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Bottom-up Assembly of Nanocellulose Structures

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Bottom-up Assembly of Nanocellulose Structures

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Highlights

- Bottom-up assembly of cellulose nanocrystal and cellulose nanofibril structures
- Discrete nanocellulose-only particles to bulk nanostructured materials
- Bottom-up assembly techniques and driving forces to produce well-defined structures
- Potential applications and research directions for nanocellulose-only structures

Abstract

Nanocelluloses, both cellulose nanofibrils and cellulose nanocrystals, are gaining research traction due to their viability as key components in commercial applications and industrial processes. Significant efforts have been made to understand both the potential of assembling nanocelluloses, and the limits and perspectives of the resulting structures. This Review focuses on bottom-up techniques used to prepare nanocellulose-only structures, and details the intermolecular and surface forces driving their assembly. Additionally, the interactions that contribute to their structural integrity are discussed along with alternate pathways and suggestions for improved properties. Six categories of nanocellulose structures are presented: (1) powders, beads, and droplets; (2) capsules; (3) continuous fibres; (4) films; (5) hydrogels; and (6) aerogels and dried foams. Although research on nanocellulose assembly often focuses on fundamental science, this Review also provides insight on the potential utilization of such structures in a wide array of applications.

Keywords Nanocellulose; bottom-up assemblies; structures; cellulose nanocrystals; cellulose nanofibrils

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1. Introduction

The utilization of nanocelluloses in the production of new functional materials has become a fast-growing area of interest in both research and industry due to the exceptional versatility of these nanoscale materials. Both the physical and chemical adaptability of nanocelluloses make them the ideal substitute for inorganic and petroleum-based materials, in many applications. Additionally, their natural abundance and sustainability, recyclability and inherent biocompatibility allow for nanocelluloses to be implemented not only in industrial applications but also in niche applications such as sensors, pharmaceuticals, food, household products and cosmetics.

Physically, nanocellulose offers a material that has an exceptionally high surface area to volume ratio and exhibits high strength both as crystalline nanoparticles and as entangled fibrillar networks. All of these attributes are beneficial in the bottom-up assembly of nanocellulosic structures, where larger assemblies can be prepared using nanocellulose as the building blocks. The key in designing and fabricating these structures is to understand and control the physical and chemical interactions between nanocellulose particles and fibrils. However, because nanocelluloses range from short, rod-shaped particles (cellulose nanocrystals (CNCs)) to long, flexible fibrils/ribbons (cellulose nanofibrils (CNFs) and bacterial cellulose (BC)) the choice of which type to use in which structure is fully dependent on the desired properties of the final material.

CNFs, for example, are typically implemented in structures that require both strength and flexibility. This type of nanocellulose, with diameters in the nanometer scale and lengths in the micrometer range (Pääkko et al., 2007; Sani & Dahman, 2010; Wågberg et al., 2008), is able to form complex, entangled networks that are often used to form 3-dimensional structures such as hydrogels and aerogels (De France et al., 2017), hierarchical fibres (Clemons, 2016; Lundahl et al., 2017) and films (Kontturi et al., 2006), with, for example, very low gas permeability (Henriksson et al., 2008; Sehaqui et al., 2011). On the other hand, CNCs differ in that they are relatively stiff rod-shaped particles (ca. 3 – 7 nm wide and 100 – 350 nm long (Beck-Candanedo et al., 2005; Habibi, Lucia, et al., 2010; Reid et al., 2017)) when derived from plant sources) with a specific Young's modulus comparable to that of steel and Kevlar® (with a bending strength of 10 GPa, an elastic modulus of 150 GPa and exceptionally high specific modulus when normalized by density) (Eichhorn et al., 2010)) and, exhibit high colloidal stability and interesting optical properties. The use of CNCs in “cellulose-only” materials has proven difficult, due to the brittle nature of the resulting structures. As such, they are more often used in supported thin film/coating applications (Ferrer et al., 2017) and as rheological modifiers, and reinforcing agents in hybrid/composite materials (Hubbe et al., 2008). Recently though, CNCs have also found application in hydrogel and aerogel structures (De France et al., 2017), and even as stabilizers in Pickering emulsions and foams (Gestranus et al., 2017; Kalashnikova et al., 2011, 2012, 2013; Ougiya et al., 1997; Winuprasith & Suphantharika, 2015).

From a surface chemistry and functionalization perspective, the potential of nanocelluloses is far reaching. The abundance of hydroxyl groups on the surface of the nanoparticle/fibril allows them to form strong, hydrogen bonded structures when dry, which, owing to the nanoscale size of the cellulose, can lead to densely packed materials. However, the high capacity to form hydrogen bonds also results in the overall hydrophilic nature of nanocelluloses; a property which limits their use in water sensitive applications and reduces their compatibility with non-polar environments. Nonetheless, these hydroxyl groups also facilitate the surface modification of nanocelluloses using well-known carbohydrate and synthetic chemistries. Functionalization routes such as esterification (Braun et al., 2009), acetylation (Cetin et al., 2009), oxidation (Habibi et al., 2006), cationization (Hasani et al., 2008), silylation (Gousse & Chanzy, 2002), and polymer grafting (Kedzior et al., 2018) have been demonstrated to alter the inherent nature of cellulose, promote otherwise unlikely surface interactions, and impart added functionality. For a more comprehensive take on the multitude of surface modification routes available for nanocellulose, the reader is referred to recent reviews (Heise et al., 2020; Rol et al., 2019; Zoppe et al., 2020).

Table 1 summarizes the contents of this Review, which focuses on the controlled bottom-up assembly of hierarchical **nanocellulose-only** structures, ordered from discrete particles in the form of powders, beads and droplets, to bulk nanostructured materials. The most common routes to prepare such structures and their potential applications are highlighted. We focus on the fundamental mechanisms and intermolecular and surface forces that govern structure assembly. In this Review, only materials where nanocellulose is the major component or plays the dominant role are presented, despite the importance of hybrids/composites where nanocellulose is an additive or minor component – such materials are reviewed elsewhere (Eichhorn et al., 2010; Moon et al., 2011). Additionally, this Review does not go into detail about the optical properties of CNCs that result from their ability to *self-assemble*, i.e., form chiral nematic liquid crystals; for in-depth coverage, the reader is referred to comprehensive reviews available in the literature (Abitbol & Cranston, 2014; Gray, 2016, 2018; Lagerwall et al., 2014; Meseck et al., 2017; Pan et al., 2010; Parker et al., 2018; Tran et al., 2020).

When producing hierarchical nanocellulose assemblies through bottom-up techniques, self-assembly is rarely implemented due to its sensitivity to contaminants and the surrounding environmental conditions, and the long wait times needed for thermodynamically driven ordering and the evaporation of water. Rather, various *controlled* methods are used to manipulate nanocellulosic materials into defined alignments, shapes and topographies, to produce structures with a specific role and function. In this Review, we will discuss the bottom-up techniques used to assemble the following structures, 1) powders, beads, droplets, 2) capsules, 3) continuous fibres, 4) supported thin and free-standing films, 5) hydrogels, and 6) aerogels and dried foams. These structures are ordered from discrete particles to bulk nanostructured materials. The driving forces that need to be controlled to produce well-defined structures are described in each section, and potential applications and research directions are noted. It is important to keep in mind,

however, that the utilization of nanocelluloses in commercially relevant applications is an emerging field and as such, the majority of the applications described below are ones which, as of yet, have only been proposed. Regardless, the necessary shift toward greener and more sustainable materials in all commercial products will inevitably result in the implementation of nanocellulose in a broad range of applications, likely in the foreseeable future.

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2. Nanocellulose Powders, Droplets and Beads

Nanocellulose can be assembled into hierarchical discrete objects or particles from liquid suspensions following a range of drying methods. Since the particles contain many CNCs or CNFs, they range from hundreds of nanometers to millimeters in size. Some methods give uniform particles with low size polydispersity (i.e., beads) while others are more random (i.e., powders). One of the primary reasons to dry nanocellulose suspensions (in bulk) is to facilitate transportation, shipping and storage, and to increase the range of processing routes for nanocellulose containing materials. For example, to produce melt compounded thermoplastic nanocomposites, adding nanocellulose as a dry powder avoids the complications of adding liquids that may not be compatible with some equipment and furthermore can lead to side reactions with other reactants and promote thermal degradation of cellulose (Kedzior et al., 2016; Oksman & Mathew, 2014; Peng et al., 2015).

In general, dried nanocellulose is expected to be redispersible in liquid media, meaning that the individual CNCs or CNFs are completely separated, and minimal aggregation of nanoparticles remains after redispersion (Peng et al., 2013). Unless of course, the opposite is required – a material that holds together and is permanently aggregated, in which case, additional chemicals, treatments or crosslinking agents can be added. A great deal of focus has gone into understanding the best drying methods and additives needed to ensure redispersibility. Note that dried CNCs have been shown to be fully redispersible (Beck et al., 2012; Cheng et al., 2015), however work remains with CNFs (Peng, Gardner, et al., 2012), and generally fibrillated celluloses are shipped as dispersions, gels or “pastes”, containing as high as 10% cellulose (90% water) if redispersion is required (Foster et al., 2018).

Liquid droplets are another form of discrete hierarchical nanocellulose “particles”. The production of uniform droplets from nanocellulose suspensions has typically been done using microfluidic devices with the goal of improving the fundamental understanding of cellulose-cellulose interactions in the bottom-up assembly of structures, or the self-assembly of CNCs in confined geometries. Alternatively, droplets and microparticles can be produced by dispensing droplets from a pipette/syringe/atomizing nozzle onto superhydrophobic surfaces or into a non-dispersing solvent. Drying of uniform droplets to form beads may offer microscale materials with controlled properties and in general, powders and beads may find applications themselves in a variety of liquid formulated products, separation agents, cosmetics (e.g. replacement for plastic microbeads), foods or pharmaceuticals. Table 2 lists the main assembly methods to produce powders, droplets and beads, the key interaction forces during drying and between cellulose, and some characteristic properties of the obtained materials.

2.1. Preparation of Discrete Nanocellulose Particles

2.1.1. Powders

As discussed, drying nanocelluloses is considered an essential stage in the commercial development of CNC and CNF applications, manufacturing scale-up and market acceptance. In addition to which, in many cases the use of dried cellulose powders is more efficient than using suspensions or gels, especially when incorporating them into non-polar systems (Peng, Gardner, et al., 2012). The goal of drying is to remove water without permanently losing the nanostructure of CNCs and CNFs and to do so, it is of vital importance to understand the interactions and higher order structures that result from drying. If cellulose comes into contact with itself, strong cellulose-cellulose interactions occur, namely van der Waals forces, hydrogen bonding, and in some situations (the highly debated) hydrophobic interactions (Glasser et al., 2012; Medronho et al., 2012; Nishiyama, 2018). Furthermore, if heated, hornification can also occur. Hornification is the formation of irreversible (or at best, partially reversible) bonds between cellulose hydroxyl groups (Ding et al., 2019). The most common drying methods to obtain powdered nanocelluloses are described below.

Spray drying is the process of atomizing a liquid into small droplets that are then quickly dried with hot gas forming dried particles with a consistent particle size distribution. It is a continuous process that is used industrially in the manufacturing of powders, such as those intended for food, pharmaceutical and detergent products, for example. The forces at play during spray drying are well described in the literature (Peng, Gardner, et al., 2012; Vehring, 2008), and eventually individual cellulose nanoparticles come into molecular contact where hydrogen bonds and van der Waals forces dominate.

When CNCs are spray dried from the sodium salt form (meaning they have been neutralized from the acid form with NaOH to have Na⁺ counterions on the surface charge groups) they form a uniform white powder of agglomerated nanocrystals with a rounded granular shape (Beck et al., 2012; Khoshkava & Kamal, 2014a) or spheres (Peng, Gardner, et al., 2012; Z. Zhu et al., 2019), and sizes ranging from 5-30 µm (Figure 1a and Figure 1b). Depending on the spray drying process parameters, particle size and surface roughness can be controlled, and sometimes nanometer-sized particles are also produced. These powders are free-flowing and flour-like and can be redispersed fully when reconstituted in water at low concentrations (where water-cellulose hydrogen bonds immediately replace cellulose-cellulose hydrogen bonds) as long as energy is added in the form of ultrasonication to break van der Waals interactions (Beck et al., 2012; Reid et al., 2016). If dried from the acid form, CNCs will not redisperse easily. While spray dried CNC powders can theoretically be redispersed in organic solvents or hydrophobic polymers, their incompatibility with non-polar materials generally means that cellulose-cellulose interactions dominate and nanoparticles remain partially aggregated and not fully dispersed (Khoshkava & Kamal, 2013, 2014b, 2014a). To improve the compatibility of nanocellulose and

polymers, “masterbatches” can be prepared (Kargarzadeh et al., 2017), where a high concentration of nanocellulose and polymer are forced together into a powder (produced, for example, by spray drying) which can then be mixed in with more bulk polymer to achieve the final desired nanofiller content. Another compatibilization method has been to spray dry CNCs with lignin, making a more hydrophobic powder but as a result of changes in diffusion during the drying process, the particles have a donut shape instead of being spherical (Z. Zhu et al., 2019).

When CNFs are dried through spray drying, they lead to either spherical particles similar to those formed from CNCs, or if a portion of the long fibrils protrude outside of the atomized droplet, irregular shaped particles are obtained (Figure 1c). These materials are generally not redispersible in water or other solvents.

Freeze drying (or lyophilisation) is a batch process that dries by first freezing, then lowering the pressure and sublimating the ice; it is commonly used in preservation (sometimes of biological tissues and bioactive ingredients) and food processing. The product of freeze drying is not a free-flowing powder but in the case of nanocellulose, it is a thin lamellar flaky structure with laterally agglomerated nanocellulose that may be white or slightly iridescent (Figure 1d) and can be ground to a powder if needed. The flakes are typically a few hundred nanometers thick and ground powders have an irregular shape. The structures produced by freeze drying are highly dependent on the rate of freezing which forces cryogelation between cellulose nanoparticles but leaves large voids or pores where the ice crystals form and are then sublimated. It is believed that the lamellae interact through weak hydrophobic interactions (Peng, Gardner, et al., 2012) contributing to the ease of redispersion of freeze dried CNCs.

A subset of spray drying and freeze drying is **freeze spray drying** where a nanocellulose suspension is sprayed or dropped into a cryogenic solvent such that the droplets are immediately frozen and then dried by sublimation. Either a fibrillar skeleton morphology (Jimenez-Saelices et al., 2016) or micrometer sized granules (Cai et al., 2014) can be obtained but in both cases, the materials are highly porous (called an aerogel) and retain internal surface area similar to having individualized nanoparticles.

Preparing nanocellulose samples for **supercritical drying, or critical point drying (CPD)** requires replacing water with a volatile solvent (such as ethanol), then replacing the volatile solvent with liquid CO₂. Next, the mixture is heated to supercritical conditions and then CO₂ is removed by decompression to atmospheric conditions (Peng et al., 2013; Peng, Gardner, et al., 2012). A number of variations on this sequence and equipment exist, for example, CNCs have been dried using pressurized gas expansion (PGX) to obtain some of the highest porosities reported to date (Osorio et al., 2018). Due to the absence of capillary forces during drying, nanocellulose structures in the wet state are preserved in the dry state. The challenge is fully removing water in the initial stages which has been shown to be easier for CNFs than CNCs (Peng, Gardner, et al., 2012). Overall, supercritical drying may be the most expensive and laborious way to dry nanocellulose but is able to best preserve the nano-dimensions of the

crystals and fibrils. From a thermal stability standpoint, supercritical drying and freeze drying lead to nanocellulose powders with the lowest onset of thermal degradation and lowest degrees of crystallinity (Peng et al., 2013).

2.1.2. Droplets

Microfluidic devices have been implemented to study nanocellulose liquid droplets where the confinement within a droplet, or in a drying/shrinking droplet, gives rise to unique cellulose-cellulose interactions (Levin et al., 2018; Y. Li et al., 2016; Parker et al., 2016; Tumarkin & Kumacheva, 2009). Microfluidic devices for liquid droplet formation are highly versatile, as they allow for accurate control of the size and shape of the droplets and offer a high throughput technique where as many as a million droplets per hour can be produced and parallel assemblies are possible (S. Xu et al., 2005). Within these devices, a nanocellulose suspension (dispersed phase) and an immiscible liquid (continuous phase) are simultaneously passed through micrometer thick channels with varying geometries (depicted in Figure 1e). Junctions, pinches or other physical barriers throughout the device disrupt the flow of the dispersed phase, causing the formation of liquid droplets, which are then collected in the continuous phase. The size of the microfluidic channels is the primary parameter that can be varied to tailor droplet size, and in general, droplets are larger than 50 μm . While droplets in themselves are not, strictly speaking, bottom-up assemblies of nanocelluloses they are the precursor material for solid, nanocellulose beads, which are formed through drying of said droplets. Moreover, a lot of information about the fundamentals of nanocelluloses, and their potential applications can be learned through droplet technologies.

CNC self-assembly into liquid crystal phases has been tracked in microfluidic droplets either for CNCs alone (Parker et al., 2016, 2018) or for CNCs combined with polymer, metal, carbon or metal oxide nanoparticles (Y. Li et al., 2016). Flow focusing devices led to highly ordered liquid droplets with concentric hierarchical architectures (Y. Li et al., 2016; Parker et al., 2016) that could be dried into low porosity solid particles with vivid iridescence and photonic crystal organization (Y. Li et al., 2016; Parker et al., 2016). Microfluidic channels have also been used to produce uniform CNC droplets with the ability to crosslink, which restricts the self-assembly and densification of CNCs by tethering the particles to each other with an open pore structure (Levin et al., 2018). Due to the fact that CNFs are longer than CNCs and tend to entangle even at low concentrations, there are no literature examples of microfluidic preparation of CNF droplets or beads.

2.1.3. Beads

The formation of dried cellulose beads (also called spherical microparticles and microspheres) was first reported as early as the 1950s for a variety of applications including being used as the

column material in liquid chromatography, water purification, protein immobilization, and as drug delivery vehicles (O'Neill & Reichardt, 1951). The ability to control the bead size, shape dispersity, porosity, and surface functionality has been widely discussed (Martin et al., 2013). Generally, beads should be wet-stable, and their structure maintained throughout their application. However, the majority of cellulose beads are made from regenerated cellulose (Carrick et al., 2013; Carrick, Larsson, et al., 2014; Carrick, Lindström, et al., 2014; Luo et al., 2009; Luo & Zhang, 2010), which is not nanocellulose. In many of the examples where nanocellulose is used in microparticles, it is a minor component acting as a reinforcing or crosslinking agent, and is often combined with polymers such as chitosan (Z. Liu et al., 2012), alginate (Mohammed et al., 2015; Supramaniam et al., 2018), xylan (M. Li et al., 2016) or other functional nanoparticles (e.g. magnetic nanoparticles). Again, the focus of this Review is on materials that are *primarily* nanocellulose and as such, there are only a few examples of nanocellulose-only beads described to date.

In general, solute containing droplets can be “fixed” into more permanent bead structures by drying, ion/solvent/cryo-induced gelation, chemical crosslinking, or thermal/light-activated polymerization. A variety of post-preparation surface functionalization routes also exist (Martin et al., 2013). For nanocellulose systems, drying and cryo-gelation are the most common ways to turn droplets into beads and below we summarize two types of nanocellulose beads: (1) solid nanocellulose beads and (2) porous nanocellulose beads that have internal aerogel structures. The advantages of hierarchical micrometer-sized objects with aerogel structures is that they are extremely lightweight and have specific surface areas approaching that of a nanomaterial, which is good for binding/holding/releasing other components, while being in a convenient format for processing and the development of formulated products (“bulk” aerogels are discussed further in Section 6.1).

In the category of solid nanocellulose beads, examples include drying CNC droplets produced by microfluidics, as mentioned above, to give particles <200 μm in diameter (Y. Li et al., 2016; Parker et al., 2016), or producing semi-spherical geometries of chiral nematic CNC films by using elastomeric molds to template 4-6 mm shapes (Rofouie et al., 2018). Such dried droplets or semi-spheres will hold together if placed in water for at least a short time (minutes to hours), which can be extended if they were dried completely from an acid form CNC suspension or heat treated after drying to induce hornification (Beck et al., 2012; Ding et al., 2019). An alternative route to solid, spherical nanocellulose particles involves oxidizing cellulose nanofibrils from green algae to dialdehyde cellulose that inherently forms 1-20 μm sized beads (Lindh et al., 2014).

Highly porous nanocellulose beads with aerogel “cores” can be produced by adapting some of the procedures for solid beads; for example, by performing a reductive amination with diamine spacers on the green algae oxidized cellulose spheres, beads with 30 times higher specific surface area can be produced with pores in the 10-100 nm range (Lindh et al., 2016). Following the microfluidic approach, if CNCs are orthogonally functionalized with crosslinking groups

(e.g. aldehyde and hydrazide groups to form hydrazone crosslinks) and are combined in droplets and then allowed to dry, the removal of water forces CNCs into molecular contact enabling chemical crosslinking (Levin et al., 2018). This crosslinking precludes liquid crystalline self-assembly and instead of producing solid ordered beads, leads to highly macroporous and flexible beads in the 30-110 μm size range that do not redisperse in a range of liquids (Levin et al., 2018).

Two other types of porous nanocellulose beads have been made by depositing droplets and freezing them: in the first case, CNF suspensions were atomized into liquid nitrogen and then freeze dried giving beads in the 60-120 μm range with meso- and macropores, and if produced with an epichlorohydrin resin crosslinker and heat treated after drying, the beads were chemically crosslinked and liquid stable. In the second case, CNF gel droplets were deposited onto superhydrophobic surfaces (to keep an almost perfectly spherical shape) and then oxidized to introduce dialdehyde groups, frozen, thawed, solvent-exchanged to ethanol and then acetone, and air dried (Erlandsson et al., 2016). The final drying induced acetal bond crosslinks, but retained the meso- and macroporous internal structure, and again produced beads that kept their structural integrity in water. Porous beads produced this way are the largest stable and robust structures reported, with sizes in the 1-2 mm range (Erlandsson et al., 2016) (Figure 1f). It is worth noting that structures from CNFs tend to be more wet-stable than CNCs because of significant physical entanglement that occurs naturally in the longer, more flexible nanofibrils, thus making chemical crosslinking less crucial depending on the intended bead applications. One advantage of highly porous beads is the ability to post functionalize them since nanoparticles and polymers can easily coat both the inside and outside of the beads.

2.2. Potential Applications of Powders, Droplets and Beads

As mentioned previously, potential applications for powders, droplets and beads span a range of industries. Aside from producing a dried material that can either be redispersed or mixed to give new composite or hybrid materials, biomedical/pharmaceutical, analytical, environmental, and cosmetic uses have been discussed. For example, CNC and CNF beads have been demonstrated in water purification, as sorbents and potentially as replacements for activated carbon to remove dyes and heavy metals from the environment (Mohammed et al., 2015). The ability to load, store and release other nanoparticles and small molecules from porous beads may offer the next advances in controlled release technologies and more specifically, enzyme/protein immobilization (Martin et al., 2013) and drug delivery have been demonstrated (Luo et al., 2009). Another interesting “delivery” approach that has been envisioned, is using cellulose beads to deliver plant growth regulators (M. Li et al., 2016).

Other cosmetic/medical applications may include protective creams/coatings, exfoliating products, blood coagulants (M. Li et al., 2016) and scaffolds for cell growth and tissue engineering (Cai et al., 2014; Levin et al., 2018). In chromatography (e.g. size exclusion, affinity

or gel filtration chromatography) (Martin et al., 2013) one can imagine using uniform nanocellulose beads as the stationary phase (Luo & Zhang, 2010) and potentially even as chiral separators (M. Li et al., 2016) or solid phase synthesis supports (Martin et al., 2013). Microfluidics can offer unprecedented control for the engineering of particles with unusual structural or mechanical properties and due to the interesting optical properties of CNCs, a range of optical devices including optical chirality sorting, optical microresonators (Y. Li et al., 2016), broadband reflectors and circular polarizers (Rofouie et al., 2018) may be possible. Lastly, recent high-tech applications proposed have included nanocellulose beads as components in electrochemical charge storage for energy devices (such as electrodes in supercapacitors), when combined with functional materials like carbon nanotubes and conductive polymers) (Erlandsson et al., 2016).

3. Nanocellulose Capsules

In addition to the assemblies described above, nanocelluloses can also be used in encapsulation technologies (Figure 2a). The utilization of capsules covers a wide spectrum of applications from controlled release (Yoo et al., 2017), protection of nano- and microparticles (Ye et al., 2015), to liquid mobility (Svagan et al., 2014, 2016) and separation technologies (Paulraj et al., 2018). Nanocellulose has been shown to be a potential platform as a material in all of the aforementioned applications. The biocompatibility and non-toxicity of nanocellulose makes it ideal for sustained drug release capsules in addition to which the amphiphilic nature of CNCs can enable encapsulation of hydrophobic pharmaceuticals (Mohanta et al., 2014). Furthermore, the controllable porosity of the capsule shell network allows nanocellulose capsules to be loaded with both nano- and macroparticles, whereas their polymer-based counterparts can typically only facilitate the loading of molecules under 10 nm in diameter (Ye et al., 2015). Importantly, in comparison to the traditionally used encapsulation materials, such as alginate, nanocellulose is of particular interest as a bio-based alternative due to its robustness in low pH, high ionic strength and at elevated temperatures (Huq et al., 2017). Table 3 summarizes the preparation methods for nanocellulose-reinforced capsules. It also reviews the interactions occurring during preparation along with methods by which to lock assembled structures in to place post fabrication.

It should be noted that, while not a nanocellulose-only assembly, emulsions and latexes also warrant mentioning and are “precursors” to capsules in some cases. Due to their small size, intermediate wettability and slightly amphiphilic nature (Kalashnikova et al., 2012), nanocelluloses partition at interfaces, although they are not strictly surface active. For example, nanocelluloses can act either as interface stabilizers or as a network in the continuous phase that restricts droplet coalescence in emulsion and emulsion polymerization systems (Gestranius et al.,

2017; Z. Hu et al., 2015; Jiménez Saelices et al., 2019; Jiménez Saelices & Capron, 2018; Kalashnikova et al., 2013; Kedzior et al., 2017). Nanocelluloses can also adsorb at latex particle surfaces or reinforce dried latex films used, for example, as coatings and adhesives (Abitbol et al., 2014; Dastjerdi et al., 2017a, 2017b, 2018, 2019; Ouzas et al., 2018, 2019; Pakdel et al., 2020). However, as these structures are outside of the scope of this review, the reader is referred to a comprehensive review on the subject by Kedzior et al., 2020.

3.1. Preparation of Capsules

The formation of capsules is largely driven by electrostatic interactions, physical entanglement and crosslinking at interfaces. The most common method to prepare nanocellulose-based capsules is through **dip coating** (described in detail in Section 5.1.1), where electrostatic interactions lead to the adsorption of nanocellulose (from suspension) onto the surface of an oppositely charged sacrificial template, such as CaCO_3 (Paulraj et al., 2018), polystyrene, silica (Ye et al., 2015) or melamine formaldehyde (Mohanta et al., 2014), which can be easily dissolved to leave intact a hollow nanocellulose shell. The potential of both CNCs and CNFs has been investigated in the preparation of capsules prepared through dip coating. However, due to the brittle nature of CNC-only networks, and the relatively hydrophilic nature of cellulose, capsules are typically made from composite materials where the nanocellulose is mixed with a plasticizing polymer such as glycerol and polyethylene glycol (Y. Zhang et al., 2017), xyloglucan and pectin (Paulraj et al., 2018), polyethylenimine (Ye et al., 2015) or alginate (Huq et al., 2012, 2014) (Figure 2b). The role of these plasticizing polymers is to improve flexibility, and to encourage physical entanglement and crosslinking within the capsule shell network. Conversely, nanocellulose can be used as a filler to improve structural integrity and improve the mechanical strength of capsules (Svagan et al., 2014) (Figure 2c). This mechanical strength stems not only from the crystallinity of the cellulose, but also from the abundance of intermolecular hydrogen bonds between nanocellulose crystals (or fibrils) which result from the removal of water from the shell wall structure.

Nanocellulose capsules can also be prepared using Pickering emulsions and subsequent **interfacial polymerizations/complexation** (Svagan et al., 2014, 2016; Yoo et al., 2017). In this method, as the oil phase polymerizes through an addition polymerization (such as the polymerization of poly urea-urethane) the nanocellulose becomes embedded within the polymeric shell. Using this preparation technique, it is possible to form hollow capsules where carbon dioxide becomes trapped within the capsule, or liquid core capsules where a hydrophobic liquid is encapsulated by the nanocellulose/polymer shell (Svagan et al., 2016; Yoo et al., 2017). Oil containing capsules can also be prepared using a complexation between CNC and methylcellulose stabilized Pickering emulsions and tannic acid, where the tannic acid and methylcellulose form a colloidal complex, which results in the condensation and stiffening of the methylcellulose within the CNC shell network. Interestingly, these tannic acid treated

CNC/methyl cellulose oil capsules are so robust that they can be freeze-dried to a dry powder and then redispersed into water (Z. Hu, Marway, et al., 2016). Although not cellulose-only structures, these structures are only made possible by the partitioning of nanocellulose to the water-oil interface and are then held together by chemical crosslinks resulting from the polymerization/complexation process, and hydrogen bonds inherent to cellulose networks (Svagan et al., 2016).

Although a slightly different approach to bottom-up assembly, it is worth noting that **biofabrication** has also been used to prepare BC capsules (Greca et al., 2018). In this method, hydrophobic particles are used to stabilize a water droplet in air to create a so-called ‘liquid marble’ (McHale & Newton, 2011). These hydrophobic surfaces provide an ideal interface for bacteria to grow and synthesize BC at the air-water interface of the marble, resulting in a templated network of BC fibres held together through inter- and intramolecular hydrogen bonding and van der Waals forces. These capsules can then be isolated by simply washing out the hydrophobic particles, leaving intact a hollow BC capsule upon drying. Interestingly, these structures can also be loaded *in situ* during BC synthesis with, for example, nano- or microparticles, which results in their encapsulation.

3.2. Potential Applications of Capsules

The implementation of nanocellulose-based capsules will likely see a rise in the future, possibly affecting a wide range of applications. A major market in which such capsules could be implemented is in pharmaceuticals. Bio-based capsules show promise in areas such as controlled drug release, tailored drug delivery routes (Mohanta et al., 2014; Y. Zhang et al., 2017), protective cages for small molecules (Greca et al., 2018; Lemahieu et al., 2011; Ye et al., 2015), and drug stabilization (Huq et al., 2014). Additionally, with their ability to encapsulate liquids (Svagan et al., 2016) they could be applied in cosmetics, for the slow release of dyes (Yoo et al., 2017) or other applications requiring liquid mobility. Such capsules could also be used in separation technologies, such as those listed above for powders and beads, and for example, in applications requiring low oxygen permeability. In general, the relative robustness of nanocellulose-reinforced capsules provides a more secure encapsulation technology than many other materials currently available.

4. Continuous Nanocellulose Fibres

Manufactured cellulose-based fibres such as viscose, modal and acetate fibres are by no means a new addition to the application spectrum of cellulosic materials. However, these regenerated cellulose fibres are conventionally made using a tedious combination of cellulose derivatization and subsequent dissolution, extrusion and regeneration processes, which require vast amounts of environmentally harmful chemicals. They have, however, fulfilled the requirement for strong, continuous fibres, for use in, for example, the textile industry and separation technologies, whereas naturally occurring fibres, such as cotton fibres, are typically short and discontinuous, and so exhibit significantly lower mechanical strength (Hooshmand et al., 2015). For context, natural cotton fibres exhibit a Young's modulus < 13 GPa and a tensile strength as low as 290 MPa (X. Li et al., 2007), whereas the corresponding value for recently developed, regenerated Ioncell fibres (from cellulose dissolved in ionic liquids) is a modulus up to 34 GPa and tensile strength of almost 900 MPa (Sixta et al., 2015).

Recently, it has been reported that water-based nanocellulose suspensions can be directly spun into continuous fibres with diameters ranging from 100 nm to 500 μm , thus circumventing the need for complex chemistries, and providing a strong, greener alternative for numerous applications (Hooshmand et al., 2015; Iwamoto et al., 2011; Lundahl et al., 2016). In many cases, the process of spinning these fibres causes the nanocellulose to align much like that which occurs in nature during the biosynthesis of hierarchical fibres (Clemons, 2016). Whilst cellulose-only fibres can be spun from CNF suspensions, fibres containing CNCs are typically cellulose/polymer composite materials owing to the highly brittle nature of CNC-only structures. The use of petroleum-based polymers in these composite fibres can be avoided by combining nanocellulose with a cellulose derivative, however, this requires the same extensive processing as traditional man-made fibres. Beyond the environmental aspect, however, continuous nanocellulose-based fibres are advantageous in that they typically exhibit better mechanical properties than regenerated cellulose fibres, due to the reinforcing nature of nanocellulose as a filler, and its alignment within the fibre (which can also be induced by secondary processing such as stretching, for example) (Endo et al., 2013; Iwamoto et al., 2011). For example, Iwamoto et al. reported Young's moduli as high as 25 GPa for wood-based nanofibrils with corresponding tensile strengths of 320 MPa (Iwamoto et al., 2011), but the best mechanical properties reported to date from nanocellulose are achieved through hydrodynamic alignment, discussed further below, and boasting a modulus of 90 GPa and a tensile strength of ca. 1.6 GPa (Håkansson et al., 2014; Mittal et al., 2018). Again, this is significantly higher than cotton fibres and typical commercial regenerated cellulose fibres like modal (rayon) fibres with a Young's modulus of 15 GPa and tensile strengths of almost 500 MPa (Adusumalli et al., 2006). Furthermore, their submicron diameters allow these fibres to be spun into mats which have extremely high specific surface areas, controllable porosity and can even be transparent (Giesa & Buehler, 2013).

summarizes the typical preparation methods for nanocellulose-based continuous fibres along with the external forces present, which cause the nanocellulose to align (typically) along the axis of the fibre. Summarized are also the forces and interactions present during the formation of these assemblies and those holding the final structure together, in addition to the typical diameters of fibres produced by each method.

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4.1. Preparation of Continuous Fibres

Three distinct methods of spinning fibres are used to produce continuous nanocellulose fibres – wet spinning, dry spinning and electrospinning. The most common of these techniques is **wet spinning** where fibres are prepared by extruding an aqueous nanocellulose gel through a nozzle and passing the resulting filament through a solvent coagulation bath (Figure 3a). When the extruded filament comes into contact with a cellulose incompatible solvent (such as acetone, ethanol, isopropanol or tetrahydrofuran), the outer wall of the filament will form a skin due to the rapid removal of water through solvent exchange (Walther et al., 2011). This rapid dehydration will induce the formation of hydrogen bonding between cellulose fibrils/crystals and as a result, provides the fibre with good mechanical strength. Cellulose-cellulose interactions can also be improved by modifying the nanocellulose prior to spinning. TEMPO-mediated oxidation and carboxymethylation, for example, have been hypothesized to enhance CNF orientation and promote favourable interactions due to increased surface charge (Håkansson et al., 2014; Iwamoto et al., 2011). Whilst wet spinning of pure CNFs is possible (Hooshmand et al., 2015; Iwamoto et al., 2011; Lundahl et al., 2016; Walther et al., 2011), CNC-based fibres require a polymer matrix. In these cases, or when CNFs are combined with a polymer, nanocellulose is mixed with the polymer (such as polylactic acid (PLA) (Geng et al., 2016) or polyvinyl alcohol (Endo et al., 2013; Uddin et al., 2011)) prior to spinning; reports have shown that the shear force-driven alignment of the nanocellulose component induces favourable alignment of the polymer component as well (Endo et al., 2013). Irrespective of the polymer matrix used, in order to utilize the full potential of nanocellulose as a reinforcing agent, both homogeneous dispersion of the nanocellulose and favorable cellulose-polymer compatibility are essential.

Nanocellulose fibres can also be prepared using a **dry spinning** method in which the extruded filament, rather than being passed through a coagulation bath, is dried in the air at elevated temperatures whilst being pulled from an extrusion nozzle (Figure 3b). Similar to wet spinning, the shear forces exerted on the nanocellulose during extrusion result in aligned continuous fibres. As with wet spinning, nanocellulose-only and nanocellulose/polymer composite continuous fibres have been demonstrated using dry spinning processes (S. Chen et al., 2014; Ghasemi et al., 2018; Hooshmand et al., 2015).

Regardless of whether spun wet or dry, the performance of spun nanocellulose fibres is dependent on numerous factors ranging from the concentration and potential pre-treatment of the nanocellulose precursor gel (or suspension), spinning parameters such as shear rate, the speed at which the filament is pulled and fibre drying, along with the presence of potential additives. For a comprehensive review of factors affecting fibre performance, the reader is referred to reference (Lundahl et al., 2017). It should be noted that although spinning can be carried out using specialty equipment, both wet and dry spinning can also be done on a smaller scale using a fairly straightforward syringe pump system (Iwamoto et al., 2011).

The third spinning technique often implemented to fabricate continuous nanocellulose fibres is **electrospinning**. However, unlike wet and dry spinning, this technique is typically used to prepare non-woven fibre mats or 1-dimensional mats rather than single spooled fibres (Dong et al., 2012; Hasegawa et al., 1993). Whereas wet and dry spun fibres are frequently CNF-based, electrospinning is more often carried out using CNCs as they cause fewer rheological issues during the spinning process. While nanocellulose-only fibres have not yet been successfully spun, numerous CNC/polymer combinations are possible to electrospin into mats; these include CNCs spun with polymethyl methacrylate (Dong et al., 2012), cellulose acetate (Vallejos et al., 2012), cotton cellulose (dissolved in a dimethylacetamide/lithium chloride solvent) (He et al., 2014), PLA (Shi et al., 2012), starch (H. Wang et al., 2019) and lignin (Ago, Jakes, et al., 2012; Ago, Okajima, et al., 2012). Figure 3c shows a schematic representation of an electrospinning setup. Briefly, a high voltage is applied to the needle of a syringe out of which the nanocellulose suspension is extruded. At a point where the voltage induced electrostatic repulsion overcomes the surface tension of the suspension, the suspension is ejected in a thin stream towards a metallic collector plate (where the fibre mat is formed). As the stream moves toward the plate it thins and solidifies as a result of the electrically induced elongation forces and simultaneous solvent evaporation (Richard-Lacroix & Pellerin, 2013). Due to the magnitude of the elongation forces, electrospun fibres exhibit a high order of nanocellulose alignment along the fibre axis (Clemons, 2016).

Aside from traditional spinning techniques, a variety of novel methods to prepare high-performance nanocellulose fibres have recently been reported. One such method is the use of interfacial polyelectrolyte complexation to spontaneously form insoluble polyelectrolyte complexes. In this technique, two oppositely charged polyelectrolytes, when brought into contact, undergo an ionic condensation releasing their corresponding counterions into the system (the increase entropy in the system due to this counterion release is the driving force for complexation to occur) (Drogoz et al., 2007). Combinations of cationic CNCs with anionic TEMPO-oxidized CNFs or carboxylated CNCs have been demonstrated to produce continuous fibres, which are easily extracted from the polyelectrolyte interface by simply lifting the complex out of the nanocellulose suspension (Figure 3d) (K. Zhang & Liimatainen, 2018). Another novel method by which to form continuous fibres is using flow-focusing devices i.e. hydrodynamic alignment (Håkansson et al., 2014; Mittal et al., 2017, 2018, 2019; Nechyporchuk et al., 2019). In this method, a nanocellulose suspension is passed through a microfluidic device in which the flow of the suspension causes the nanocellulose to align within the confined channels of the device (Figure 3e). Electrostatic repulsion between the nanocellulose fibrils/crystals works to both prevent aggregation and enhance alignment. Just prior to the onset of Brownian motion induced random alignment, the aligned structure is ‘frozen’ by altering the pH or ionic strength of the suspension, causing the suspension to gel. This gelled filament is then solvent exchanged in a solvent (or coagulation) bath and allowed to dry to form a solid nanocellulose fibre. The advantage of such a flow-based assembly of continuous fibres is that it is relatively easy to scale, and produces highly orientated fibres with excellent mechanical properties (Håkansson et al.,

2014; Mittal et al., 2018). For reference, flow-focused CNF fibres exhibit tensile strengths as high as 1.6 GPa, whereas the respective values for natural cotton fibres are as low as 300 MPa (X. Li et al., 2007), and < 350 MPa for wet spun CNF fibres (Lundahl et al., 2016).

4.2. Potential Applications of Continuous Fibres

The motivation to use continuous fibres over natural fibres is that they have significantly better mechanical strength due to the lack of discontinuation typically exhibited by the latter (Hooshmand et al., 2015). Furthermore, nanocellulose fibres benefit mechanically not only from the inherent strength of nanocellulose (due to its high crystallinity) but also from the alignment of the nanocellulose fibrils and/or crystals along the fibre axis (Iwamoto et al., 2011). As such, continuous nanocellulose-based fibres have been proposed for a multitude of applications. For example, these fibres could be used as textile yarns in functional active wear or military armour. Not only are they strong and lightweight, but their relatively hydrophilic nature allows them to absorb large amounts of water (Lundahl et al., 2018). This water absorption capacity of these fibres makes them useful in applications such as hygiene products and diapers. Interestingly, when coated with silica nanoparticles (through interfacial complexation), for example, these fibres have been shown to exhibit flame retardant properties, further broadening their application spectrum to safety devices such as fire blankets (Nechyporchuk et al., 2017). From a more mechanical standpoint, continuous nanocellulose fibres could be used as structural reinforcements in advanced composites (Ganster & Fink, 2006), as a substitute for fibre glass (Goutianos et al., 2006), or in filtration devices, to name a just a few.

Whereas the aforementioned applications are ones utilizing single continuous fibres (Figure 3f and Figure 3g), electrospun fibre mats (Figure 3h) also have a wide array of possible applications. One such application is the use of these mats in filtration systems (Goetz et al., 2018; Ma et al., 2012). The ability to control, not only the porosity of the mats, but also their surface chemistries, enables them to be used in applications requiring the capture of specific particles/molecules/ions (e.g. water purification). Alternative applications, which benefit from the high surface area and tunability of electrospun mats include supports for catalysis, and biomedical applications such as tissue engineering scaffolds (He et al., 2014) and wound healing, and even sensor and actuators (Clemons, 2016).

5. Nanocellulose Films

Nanocellulose films are typically assembled as either supported or free-standing films where supported films (also called “coatings”) are ones in which the nanocellulose is attached to the surface of a flat, uniform substrate, whereas free-standing films resemble traditional paper, but

are significantly thinner. Typically, supported thin films range between <100 nm (ultrathin) and <1000 nm (thin) in thickness, whereas free-standing films have thicknesses in the micrometer range. Supported thin films of nanocellulose are diverse structures, which can be implemented in a wide array of potential applications such as protective, and antifouling coatings, sensors, drug delivery systems, or they can be used as model systems to gain fundamental understanding about nanocellulose and colloidal systems in general. On the other hand, free-standing films have potential in separation applications as membranes and filters (Mestreveli et al., 2014), as transparent substrates for flexible electronics (Hsieh et al., 2013; L. Hu et al., 2013; X. Xu et al., 2016), and as “nanopaper” (Henriksson et al., 2008; Sehaqui et al., 2011). Table 5 lists the main assembly methods and their driving forces along with the dominant forces holding nanocellulose films together and some key properties.

5.1. Preparation of Nanocellulose Films

5.1.1. Supported Thin Films

Deposition of supported thin films can be carried out using a number of different techniques. The majority of the techniques are ones that utilize the natural tendency of cellulose to assemble at interfaces. These techniques include drop (or solvent) casting, dip coating and Langmuir deposition. Conversely, other thin film deposition techniques, such as spin coating and bar coating, rely on external forces to manipulate the nanocellulose into desired conformations.

Supported thin film preparation using the **drop, or solvent, casting** method, while being facile and fairly effortless, is uncontrollable and often leads to films with unpredictable properties such as film thickness and surface roughness. The deposition of films through this method is carried out by simply dropping a given volume of a nanocellulose suspension onto a substrate and allowing it to naturally dry into a film through evaporation. Although the degree of control during drop casting is limited, it is possible to control the external parameters effecting film formation. Controlling the atmospheric conditions to allow for slower solvent evaporation and ensuring the film is undisturbed throughout the drying process will provide the best conditions for the formation of uniform films (Beck et al., 2011). Typical phenomena seen during the drying process of solvent cast nanocellulose films are dewetting and the “coffee stain” effect (Teramoto, 2020; Uetani & Yano, 2013). These occur when the affinity of the cellulosic material toward the substrate is limited, and when the volume of the cast suspension is small.

Simply put, dewetting is the retraction of the suspension to minimize contact with the substrate surface. The effects of dewetting can be seen in the resulting films as unique patterns made up of, for example, coffee rings (Klockars et al., 2019), striations (Niinivaara, Wilson, et al., 2016), or fractals (Niinivaara & Kontturi, 2014). Recent work has also shown the potential of producing patterned aerogel films, by drop casting a crosslinked hydrogel (further discussed in Section 6.1)

onto patterned mould, applying pressure and subsequently lyophilizing to remove water (Or et al., 2019).

Whereas the formation of supported thin films through drop casting is governed by the forces occurring during solvent evaporation and the behaviour of the nanocellulose at the air/substrate interface, the formation of films in dip coating is driven by spontaneous adsorption resulting from electrostatics or specific interactions between the surface of the substrate and the nanocellulose. In **dip coating** (Figure 4a), a substrate is lowered into a nanocellulose suspension, where a layer of material is adsorbed onto the surface of the substrate. Although a tedious process, especially if depositing several layers (i.e., **layer-by-layer deposition** to form multilayer films (Decher & Schlenoff, 2002)), dip coating is a straightforward procedure yielding films of controllable thickness (by controlling suspension concentration) with relatively low surface roughness (Cranston, 2013).

Langmuir deposition also relies on the interfacial assembly of nanocelluloses, however at the air/water interface. In this method, the amphiphilic nature of cellulose is utilized to spread a layer of nanocellulose at the air/water interface with its polar moieties in contact with the water, and non-polar ones in contact with the air. Using horizontal barriers sliding over the surface of the water phase, the nanocellulose is then compressed to form a stable, uniform film on the surface of the water. It is important to note that the most important requirement for Langmuir deposition is the ability of the nanocellulose to form these stable films at the air/water interface. While CNCs are able to assemble naturally in this manner (Bertsch et al., 2018) (owing to the hydrophobic edge of their crystal structure (Kalashnikova et al., 2012)) or with the help of surfactants (Habibi et al., 2007; Habibi, Hoeger, et al., 2010), CNFs require a hydrophobic surface functionalization to aid in their assembly at the air/water interface for Langmuir deposition (Xhanari et al., 2011).

Nonetheless, once in the form of a compressed, uniform film at the air/water interface, the nanocellulose is then transferred onto the surface of a substrate. This can be carried out either by passing the substrate perpendicularly (Langmuir-Blodgett deposition) through the film into the water phase and then retracting it (forming a bilayer), or by bringing it into contact parallel (Langmuir-Schaefer deposition) to the film and retracting (forming a monolayer) (Figure 4b). As the deposition of nanocellulose films using this method yields a single layer or bilayer at a time, control of the film thickness is very accurate, however, thin film preparation using Langmuir deposition is slow and requires specialty equipment.

One of the more accessible pieces of equipment for thin film deposition is a spin coater, which is a fast and relatively simple method to produce films of varying thicknesses with high reproducibility (Schubert & Dunkel, 2003). **Spin coating** (Figure 4c) utilizes high rotational speeds to dry a droplet of solution or suspension onto the surface of a substrate and can be used with any form of nanocellulose (Ahola et al., 2008; Edgar & Gray, 2003; Kontturi et al., 2003, 2007; Notley, Eriksson, Wågberg, Beck-Candanedo, et al., 2006). Due to the nature of this

technique, however, spin coated films are not in thermodynamic equilibrium but in a metastable configuration brought on by the forces involved in the film formation process and the rapid evaporation of the solvent. By varying parameters such as acceleration, rotational speed and suspension concentration, the thickness, uniformity and roughness of the resulting film can be controlled. A fast acceleration and high rotational speed typically result in thin, highly uniform films whereas a high concentration, and therefore viscosity, will lead to thicker films with higher surface roughness. The duration of the spinning cycle is greatly governed by the boiling point and vapour pressure of the solvent used but is also directly affected by atmospheric conditions such as temperature and relative humidity.

The final method by which to prepare supported nanocellulose films is through **bar coating** (Lavoine et al., 2014) (Figure 4d). In this technique, a volume of nanocellulose suspension is dropped onto the surface of a substrate after which a bar is pushed/or pulled through the suspension horizontally along the surface of the substrate all the while spreading the nanocellulose suspension out evenly. Once it has fully covered the surface of the substrate, the resulting film of nanocellulose is allowed to dry. One of the main advantages of bar coating, is that the shear forces caused by the movement of the bar over the nanocellulose causes the nanocellulose crystals/fibrils to align (Hoeger et al., 2011). An added benefit of this method of coating is that it can be done over significantly large surface areas, however, in comparison to the aforementioned techniques the uniformity of films suffers.

5.1.2. Free-Standing Films

Free-standing nanocellulose films are typically prepared by making thick films using drop casting, layer-by-layer deposition, or bar coating, as described above, and then peeling the film from the substrate. Alternatively, they can be made through a simple filtration method (similar to that used in traditional papermaking). The filtration process generates films commonly referred to as “nanopaper” (Henriksson et al., 2008; Sun et al., 2018) where a CNF suspension is vacuum filtered using a filtration aid or membrane and is then recovered and allowed to dry via evaporation or with the aid of an external heat source, such as hot pressing (Österberg et al., 2013) (Figure 5a and Figure 5b). Whilst vacuum filtered CNC films have also been demonstrated (Q. Chen et al., 2014), free-standing CNC films are more typically produced through simple evaporation processes (Beck et al., 2011). However, due to the brittle nature of CNC-only materials these films have almost no structural integrity and as such necessitate a minor amount of additives such as glycerol (Dorris & Gray, 2012; M. Xu et al., 2018), surfactants (Bardet et al., 2015; Guidetti et al., 2016) or flexible polymer (e.g. polyethylene glycol (Q. Zhou et al., 2009)) (Figure 5c) to allow for handling or integration into industrial processes. Interestingly, recent reports have shown the potential to produce “nanopaper” through a novel **spray coating** method, which enables high throughput production of uniform, smooth

(on the substrate side) films of nanocellulose (Beneventi et al., 2014, 2015; Shanmugam et al., 2017, 2018).

5.2. Potential Applications of Nanocellulose Films

5.2.1. Supported Thin Films

Supported thin films of nanocelluloses are widely used in fundamental research as model systems (Kontturi et al., 2006) (Figure 5d) to elucidate the viability of nanocellulose as a component in functional materials. Importantly, model systems have been used to mimic the interactions of native cellulose in the plant cell wall (Benselfelt et al., 2016; Notley et al., 2004; Notley & Norgren, 2006; Stiernstedt et al., 2006; Villares et al., 2015), have provided vital information on cellulose surface interactions (Ahola et al., 2008; Eriksson et al., 2007; Lombardo & Thielemans, 2019; Notley, Eriksson, Wågberg, Beck, et al., 2006), moisture sensitivity (Ahola et al., 2008; Aulin et al., 2009; Brett et al., 2019; Kittle, 2012; Niinivaara et al., 2015; Niinivaara, Faustini, et al., 2016; Reid et al., 2016), particle binding (Kontturi et al., 2018), and biomedical viability (Jorfi & Foster, 2015; Orelma et al., 2012) of nanocellulose, to name only a few.

From a more practical standpoint, supported nanocellulose thin films have been implemented in a number of different applications. A significant amount of work has been carried out to demonstrate the potential of thin film coatings in the packaging industry (Ferrer et al., 2017). As mentioned previously, due to the ability of both CNCs and CNFs to form densely packed structures, nanocellulose coatings have the potential to not only provide additional strength to packaging materials but also instill barrier properties (Shanmugam et al., 2019). Such coatings could be implemented in food packaging applications as barriers against either air (oxygen) to prevent food spoilage, for example, or grease. While applicable in barrier applications for hydrophobic components, the hydrophilic nature of cellulose prevents the use of nanocellulose coatings in a number of different applications where moisture sensitivity is an important factor. Water is able to penetrate the nanocellulose network and compete with the intermolecular hydrogen bonds, compromising the structural integrity of the films, significantly diminishing the barrier potential of nanocellulose films. Fortunately, as mentioned earlier, this significant drawback of cellulose can be circumvented through surface functionalization, through which nanocelluloses can be made more compatible for their intended use. For a comprehensive review on nanocellulose in packaging applications, please refer to reference (Hubbe et al., 2017).

On the other hand, the moisture sensitivity of cellulose can instead be exploited in thin film applications such as in humidity sensors and intelligent packaging. Such applications utilize the swelling and subsequent change in Bragg's reflection (visible colour change) of chiral nematic CNC films (Ping et al., 2013), or changes in thin film interference colors for non-chiral nematic films (Cerclier et al., 2011), upon exposure to humid conditions or enzymes that breakdown cellulose. Such colour indicating films offer a facile and affordable alternative to those currently available to monitor the quality of humidity sensitive goods such as foods, pharmaceuticals and certain chemicals. Another interesting possibility to utilize the chiral nematic behaviour of CNC films is to apply them as anticounterfeit films in security and high-value papers (Pan et al., 2010). Decorative coatings with CNC and CNF films (with and without liquid crystalline order) have also been demonstrated in a number of artistic applications (Figure 5e) (Blonder et al., 2017; Klockars et al., 2019).

The ability to use external forces such as electric (Csoka et al., 2011) and magnetic fields (Sugiyama et al., 1992), and shear forces (Csoka et al., 2011) to tune the alignment of CNCs in suspension and films, shows great promise in a number of different applications. CNC films with tunable long-range order have been proposed as templates in the formation of chiral, mesoporous materials, which can be implemented in antireflective coatings, plasmonic and photonic devices (Giese et al., 2015). Additionally, aligned supported CNC films have also been implemented in the development of bio-based microelectromechanical systems (MEMS), which are used in, for example, the medical, communication and transportation industries (Saha et al., 2018). It has also been speculated, that combined with the piezoelectric properties of nanocellulose films (Rajala et al., 2016), CNC MEMS could be used in actuation and sensing applications (Saha et al., 2018).

5.2.2. Free-standing Films

The use of free-standing CNF films as supports in separation applications, such as membranes and other filtration aids, have also been investigated (Metreveli et al., 2014). Due to their high surface area and significant porosity, structures made of nanocellulose, when functionalized appropriately or combined with the correct additives, have the ability to capture small molecules, metal ions, bacteria and other organic pollutants (Carpenter et al., 2015; Voisin et al., 2017).

Recently, the investigation of free-standing CNF "nanopaper" in various applications has gained popularity (Barhoum et al., 2017). Not only are these films highly flexible, but also lightweight and remarkably strong regardless of their porosity (Henriksson et al., 2008). Furthermore, owing to the nanoscale of the cellulose fibres, these structures are extremely densely packed rendering them opaque or even transparent. An interesting use for these film properties is in the field of flexible conductive films (L. Hu et al., 2013) and electronics (Hsieh et al., 2013; X. Xu et al., 2016; Zheng et al., 2013). While cellulose itself is a non-conductive polymer, it shows great promise in being utilized as a transparent and flexible substrate material in the aforementioned applications. Coupled with conductive materials such as carbon nanotubes, graphene, metal

oxides and conductive polymers CNFs could be used to form highly conductive films capable of for example, energy storage (Zheng et al., 2013). Similarly, CNCs, although too fragile to use as free-standing cellulose-only structures, have the potential to be used as substrates to support more flexible polymers. Such structures have, for example, demonstrated potential as recyclable, organic solar cells (Yinhua Zhou et al., 2013). In general, the application potential of nanocelluloses in functional materials increases exponentially when they are utilized as building blocks *in combination* with other materials to form nanocomposites; however, such materials are outside the scope of this Review.

6. Nanocellulose Hydrogels, Aerogels and Dried Foams

Hydrogels are highly porous 3-dimensional network structures, that are able to hold significant amounts of water whilst maintaining their structural integrity. Networked structures can be held together by physical crosslinks (i.e., weak intermolecular forces that link moieties to each other or entanglement), chemical crosslinks (i.e., covalent bonds between individual CNFs/CNCs and/or to a polymer matrix) (Liang et al., 2020), or a combination of the two. Nanocellulose hydrogels can be either comprised solely of nanocellulose, “nanocellulose-only”, or are a combination of hydrophilic polymers reinforced with nanocellulose. Hydrogels have traditionally been used in applications ranging from cosmetics, foods, biomedical devices, absorbents and even in niche technologies such as chromatography and electrophoresis (Chirani et al., 2015). The natural tendency of high aspect ratio nanocellulose to form percolated networks and “gel” makes it ideal for the formation of hydrogels (Pääkko et al., 2007). (Note that aspect ratio is the ratio of a particle’s major dimension to minor dimension, length divided by diameter for rods, and by some definitions, anything that is over 1, i.e., not a sphere, is considered high aspect ratio – in general, CNFs have larger aspect ratios than CNCs (Lavoine et al., 2019).) In fact, a large amount of research has been carried out on the viability of both CNCs and CNFs in these structures, as covered in an extensive review summarizing the 200+ articles available in the literature (De France et al., 2017). The inherent non-toxicity, biodegradability, functionalizability, and high aspect ratio of nanocelluloses are distinctly advantageous in their use as hydrogel materials. While CNF and CNC-only hydrogels are widely reported, significant research efforts have been made to produce structurally more robust hydrogels (especially in the case of CNC-only gels, which lack physical entanglement due to the rigid-rod like behavior of CNCs). Hydrogels with improved mechanical properties can be prepared by promoting chemical crosslinks through surface modification or through the addition of external crosslinking agents.

The mechanical strength of hydrogels is an important factor since they are the “precursor” material for preparing aerogels. Typically, aerogels are produced from hydrogel assemblies by substituting the liquid phase (water) with a gas phase (air) through sublimation or supercritical drying (Figure 6a and Figure 6b). Conversely, foams are structures in which air bubbles have been dispersed and stabilized within a liquid or solid structure (generally called aqueous foams or solid foams, respectively). Nonetheless, both aerogels and dried foams are extremely lightweight, high porosity structures (>90% for aerogels and >50% for foams (Lavoine & Bergström, 2017)) in which air is the main component. Aqueous nanocellulose foams in which air bubbles have been dispersed and stabilized in an aqueous nanocellulose suspension have only been reported in a few cases where the surface activity of nanocellulose was improved through functionalization (Cervin et al., 2013; Z. Hu, Xu, et al., 2016). Table 6 summarizes the dominant forces and interactions occurring during gel preparation, the forces that hold them together, and some examples of crosslinking chemistries demonstrated.

6.1. Preparation of Hydrogels, Aerogels and Dried Foams

6.1.1. Hydrogels

The main contributors to the gelation of unmodified nanocelluloses are physical entanglement (Pääkko et al., 2007), attractive intermolecular cellulose-cellulose interactions such as van der Waals forces, and electrostatic screening or ion-mediated gelation (which destabilizes CNC/CNF colloidal stability (Fall et al., 2011; Nordenström et al., 2017) leading to particle aggregation and often decreasing the percolation threshold) (Figure 6c). It should be noted that in hydrated structures, such as hydrogels, hydrogen bonding between cellulose does not play a vital role (Nishiyama, 2018). Pore sizes in hydrogels are challenging to measure (without drying artefacts) and are generally assumed to be in the nanometer range but can be as large as 10 μm for gels templated by ice or sacrificial templates. Entanglement is a dominant gelation mechanism for CNFs but is less likely for shorter rigid CNCs, which generally require surface functionalization, chemical crosslinkers/additives or other polymers to form networked structures. As a result, significantly more work has been carried out on formulating nanocellulose-only gels from the more flexible, higher aspect ratio, CNF materials.

The production of stable hydrogels is a far more simple task than that of forming aerogels. As mentioned, nanocellulose will naturally aggregate to form gels above a threshold concentration, which depends on the medium, the nanocellulose type and dimensions, and the pH/ionic strength. For plant-derived CNCs in water this is approximately 10 wt% (Ure et al., 2011) whereas it is significantly lower for CNFs (often under 2 wt%) (Foster et al., 2018). This critical concentration can, however, be decreased by screening electrostatic repulsion through an increase in ionic strength or by inducing instability through a decrease in pH (Fall et al., 2011), or by decreasing nanocellulose surface charge density through elevated temperatures (Lewis et

al., 2016). Multivalent ions have also been demonstrated as effective gelation agents by inducing ionic bridging between CNCs (Chau et al., 2015). These methods, which induce gelation in nanocellulose suspensions, do so through DLVO destabilization (named after Boris Derjaguin, Lev Landau, Evert Verwey and Theodoor Overbeek). The stability of colloids is governed by the DLVO theory, which accounts for the attractive effect of van der Waals forces and the electrostatic repulsion of similarly charged particles (Derjaguin & Landau, 1941; Verwey & Overbeek, 1955). In a stable colloid, these two forces are balanced at small separations, however, off-setting this balance by altering ionic strength, concentration, surface charge, pH or temperature will result in destabilization, and subsequent gelation.

Whilst DLVO destabilization is an effective method by which to induce gelation in nanocellulose suspensions, a number of alternative routes can also be taken to prepare even more robust cellulose-only hydrogels. CNF gelation, for example, can be induced through a homogenization process in which the degree of fibrillation and subsequent mixing (entanglement) of the CNFs are maximized, resulting in strong hydrogel networks (Pääkko et al., 2007). For CNCs, on the other hand, which are unable to physically entangle, strong cellulose-only hydrogels can be prepared through chemical crosslinking. For example, covalent hydrazone crosslinks occur between CNCs surface functionalized with aldehyde and hydrazide groups (Osorio et al., 2018; X. Yang & Cranston, 2014). Another unique example is that cellulose-only hydrogels can be prepared by physically entrapping CNCs within an entangled cellulose derivative polymer matrix (Y. Wang & Chen, 2011).

Although cellulose-only hydrogels have been demonstrated, the potential of nanocellulose-based hydrogels is vastly expanded by their incorporation into a hydrophilic polymeric matrix. While these hydrogels are in fact composites, they are worth discussing here as the nanocellulose plays a key role in the mechanical properties of the resulting material. For example, the mechanical properties of polyvinyl alcohol hydrogels can be vastly improved by the simple physical entanglement of CNCs within the polymer matrix (Abitbol et al., 2011). The reinforcing potential of nanocellulose can be enhanced even further by chemically entrapping it within the polymer matrix either through chemical crosslinking or through polymerization (J. Wei et al., 2016; J. Yang et al., 2013) in the presence of the nanocellulose. Through these methods, nanocellulose acts as either the crosslinker between polymer chains or is itself chemically crosslinked to the polymer, which provides the hydrogel with both chemical robustness and physical strength (De France et al., 2017). Regardless of crosslinking mechanism, the nanocellulose component must typically undergo a surface modification in order to promote the formation of covalent bonds between the cellulose and the polymer (Chau et al., 2016; Domingues et al., 2015; García-Astrain et al., 2016; Köhnke et al., 2014; McKee et al., 2014). Typically, these surface modifications include polymer grafts (Atifi et al., 2014; J. Yang et al., 2014; Yiming Zhou et al., 2013), silylation (J. Yang et al., 2014) or the addition of carboxyl (Mihiranyan, 2013) or aldehyde groups (Chau et al., 2016).

6.1.2. Aerogels and Dried Foams

As already mentioned, the formation of aerogels essentially involves processing a nanocellulose hydrogel in such a way that the liquid component of the gel is replaced with air while maintaining its structural integrity (Figure 6d) and porous network structure (Figure 6e and Figure 6f). For the preparation of dried foams (Figure 6g) however, an aqueous precursor foam (Figure 6h) must be prepared, which then undergoes the same liquid to gas substitution as the hydrogel precursor in aerogel preparation. It is worth remembering here, that typically, aerogels are produced from hydrogel assemblies by substituting the liquid phase with a gas phase whereas foams are structures in which air bubbles have been dispersed and stabilized within a liquid or solid structure.

The preparation of foams requires nanocellulose to partition at the interface between hydrophobic and hydrophilic substances, which in the case of foams, is the air-water interface. The most common way to prepare a nanocellulose foam is to combine a surfactant and a nanocellulose suspension and agitate or homogenize the mixture. This agitation causes air bubbles to be dispersed into the suspension and become stabilized by surfactant, which then results in the partitioning of the nanocellulose to the “surfactant-coated” air-water interface. Numerous nanocellulose/surfactant combinations have been reported to make stable precursor foams such as TEMPO-oxidized CNFs with a non-ionic surfactant (Gordeyeva et al., 2016), unmodified CNFs with a cationic surfactant (Mariano et al., 2018), and polymer grafted CNCs with non-ionic surfactant (B. Wei et al., 2017). Additionally, surface functionalized CNCs (through amine adsorption) were foamed in water (Cervin et al., 2013, 2016) as was a cellulose-only system where foams were stabilized using CNCs and methyl cellulose (Z. Hu, Xu, et al., 2016). Some of these aqueous foams can be dried by oven drying or freeze-drying, however, some collapse upon drying. Foams normally have large pores of over 50 μm , stemming from the size of the trapped air bubbles – the final structures may have discreet pores or interconnected pores depending on the gas volume and preparation method.

Several techniques have been demonstrated to process nanocellulose hydrogels or solvogels to aerogels such as freeze drying (Lavoine & Bergström, 2017), CPD (Heath & Thielemans, 2010; Liebner et al., 2010), and PGX processing (Osorio et al., 2018). Note that freeze drying requires freezing whereas it is an optional pre-processing step with CPD such that cryo-templating (De France et al., 2017; Osorio et al., 2018) is sometimes referred to as an aerogel processing method but freezing alone is not sufficient – it must be followed by a drying step.

In freeze drying (described in Section 2.1.1), the hydrogel or other precursor gel is frozen and then the ice is sublimated, leaving in place a stable, porous, low density aerogel (Lavoine &

Bergström, 2017). Freeze drying parameters can be altered in order to control the structure of the resulting aerogel. For example, a slower freezing rate can be used to promote the formation of ice crystals which will exclude the nanocellulose particles from the water phase (Osorio et al., 2018). In this technique, known as cryo-templating, the directional formation of ice crystallites gives form to aerogels with a specific anisotropy (De France et al., 2017). Cryo-templating can be used further to induce anisotropy within an aerogel by controlling the temperature, cold source, and even freezing style of the precursor hydrogel (Y. Chen et al., 2019). Pore sizes in aerogels produced from ice templating followed by drying are normally >50 nm and often with large macropores (μm) resulting from ice crystals. When spray freeze dried, however, the rapid freezing rate results in nanocellulose aerogels that exhibit pore sizes as low as tens of nanometers (Jimenez-Saelices et al., 2016). In the case of chemically crosslinked nanocellulose aerogels, their pore structure is often bimodal, with mesopores < 20 nm between individual particles and macropores surrounded by sheets of crosslinked nanocellulose (X. Yang & Cranston, 2014).

As outlined in Section 2.1.1, supercritical drying or CPD differs from freeze drying in that the liquid filling the gel pores is solvent exchanged with a super critical fluid and then depressurized to ambient conditions, leaving an intact, dry, porous aerogel (Heath & Thielemans, 2010; Liebner et al., 2010). The basic premise in aerogel formation through PGX processing is very similar to CPD, however, solvent exchange does not need to be carried out in a step-wise process but the hydrogel can be subjected to a mixture of, for example, ethanol and carbon dioxide, which causes a rapid and homogeneous dehydration of the gel upon depressurization (Osorio et al., 2018). Such processes are vital in the removal of water from the nanocellulose structure, as uncontrolled drying causes them to collapse due to capillary pressure resulting from evaporation (Lavoine & Bergström, 2017). The forces and interactions at play in these drying techniques were discussed in Section 2.1.1 and Table 2. If CPD or PGX is performed on nanocellulose hydrogels without a freezing step, the specific surface area is normally larger and the pores smaller, typically in the <100 nm range.

Although not a preparation method per se, it should be noted that a number of aerogel applications require the structure to exhibit a degree of hydrophobicity (such as selective absorption). A relatively facile method to impart specific surface functionalities to aerogel structures is to carry out a post-treatment. For example, gas phase chemistries can be used to esterify the nanocellulose (Fumagalli et al., 2013), or to deposit hydrophobic moieties such as silanes (Jiang & Hsieh, 2014) or titanium dioxide (Kettunen et al., 2011) through chemical vapour deposition. This can also be considered a type of crosslinking post-treatment. Alternatively, aerogels can be modified using a layer-by-layer assembly (described in Section 5.1.1) for example, to induce conductivity through the adsorption of conductive polymers or nanoparticles (Hamedi et al., 2013).

6.2. Potential Applications of Nanocellulose Hydrogels, Aerogels and Foams

Both nanocellulose-only and nanocellulose composite hydrogels have been proposed for a number of potential applications. Nanocellulose hydrogels have primarily found their niche in the biomedical field. For example, as drug delivery systems (Lin et al., 2012), as cell and biomolecule transportation systems (K. Wang et al., 2016), and as biomimetic scaffolds for tissue engineering (Chau et al., 2016; Curvello et al., 2019; Dugan et al., 2010). Additionally, outside of the biomedical field, nanocellulose hydrogels have been explored as selective absorbents (Yiming Zhou et al., 2013, 2014), photonic and optoelectronic materials (Kelly et al., 2013) and in the case of bacterial cellulose, in its hydrogel form, it is used in the dessert, nata de coco.

As with their hydrogel counterparts, nanocellulose-based aerogels have also been proposed for use in a multitude of different applications. One such application is the utilization of these aerogels as support structures to hold, for example, super-capacitor nanoparticles or conductive polymers/particles to function as electrodes/current collectors in energy production and storage (X. Yang et al., 2015) or to improve the processing of organic metal frameworks for water purification applications (H. Zhu et al., 2016). As a result of their large surface area and high porosity, nanocellulose aerogels also have the potential of acting as sorbents (Köse et al., 2020; H. Liu et al., 2017; H. Zhu et al., 2016) provided the aerogel maintains structural integrity upon wetting, which can generally be achieved through chemical crosslinking. Furthermore, aerogels have been demonstrated in shock absorbing materials, as sound and thermal (Kobayashi et al., 2014) insulators and in hygiene products. Interestingly, CNC-based gels have also been used as injectable and space-filling bioscaffolds (Ferreira et al., 2020), and for example, have been shown to speed up bone growth when tested in animal models (Osorio et al., 2019).

Nanocellulose foams, on the other hand, have been proposed in applications such a selective adsorption (H. Zhang et al., 2019), thermal insulation (Wicklein et al., 2015), enhanced oil recovery (B. Wei et al., 2017) or even as substitutes for packaging materials traditionally made from polystyrene and polyurethane (Cervin et al., 2013).

7. Summary

Nanocellulose, in both its fibrillated and crystalline form, provides an excellent platform with which to address the current (and immediate) necessity to shift away from our reliance on petrochemical-based materials. From investigating the fundamental interactions of bio-based

materials (e.g., thin films), to building biomedical scaffolds (e.g., hydrogels), reinforcing textiles (e.g., continuous fibres), and even remediating polluted bodies of water (e.g. with absorbent aerogels and foams), the variety of structures which can be assembled from nanocelluloses is broad and far reaching.

Identified in this Review are six classes of nanocellulosic structures assembled using a multitude of bottom-up techniques. Whether assembled through the natural tendency of cellulose to align or partition at interfaces or through the use of external forces, each of these structures are held together by a specific set of underlying interactions, the most prevalent of which (in dry materials) are hydrogen bonds and van der Waals interactions. Nonetheless, the structural integrity of nanocellulosic structures can be vastly improved (especially in cases where water is present) by introducing ‘artificial’ interactions in the form of physical and/or chemical crosslinking, hornification, electrostatic and hydrophobic interactions, and even by inducing physical entanglement.

Regardless of these available interactions, a key challenge in designing and preparing nanocellulose-only structures is the limitations that their physical structures pose. Where the fibrillar structure of CNFs allows for the preparation of highly entangled networks, the low gelation concentration (and high viscosity) prevents them from being utilized in assembly techniques involving shear forces, such as electrospinning, for example. On the other hand, while the shear thinning and amphiphilic behaviour of CNCs enable their use in producing continuous fibres, their rigidity results in highly brittle CNC-only structures.

Fortunately, it is possible to overcome a number of these structural issues through the use of nanocelluloses in bio-nanocomposites. Whilst these are outside of scope for this Review, it is worth mentioning that a vast amount of work is currently being carried out in designing and implementing nanocellulose-based composite materials, both polymeric and inorganic in nature. The drawback of these materials, however, is that they typically involve synthetic hydrophobic polymer matrices, which have limited compatibility with cellulose. Numerous surface modification routes for nanocellulose have been reported in the literature to improve this compatibility, however, few industrially feasible, not to mention, green alternatives have been discovered. It seems likely that research focus will remain on investigating the possibility of green surface modifications for nanocellulose, or shift toward finding environmentally sustainable alternative to use as the polymer matrices.

In conclusion, it is important to highlight that the manufacture of both CNFs and CNCs on an industrial scale is still in its early days, and as such, the majority of the potential applications of nanocellulose structures outlined in this Review are not commercially available but remain at the laboratory scale. Furthermore, due to the relatively young age of “the nanocellulose revolution”, further work must be carried out to understand the long-term effects of nanocelluloses on the environment and in the body (De France et al., 2019; Roman, 2015), in order to encourage both market and consumer acceptance.

CRedit authorship contribution statement

Elina Niinivaara: Conceptualization, Writing - Original Draft, Writing - Review & Editing, Visualization, Funding acquisition.

Emily Cranston: Conceptualization, Writing - Original Draft, Writing - Review & Editing, Visualization, Supervision, Project administration, Funding acquisition.

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Figure 1. Photograph of a) a spray-dried CNC powder (dried from suspension) and scanning electron micrographs of spray dried b) CNC powder (Reprinted (adapted) with permission from (Beck et al., 2012). Copyright 2012 American Chemical Society), and c) CNF powder (Reprinted (adapted) from (Peng, Han, et al., 2012). Copyright 2012 American Chemical Society). A photograph of d) freeze-dried CNC flakes (dried from suspension) (Reprinted (adapted) with permission from (Beck et al., 2012). Copyright 2012 American Chemical Society). Microfluidic devices are a common way to confine nanocellulose into droplets as shown in e) where CNC droplets are generated in a continuous oil phase inducing orientation of CNCs visible as blue and yellow domains in the polarized optical microscope (Reprinted (adapted) with permission from (Parker et al., 2016). Copyright 2016 American Chemical Society). Droplets of CNF suspensions can be dried to form f) dried beads (Reprinted from (Erlandsson et al., 2016), Copyright 2016, with permission from Elsevier).

Figure 2. a) Schematic representation of a CNC capsule; scanning electron micrographs of b) an alginate/CNC nanocomposite capsule (adapted from reference (Lemahieu et al., 2011) Copyright © 2011 WILEY- VCH Verlag GmbH & Co. KGaA, Weinheim) and c) a CNF/CNC nanocomposite capsule (Reprinted (adapted) with permission from (Svagan et al., 2014) Copyright 2014 American Chemical Society).

Figure 3. Schematic representations of three main spinning techniques a) wet spinning (adapted from reference (Walther et al., 2011) Copyright © 2011 WILEY- VCH Verlag GmbH & Co. KgaA, Weinheim), b) dry spinning (Reprinted (adapted) with permission from (S. Chen et al., 2014) Copyright 2014 American Chemical Society), and c) electrospinning (Reprinted (adapted) with permission from (Richard-Lacroix & Pellerin, 2013) Copyright 2013 American Chemical Society), d) a photograph of the pulling of a fibre through interfacial complexation (adapted from reference (K. Zhang & Liimatainen, 2018) © 2018 WILEY- VCH Verlag GmbH & Co. KgaA, Weinheim), and e) hydrodynamic alignment (Reprinted (adapted) with permission from (Mittal et al., 2018) Copyright 2015 American Chemical Society) used to prepare nanocellulose-based continuous fibres. Along with f) a photograph of a dry spun continuous nanocellulose fibre, g) a scanning electron micrograph of its cross-section (Reprinted (adapted) with permission from (Hooshmand et al., 2015) Copyright 2018 American Chemical Society) and h) a scanning electron micrograph of an electrospun nanocellulose fibre mat (This work is licensed under the Creative Commons Attribution 4.0 International License. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/> or send a letter to Creative Commons, PO Box 1866, Mountain View, CA 94042, USA) (Clemons, 2016).

a) Dip coating

b) Langmuir deposition

c) Spin coating

d) Bar coating

Figure 4. Schematic representation of nanocellulose thin film deposition on to a substrate through a) dip coating, b) horizontal Langmuir deposition (Langmuir-Schaefer deposition) and vertical Langmuir deposition (Langmuir-Blodgett deposition) (Reprinted from (Niinivaara, Wilson, et al., 2016), Copyright 2015, with permission from Elsevier), c) spin coating (Reprinted from (Niinivaara, 2016)), and d) bar coating.

Figure 5. a) Photograph of a transparent polished CNF film (adapted from reference (Nogi et al., 2009) Copyright © 2009 WILEY- VCH Verlag GmbH & Co. KGaA, Weinheim), b) scanning electron micrograph of the cross section of a representative CNF film (Reprinted (adapted) with permission from (Rajala et al., 2016) Copyright 2015 American Chemical Society), c) photograph of a flexible CNC/polyethylene glycol composite film (Reprinted (adapted) with permission from (Bardet et al., 2015) Copyright 2015 American Chemical Society), d) atomic force microscopy topography images of representative spin coated CNF and CNC films (Reprinted with permission of Royal Society of Chemistry, from (Foster et al., 2018) 2018; permission conveyed through Copyright Clearance Center, Inc.) and e) scanning electron micrograph of a self-assembled chiral nematic CNC film (adapted from reference (Guidetti et al., 2016) © 2016 The Authors. Published by WILEY- VCH Verlag GmbH & Co. KGaA, Weinheim) with photographs of iridescent butterflies made from chiral nematic CNC films (adapted from (Blonder et al., 2017)).

Figure 6. Schematic representation of a) a nanocellulose hydrogel and b) a nanocellulose aerogel listing methods to remove water from a hydrogel, and photographs of c) a nanocellulose hydrogel of high solids content (Republished with permission of Royal Society of Chemistry, from (Foster et al., 2018) 2018; permission conveyed through Copyright Clearance Center, Inc.) and d) a nanocellulose aerogel resting on a dandelion (Reprinted (adapted) with permission from (X. Yang & Cranston, 2014) Copyright 2014 American Chemical Society). Panel e) shows a x-ray micro computed tomography scan of a nanocellulose aerogel (Reprinted from (Osorio et al., 2019), Copyright 2019, with permission from Elsevier) and f) a scanning electron micrograph of the mesopore structure of a nanocellulose aerogel sheet. Also shown are photographs of a g) dried nanocellulose foam and h) a wet nanocellulose foam (or aqueous precursor foam)

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Table 1. Bottom-up assembled nanocellulose-only (or primarily nanocellulose) structures: ordered from discrete particles to bulk nanostructured materials including their most common characteristic dimension and approximate size, methods of assembly, current research directions and potential applications.*,**

Assembled Structure	Characteristic Dimension	Methods of Assembly	Current Research Directions and Potential Applications
1. Powders, beads, droplets	Radius (μm)	Spray drying, spray freeze drying, super critical/expanded gas drying, microfluidics	Understanding drying/redispersion of nanocellulose, self-assembly in confined geometries, hybrid/composite materials, master batching, plastic microbeads, chromatography, controlled release, sorbents, components for energy devices
2. Capsules	Radius (nm – mm)	Interfacial reactions or heterogeneous polymerization, layer-by-layer deposition, biofabrication	Controlled drug release, cell scaffolds, pharmaceutical encapsulation, separation technologies
3. Continuous fibres	Cross-section (μm)	Microfluidic devices, flow-focusing channel systems, electrospinning/spraying, wet-spinning, dry spinning, wet-extrusion	Super-strong fibre assemblies, reinforcing fibres for composite materials, textiles
4. Films	Thickness Supported (nm – μm) Free-standing (μm – mm)	Drop casting, dip coating, Langmuir deposition, bar coating, spin coating, (ultra)filtration	Model surfaces, chiral nematic films and templates, barrier and coating materials, advanced functional materials, optical devices, sensors, packaging, templates, membranes, filters
5. Hydrogels (wet)	Crosslink density (mol/m^3)	Physical entanglement, forced gelation, physical/chemical crosslinking	Drug delivery systems, cell and biomolecule transportation systems, biomimetic scaffolds, absorbents, biomedical devices, rheological modifiers for oil and gas extraction, food, cosmetics
6. Aerogels and foams (dry)	Pore size (μm)	Freeze drying, critical point drying (CPD), cryo-templating, pressurized gas expansion (PGX) processing, oven drying	Support/template structures, sorbents, sound and thermal insulators, hygiene products, components for energy devices, tissue engineering scaffolds

*Comprehensive references are provided below in the individual sections as this table is intended as a general overview only. ** The ‘nanocellulose’ in the schematics represents either CNCs or CNFs.

Table 2. Summary of dominant interactions in discrete nanocellulose particles (i.e., assembled powders, droplets and beads) and some key properties.

Preparation Method	Particle Type	Forces/Interactions during Preparation	Forces Holding Dry Particles Together	Internal structure	Average Particle Size
Spray drying ¹	Powder	<ul style="list-style-type: none"> • Water evaporation and water diffusion • Capillary forces 	<ul style="list-style-type: none"> • van der Waals forces • Hydrogen bonding • Possible hornification 	Solid or hollow depending on process parameters	5 to 30 μm
Freeze drying ²	Flaky structure (sometimes ground to powder)	<ul style="list-style-type: none"> • Cryo-gelation/aggregation • Ice crystals prevent hydrogen bonding between lamellae • Minimal capillary forces 	<ul style="list-style-type: none"> • van der Waals forces • Hydrogen bonding • Hydrophobic interactions between lamellar sheets 	Lamellar (flaky) with large pores	<1 μm (lamellae thickness)
Freeze spray drying ³	Beads or foam	<ul style="list-style-type: none"> • Cryo-gelation/aggregation • Minimal capillary forces 	<ul style="list-style-type: none"> • van der Waals forces • Hydrogen bonding • Optional: chemical crosslinking 	Meso and macropores	60 to 120 μm (beads)
Supercritical drying, or critical point drying (CPD) ⁴	Foam (sometimes ground to powder)	<ul style="list-style-type: none"> • No capillary forces or surface tension 	<ul style="list-style-type: none"> • van der Waals forces • Hydrogen bonding • Optional: chemical crosslinking 	Highly porous	N/A
Microfluidics ⁵	Droplets/ Beads (solid and aerogel beads)	<ul style="list-style-type: none"> • Shear • Liquid confinement can induce liquid crystal self-assembly (CNCs) • Upon drying: capillary forces 	<ul style="list-style-type: none"> • van der Waals forces • Hydrogen bonding • Optional: chemical crosslinking 	Randomly aligned/ chiral nematic (CNCs) or porous	>50 μm (droplets) 30 to 200 μm (beads)
Droplet deposition/ cryogelation ⁶	Beads (aerogel beads)	<ul style="list-style-type: none"> • Cryo-gelation/aggregation • Minimal capillary forces due to solvent exchange 	<ul style="list-style-type: none"> • Entanglement (CNFs) • Crosslinking • van der Waals forces • Hydrogen bonding 	Interconnected macropores	1 to 2 mm

¹ Peng et al., 2012; Vehring, 2008; Beck et al., 2012; Khoshkava & Kamal, 2014a; Z. Zhu et al., 2019

² Peng et al., 2012

³ Cai et al., 2014; Jimenez-Saelices et al., 2016

⁴ Peng et al., 2012, 2013; Osorio et al., 2018

⁵ Y. Li et al., 2016; Parker et al., 2016, 2018; Levin et al., 2018

⁶ Z. Liu et al., 2012; Martin et al., 2013; Mohammed et al., 2015; M. Li et al., 2016; Supramaniam et al., 2018

Table 3. Summary of dominant interactions and mechanisms in the formation of capsules.

Preparation Method	Forces/Interactions during Preparation	Examples of How Nanocellulose Shells are “Set”	Sizes
Layer-by-layer deposition ⁷	<ul style="list-style-type: none"> • Electrostatic interactions • Cellulose-cellulose interactions 	<ul style="list-style-type: none"> • Annealing with heat to induce hydrogen bonding • Chemical crosslinking 	Hundreds of nm to μm
Interfacial polymerization or complexation ⁸	<ul style="list-style-type: none"> • Ability of nanocellulose to partition at water-oil interfaces (intermediate wettability) 	<ul style="list-style-type: none"> • Physical entrapment within polymer • Added complexation/ crosslinking agents that react with nanocellulose 	Hundreds of nm to μm
Biofabrication ⁹	<ul style="list-style-type: none"> • Hydrogen bonding • van der Waals forces 	<ul style="list-style-type: none"> • Inherent intra- and intermolecular bonding in BC mat 	μm to cm

Table 4. Summary of the typical preparation methods for nanocellulose-based continuous fibres, the external forces causing nanocellulose alignment, the structural forces at play in the resulting assemblies and the typical diameters of fibres resulting from each method.

Preparation Method	External forces causing nanocellulose alignment	Forces/Interactions during Preparation	Typical diameter of fibres
Solution (wet and dry) spinning ¹⁰	<ul style="list-style-type: none"> • Shear forces from filament extrusion and pulling 	<ul style="list-style-type: none"> • Physical entanglement • Hydrogen bonding 	100 to 500 μm
Electrospinning ¹¹	<ul style="list-style-type: none"> • Electrostatic fields • Shear forces • Physical confinement 	<ul style="list-style-type: none"> • Physical entanglement • Hydrogen bonding 	100 nm to μm
Interfacial complexation ¹²	<ul style="list-style-type: none"> • Shear forces 	<ul style="list-style-type: none"> • Electrostatic interactions (complexation) 	$\leq 1 \mu\text{m}$
Hydrodynamic alignment ¹³	<ul style="list-style-type: none"> • Hydrodynamic flow 	<ul style="list-style-type: none"> • Hydrogen bonding • Electrostatic interactions (gelation) 	$<50 \mu\text{m}$

⁷ Mohanta et al., 2014; Ye et al., 2015; Paulraj et al., 2018⁸ Svagan et al., 2014, 2016; Yoo et al., 2017)⁹ Greca et al., 2018¹⁰ Iwamoto et al., 2011; Walther et al., 2011; Håkansson et al., 2014; S. Chen et al., 2014; Hooshmand et al., 2015; Lundahl et al., 2016¹¹ Ago, Jakes, et al., 2012; Ago, Okajima, et al., 2012; H. Dong et al., 2012; Vallejos et al., 2012; He et al., 2014; H. Wang et al., 2019;¹² K. Zhang & Liimatainen, 2018;¹³ Håkansson et al., 2014; Mittal et al., 2017, 2018, 2019; Nechyporchuk et al., 2019

	<ul style="list-style-type: none"> • Electrostatic repulsion 		
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Table 5. Summary of dominant interactions in nanocellulose films and their properties.

	Forces/Interactions during Preparation	Forces Holding Dry Films Together	Appearance	Thickness	Surface Roughness
Drop coating ¹⁴	<ul style="list-style-type: none"> • Solvent evaporation • Nanocellulose self-assembly • Dewetting 	<ul style="list-style-type: none"> • Hydrogen bonding • van der Waals forces 	Transparent or iridescent (from CNC liquid crystal ordering)	<100 μm	<50 nm
Dip coating ¹⁵	<ul style="list-style-type: none"> • Electrostatics • Specific substrate-cellulose interactions 	<ul style="list-style-type: none"> • Electrostatics • Hydrogen bonding • van der Waals forces 	Transparent	Monolayer: <20 nm Multilayer: 5 nm to 10 μm	<50 nm
Langmuir deposition ¹⁶	<ul style="list-style-type: none"> • Nanocellulose assembly at air-water interface • Electrostatics/ specific interactions with substrate 	<ul style="list-style-type: none"> • Electrostatics • Hydrogen bonding • van der Waals forces 	Transparent	<100 nm	<10 nm
Spin coating ¹⁷	<ul style="list-style-type: none"> • Shear forces (radial) • Solvent evaporation 	<ul style="list-style-type: none"> • Hydrogen bonding • van der Waals forces 	Transparent or iridescent (from thin film interference)	5 nm to 1 μm	<10 nm
Bar coating ¹⁸	<ul style="list-style-type: none"> • Shear forces • Solvent evaporation 	<ul style="list-style-type: none"> • Hydrogen bonding • van der Waals forces 	Transparent to hazy	<1 mm	<10 nm
Filtration ¹⁹	<ul style="list-style-type: none"> • Solvent evaporation 	<ul style="list-style-type: none"> • Hydrogen bonding • Physical entanglement • van der Waals forces 	Transparent, hazy, or white	10 μm to 1 mm	<10 nm

¹⁴ Beck et al., 2011

¹⁵ Cranston, 2013

¹⁶ Habibi et al., 2007; Habibi, Hoeger, et al., 2010; Xhanari et al., 2011; Bertsch et al., 2018

¹⁷ Edgar & Gray, 2003; Kontturi et al., 2003, 2007; Notley, Eriksson, Wågberg, Beck-Candanedo, et al., 2006; Ahola et al., 2008

¹⁸ Hoeger et al., 2011; Lavoine et al., 2014

¹⁹ Henriksson et al., 2008; Österberg et al., 2013; Q. Chen et al., 2014

Spray Coating ²⁰	<ul style="list-style-type: none"> • Shear forces • Solvent evaporation 	<ul style="list-style-type: none"> • Hydrogen bonding • Physical entanglement • van der Waals forces 	White, optically uniform	50 – 300 μm	< 20 nm
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Table 6. Summary of dominant interactions in nanocellulose-only hydrogels, aerogels and foams, and some examples of added crosslinking chemistries (similar to those reviewed by (Liang et al., 2020)).

	Preparation Method	Forces/Interactions during Preparation	Forces Holding Aerogel/Hydrogel Together	Eg. of Covalent Crosslinking Chemistries
Nanocellulose-only Hydrogels	Concentrating CNC/CNF suspension ²¹	<ul style="list-style-type: none"> • Surpassing nanocellulose percolation/entanglement threshold 	<ul style="list-style-type: none"> • Entanglement • van der Waals forces 	N/A
	Electrostatic destabilization of CNC/CNF suspension (pH, salt, temp.) ²²	<ul style="list-style-type: none"> • DLVO destabilization • Decrease in percolation/entanglement threshold 	<ul style="list-style-type: none"> • Entanglement • van der Waals forces 	Amine or carboxyl functionalization (pH responsive)
	Ion-mediated gelation ²³	<ul style="list-style-type: none"> • DLVO destabilization • Decrease in percolation/entanglement threshold • Ionic bridging 	<ul style="list-style-type: none"> • Ionic bridging (with multi-valent ions) 	N/A
	Crosslinking agents or surface functionalization of CNCs/CNFs ²⁴	<ul style="list-style-type: none"> • Chemical crosslinking • Decrease in percolation threshold 	<ul style="list-style-type: none"> • Covalent/ionic bonds 	<ul style="list-style-type: none"> • Hydrazone crosslinking, • paper wet-strength additives (e.g. PAE, Kymene) • Butanetetracarboxylic acid • Maleimide • Epichlorohydrin
	<i>In situ</i> polymerization around CNCs/CNFs ²⁵	<ul style="list-style-type: none"> • Chemical crosslinking 	<ul style="list-style-type: none"> • Covalent bonds • Physical entrapment • Entanglement 	<ul style="list-style-type: none"> • Free radical polymerization

²⁰ Beneventi et al., 2014, 2015; Shanmugam et al., 2017, 2018

²¹ Pääkko et al., 2007; Ure et al., 2011

²² Fall et al., 2011; Nordenström et al., 2017; Lewis et al., 2016

²³ Chau et al., 2015

²⁴ Osorio et al., 2018; X. Yang & Cranston, 2014; Köhnke et al., 2014; McKee et al., 2014; Domingues et al., 2015; García-Astrain et al., 2016; Chau et al., 2016

²⁵ J. Yang et al., 2013; J. Wei et al., 2016

Nanocellulose-only Aerogels	Freeze drying ²⁶	<ul style="list-style-type: none"> • Cryo-gelation/aggregation • Ice crystals prevent hydrogen bonding between lamellae • Minimal capillary forces 	<ul style="list-style-type: none"> • van der Waals forces • Hydrogen bonding • Hydrophobic interactions 	<ul style="list-style-type: none"> • Hydrazone crosslinking • Acetal formation • Citric acid crosslinking
	Critical point drying ²⁷	<ul style="list-style-type: none"> • Rapid dehydration • Hydrogel structure locked into place 	<ul style="list-style-type: none"> • van der Waals forces • Hydrogen bonding • Hydrophobic interactions 	<ul style="list-style-type: none"> • Hydrazone crosslinking • Acetal formation • Citric acid crosslinking
	Pressurized gas expansion (PGX) ²⁸	<ul style="list-style-type: none"> • Rapid dehydration • Hydrogel structure locked into place 	<ul style="list-style-type: none"> • van der Waals forces • Hydrogen bonding 	<ul style="list-style-type: none"> • Hydrazone crosslinks
	Spray freeze drying ²⁹	<ul style="list-style-type: none"> • Cryo-gelation/aggregation • Minimal capillary forces 	<ul style="list-style-type: none"> • van der Waals forces • Hydrogen bonding 	<ul style="list-style-type: none"> • Kymene
Foams	Homogenization (aqueous foams) with drying (dry foams) ³⁰	<ul style="list-style-type: none"> • Ability of nanocellulose to partition at air-water interfaces (with surfactant additives needed) 	<ul style="list-style-type: none"> • Hydrogen bonds • Hydrophobic interactions 	N/A

²⁶ Lavoine & Bergström, 2017

²⁷ Heath & Thielemans, 2010; Liebner et al., 2010

²⁸ Osorio et al., 2018

²⁹ Cai et al., 2014; Jimenez-Saelices et al., 2016

³⁰ Cervin et al., 2013, 2016; Gordeyeva et al., 2016; Z. Hu, Xu, et al., 2016; B. Wei et al., 2017; Mariano et al., 2018