- and nanocomposites: A review, *Intern. J. Polym. Sci.* 35, 2011.
98. R. J. Moon, A. Martini, J. Nairn, J. Simonsen, and J. Youngblood, Cellulose nanomaterials review: Structure, properties and nanocomposites, *Chem. Soc. Rev.* 40, 3941–3994, 2011.
99. H. P. S. Abdul Khalil, A. H. Bhat, and A. F. I. Yusra, Green composites from sustainable cellulose nanofibrils: a review, *Carbohydr. Polym.* 87, 963–979, 2012.

100. E. M. Fernandes, R. A. Pires, J. F. Mano, and R. L. Reis, Bionanocomposites from lignocellulosic resources: Properties, applications and future trends for their use in the biomedical field, *Progress Polym. Sci.*, 38(10–11), 1415–1441, 2013.
101. D. Ray and S. Sain, *In situ* processing of cellulose nanocomposites, *Compos. Part A: Appl. Sci. Manuf.* 83, 19–37, 2016.

