Current Opinion in Colloid & Interface Science 19 (2014) 383–396

Contents lists available at ScienceDirect

Current Opinion in Colloid & Interface Science

journal homepage: www.elsevier.com/locate/cocis

Nanocellulose properties and applications in colloids and interfaces☆

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ARTICLE INFO

Article history:
Received 1 July 2014
Received in revised form 16 October 2014
Accepted 17 October 2014
Available online 30 October 2014

Keywords:
Nanocellulose
Cellulose nanofibrils
Cellulose nanocrystals
Nanoparticles
Self-assembly
Anisotropic particles

ABSTRACT

In this review we introduce recent advances in the development of cellulose nanomaterials and the construction of high order structures by applying some principles of colloid and interface science. These efforts take advantage of natural assemblies in the form of fibers that nature constructs by a biogenetic bottom-up process that results in hierarchical systems encompassing a wide range of characteristic sizes. Following the reverse process, a top-down deconstruction, cellulose materials can be cleaved from fiber cell walls. The resulting nanocelluloses, mainly cellulose nanofibrils (CNF) and cellulose nanocrystals (CNC, i.e., defect-free, rod-like crystalline residues after acid hydrolysis of fibers), have been the subject of recent interest. This originates from the appealing intrinsic properties of nanocelluloses: nanoscale dimensions, high surface area, morphology, low density, chirality and thermo-mechanical performance. Directing their assembly into multiphase structures is a quest that can yield useful outcomes in many revolutionary applications. As such, we discuss the use of non-specific forces to create thin films of nanocellulose at the air–solid interface for applications in nano-coatings, sensors, etc. Assemblies at the liquid–liquid and air–liquid interfaces will be highlighted as means to produce Pickering emulsions, foams and aerogels. Finally, the prospects of a wide range of hybrid materials and other systems that can be manufactured via self and directed assembly will be introduced in light of the unique properties of nanocelluloses.

1. Cellulose nanofibrils (CNF) and nanocrystals (CNC)

Cellulose constitutes the most abundant renewable polymer resource available. As a raw material, it is generally well known for its use in the form of fibers or derivatives in a wide spectrum of products and materials. Cellulose fibrils are structural entities formed through a cellular manufacturing process, cellulose biogenesis, stabilized by hydrogen bonds and van der Waal forces [85,135]. The fibrils contain crystalline and amorphous regions that can be generally separated from the given cellulose source into amorphous and/or crystalline components, by mechanical, chemical or a combination of mechanical, chemical or enzymatic processes [135], yielding cellulose nanofibrils (CNF) or cellulose nanocrystals (CNC). Both, CNF and CNC have been used recently to engineer new materials. The current regulatory efforts and name standardization for these nanocelluloses is a testament of rapidly evolving activity in this field (for instance, CNF has been also referred to as nanofibrillar cellulose NFC, while CNC has been cited as nanocrystalline cellulose NCC, cellulose nanowhiskers, etc.)

The unique properties of nanocellulose (CNF and CNC) such as low density, biodegradability, high aspect ratio, high strength and stiffness have been discussed in several reviews ([45,49,50,67,98,110,135,168], among others). The abundance of OH groups on the surface of cellulose favors the formation of hydrogen bonding, causing the cellulose chains to assemble in highly ordered structures [85]. Hydrogen bonding plays a critical role in the nature of adhesion between nanocellulose with other polymeric materials present in the cell wall of fibers [61].

CNF are fibrils with lengths and widths in the micrometer and nanometer scales, respectively and they readily form networks and structures when dispersed in, for example, aqueous media. CNF is usually prepared by liberation from the constituent fiber matrix and microfiber bundles [12,55,178,198] (Fig. 1). These nanofibrils contain both amorphous and crystalline cellulosic regions [10] and can be differentiated from CNC, which has a smaller aspect ratio and are prepared from fibers or fibrils via acid hydrolysis that degrades the amorphous regions, yielding highly crystalline cellulose nanoparticles [11] (Fig. 1). CNCs have garnered a tremendous level of attention in the materials community. Biopolymeric assemblies, based on CNF and CNC warrant such attention

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☆ Special Volume for Current Opinion in Colloid and Interface Science Volume on "*Synthesis and Novel Applications of Biopolymer and Biologically Derived Particles,*" Krassimir P. Velikov, Orlin D. Velev (Eds.).

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http://dx.doi.org/10.1016/j.cocis.2014.10.003
1359-0294/

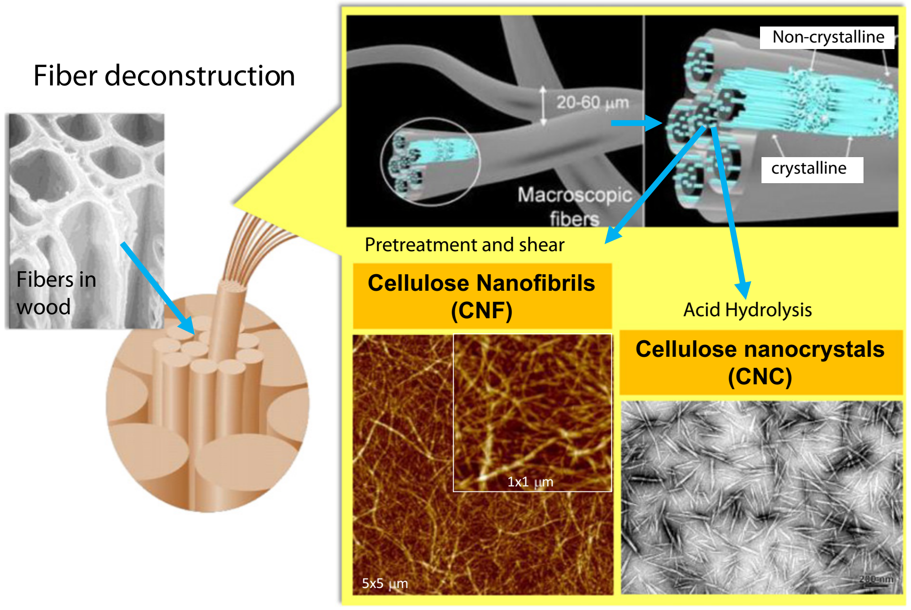

Fig. 1. Schematic illustration of CNF and CNC production from fiber cell walls by mechanical and chemical treatments, respectively (Adapted from [77] with permission from The Royal Society of Chemistry and from Ref. [202] Copyright © 2004 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim).

not only because of their unique physical and chemical properties, but also because of their inherent abundance, renewability and sustainability. They have been the subject of a wide spectrum of research efforts in the development of rheology modifiers, coating components, optical devices, stabilizers of multiphase systems and as reinforcing agents in (nano)composites, all exploiting CNF and CNC intrinsic nanoscale dimensions, morphology, light weight and assembly behavior. Here we highlight advances in nanocellulose utilization taking advantage of their colloid and interfacial behavior and their assembly at interfaces in solid films, emulsions, foams and aerogels.

As in typical colloidal systems, the size, shape and high surface area of nanocelluloses influence the properties in aqueous media, for example, the optical characteristics, stability and rheology of their suspensions. At relatively high concentrations the cellulose nanocrystals self-assemble into a chiral nematic liquid crystalline phase, a property that has been exploited in the preparation of functional films, as discussed in the next section.

2. Nanocellulose structuring in solid films

Orientation and alignment of nanocellulose have received increased attention due to their suitability to form ordered structures, for example, in sensors and in optical devices. CNC is of special interest in such applications due to their aspect ratio, cylindrical shape, rigidity and chiral ordering, all leading to optical effects in aqueous media, in films or in solids templated from such structures. There is still a debate on the origins of the chirality of CNC. The nematic ordering in colloidal dispersions is typically ascribed to the shape-anisotropy of CNC leading to ordered arrangements and thus the ordering has been suggested to originate from chirality of the cellulose chains, the interaction between the chiral surfaces and the twisted morphology of CNC [9,130]. Khandelwal and Windle [91] have presented a thorough investigation on the role of CNC twisting concluding that it affects chirality and chiral alignment of cellulose in several length scales.

Observations regarding the alignment and structuring of CNC dispersions have been extensively reported. In concentrated dispersions CNC forms cholesteric ordering and arrange as a chiral nematic liquid crystal. In such structures the nanoparticles align their long edges parallel to the horizontal plane of the aqueous dispersion and the crystal layers forming a circular structure in the normal direction [154,155]. The direction of the crystal axis is slightly rotated towards the planes below or above causing a helical alignment, with the pitch distance of the system defined as the spacing for the crystal layers on a plane to complete a full rotation. Intrinsic properties such as CNC dimensions and surface charge affect ordering in the dispersed state. For example, short CNC order with a shorter pitch (shorter wavelengths) compared to long CNC. The CNC surface charge originating from sulfate half-ester groups introduced during preparation with sulfuric acid hydrolysis increases the electrostatic repulsion between the particles [54] while increased particle concentration increases the pitch [146]. The chiral structure and assemblies formed by dispersed CNC are also affected by the ionic strength as well as the nature of counter ions [43,44]; for example, the pitch decreases with the increase of the ionic strength [146]. The reader is referred to the review by Abitol and Cranston [2] summarizing related effects.

When CNC dispersions are casted on a solid support to prepare solid films the particles can maintain their alignment to form iridescent structures with chiral nematic ordering [125,126] (see Fig. 2). The films reflect polarized light on a wavelength determined by the pitch of the liquid crystals [46]. Hence, the optical characteristic of the films and the alignment of CNC in the films, as was the case for the aqueous dispersion, can be adjusted by changing the pitch as described above [146]. Reflected light and hence the color of dry films of CNC can also be varied by the thickness of the films, for example, as defined by constructing a multilayer system consisting of alternating deposition of CNC and a cationic polymer [30].

A recent approach reports on ultrasound treatment to change the chiral nematic pitch in CNC suspensions and the resultant dry films [15]. Sonication not only helped to reduce aggregation but was a suitable mean to control the film iridescent color with no need for additives (Fig. 3a). Sonication energy increases the wavelength of the light reflected indicating a change in CNC alignment. External stimuli, electric or magnetic fields can also affect CNC orientation in aqueous dispersions [3,31,33,34,71]. A few efforts have been made to align CNCs into a dry film by shear casting, convective assembly, and under electric or magnetic fields (Fig. 3b and c). An early work by Yoshiharu et al. reported on the preparation of oriented film using a rotating glass vial [194]. The highly ordered film was formed using the CNC dispersion below