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Cellulose Nanocrystals: From Classical Hydrolysis to the Use of Deep Eutectic Solvents

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Abstract

During the last two decades, interest in cellulosic nanomaterials has greatly increased. Among these nanocelluloses, cellulose nanocrystals (CNC) exhibit outstanding properties. Indeed, besides their high crystallinity, cellulose nanocrystals are interesting in terms of morphology with high aspect ratio (length 100–1000 nm, width 2–15 nm), high specific area, and high mechanical properties. Moreover, they can be used as rheological modifier, emulsifier, or for barrier properties, and their surface chemistry opens the door to numerous feasible chemical modifications, leading to a large panel of applications in medical, electronic, composites, or packaging, for example. Traditionally, their extraction is performed via monitored sulfuric acid hydrolysis, leading to well-dispersed aqueous CNC suspensions; these last bearing negative charges (half-sulfate ester groups) at their surface. More recently, natural chemicals called deep eutectic solvents (DESs) have been used for the production of CNC in a way of green chemistry, and characterization of recovered CNC is encouraging.

Keywords: cellulose, sulfuric acid hydrolysis, cellulose nanocrystals, bio-based nanomaterials, deep eutectic solvents

1. Introduction

As renewable and biodegradable nanomaterials, nanocelluloses have raised a huge interest for several decades. Indeed, their natural available and abundant source—the biomass—as well their interesting properties makes them materials of choice for new nanomaterial science in a large panel of applications. Two types of nanocelluloses exist: cellulose nanofibrils (CNF) and cellulose nanocrystals (CNC) differing from each other in their properties as well in their isolation process. As presented in **Figure 1**, the exponential evolution of the number of publications and patents dealing with cellulose nanocrystals confirms the large interest generated by these nanomaterials.

This chapter aims to describe CNC isolation from cellulose using classical or more recent methods, as well as their properties and applications.

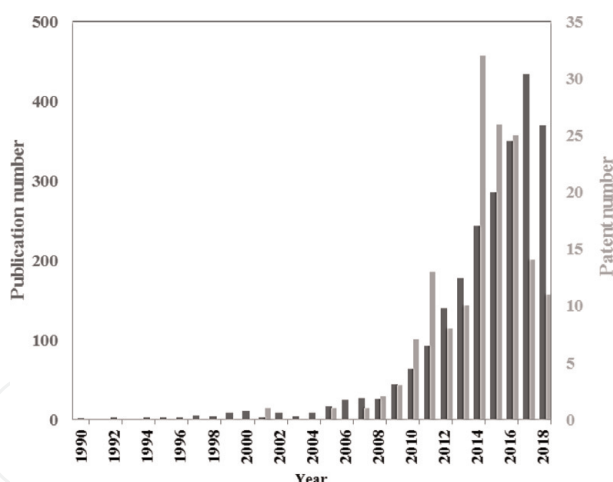


Figure 1.

Noncumulative evolution of the number of publications and patents dealing with CNC (source: SciFinder, April 2019—Descriptors, cellulose nanocrystal, cellulose nanorod, rodlike cellulose, cellulose nanowire, cellulose crystallite, cellulose nanoparticle, cellulose whiskers, nanocrystalline cellulose—Language, English).

2. Cellulose nanocrystals from classical acid hydrolysis

2.1 From cellulose to cellulose nanocrystals

2.1.1 Structure of cellulose

Cellulose can be extracted from a large variety of sources, like wood (the main source), seed fibers (cotton), bast fibers (flax, jute, ramie), some animal species (tunicates), fungi, and fruits, with different cellulose contents [1]. With more than 10^{11} tons of cellulose produced each year [2], with less than 5% is extracted for applications, cellulose is the most abundant polymer on our planet [3]. Historically, cellulose was discovered after being extracted with nitric acid from several plants by the French researcher Anselme Payen in 1838, who characterized the residual compound with chemical formula $C_6H_{10}O_5$ [3, 4]. In 1939, the name “cellulose” was for the first time introduced in the scientific community. After almost 200 years of cellulose extraction, modification, and industrial use, this sustainable and biodegradable polymer is currently used for several applications, from paper and cardboard to biomedical, building, textile, cosmetics, pharmacy, and composites [5, 6]. Indeed, intrinsic properties of cellulose fibers—abundancy, renewability, and availability—as well its fibrillary structure or mechanical properties (strength, flexibility) make them materials of choice for such applications. Indeed, in their natural form, cellulose fibers are included in hemicellulose- and lignin-based matrix like a natural composite and acts as the primary compound of plant cell walls by providing high mechanical properties and maintaining their structure.

Looking more precisely at cellulose structure, it is a linear homopolymer of β -D-glucopyranose ($C_6H_{12}O_6$) units. These anhydro-D-glucose units (AGU) are linked by β -(1-4)-glycosidic linkage, a covalent bonding between equatorial OH group in C4 and C1 carbon atom of the next unit. Every unit is twisted at 180° with respect to its surrounding environment and is in chair conformation, with the three hydroxyl groups in equatorial position. Cellobiose ($C_{12}H_{22}O_{11}$)—the combination of two anhydroglucose units (AGU)—is the repeating unit of cellulose [2, 3]. Cellulose general formula is represented in **Figure 2(a)**.

End groups of cellulose polymer are chemically different: one nonreducing end and one reducing bearing aldehyde group. Note that cellulose degree of

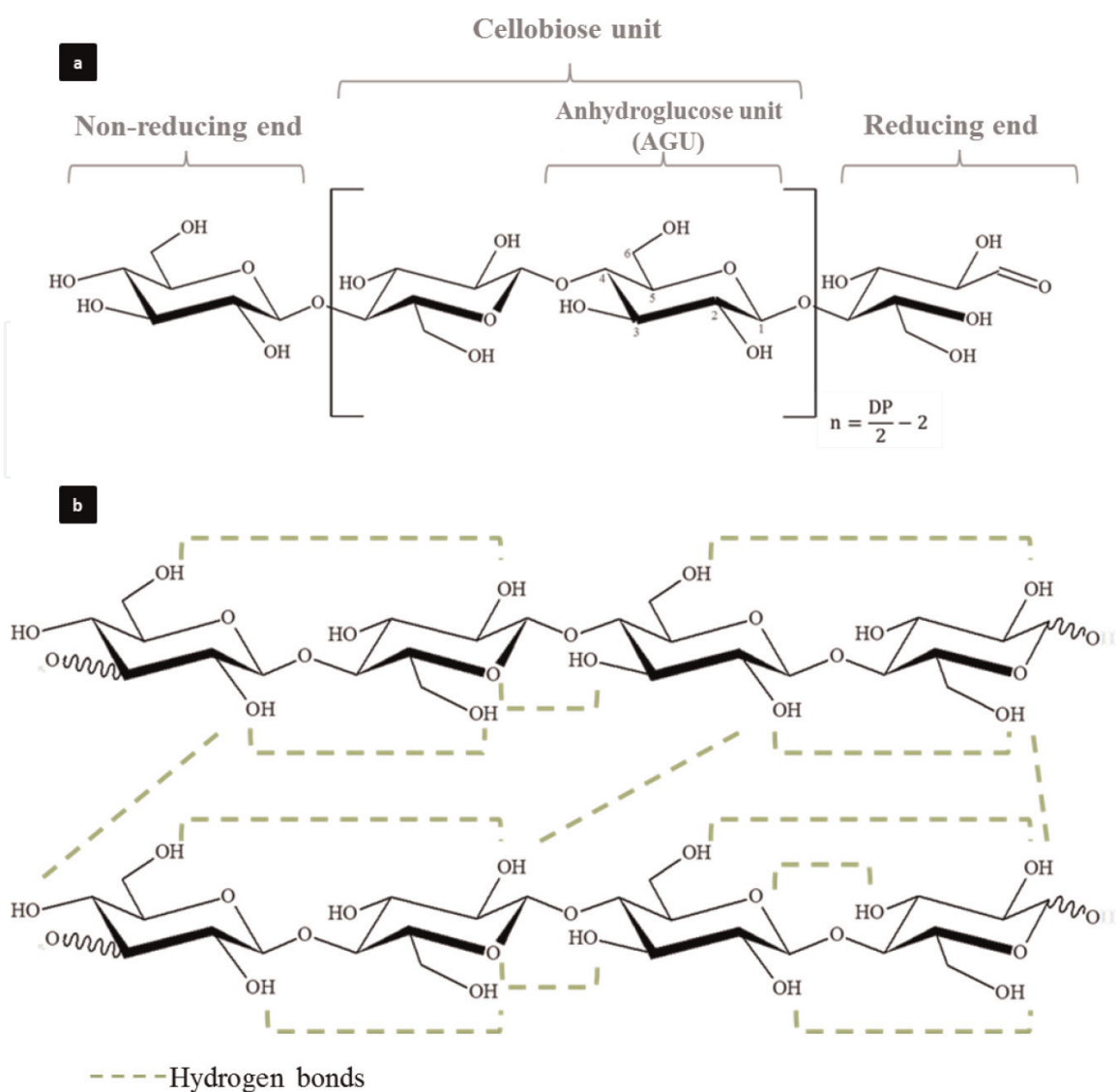


Figure 2.
 (a) Chemical structure of cellulose chain and (b) representation of some hydrogen bonds between two cellulose chains.

polymerization (DP) is expressed as a function of the AGU unit number and depends on the cellulose source and isolation process (e.g., DP between 300 and 1700 for wood pulp and 800–1000 for cotton) [3]. The numerous hydroxyl groups—three per AGU—induce possible functionalization of cellulose as well as intra- and intermolecular hydrogen bonds in and between cellulose chains. These interactions form stabilized and flexible cellulose filaments: the cellulose microfibrils (see **Figure 3(a)**).

Moreover, cellulosic chains are rearranged into different regions: the ordered crystalline and the disordered amorphous ones. Indeed, a cellulose chain can be represented as a crystalline wire connected by amorphous areas (see **Figure 3(b)**). It explains the aggregation of cellulose chains and thus their arrangement into microfibrils. The latter are assembled in bundles, themselves assembled in cellulose fibers, with a semi-crystalline structure. Cellulose crystals present four polymorphs: cellulose I, II, III, and IV. Cellulose I is the most abundant form in nature and is present under cellulose I α and I β forms whose ratio depends on the source and affect cellulose properties [3, 4]. Crystallinity of cellulose varies according to the source and is in the large range of 40–80% [3], leading to highly cohesive fibers. Looking more precisely at the level of the microfibrils, they are composed of elementary fibrils, with a diameter around 5 nm. This general structure provides

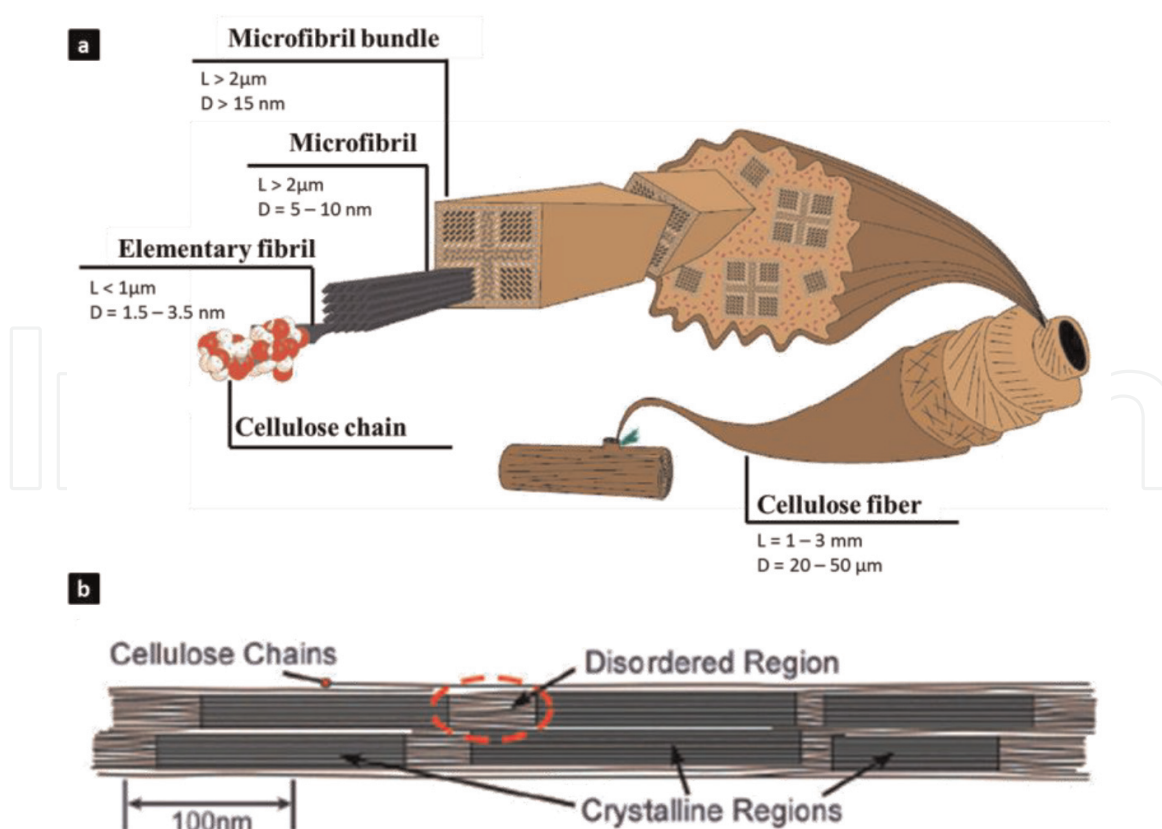


Figure 3. Schematization of a simplified (a) composition of cellulose fiber (extracted and adapted from [7]) and (b) arrangements of crystalline and amorphous domains in cellulose chains (extracted from [8]).

visualization of the different scales inside the cellulose fiber. In addition to being environmentally relevant, cellulose fibers present interesting mechanical properties, ability for further surface modification, low toxicity, low cost, and other properties making them outstanding materials for a lot of traditional as well as innovative applications.

2.1.2 Cellulose nanocrystals from cellulose

Hierarchical structure of cellulose fibers is at the origin of cellulosic nanomaterials, the nanocelluloses, having at least one dimension of nanometric scale as their name suggests. Indeed, from elementary fibrils, two types of nanocellulose can be obtained differing by their isolation procedure, as well by their properties and applications. **Figure 4** shows their different morphologies. Briefly, cellulose nanofibrils are obtained by applying high shear mechanical treatment to a cellulose suspension, and recovered nanofibrils have a length between 500 nm and 10 μm and a width between 5 and 50 nm, according to their preparation method, their source, and potential chemical treatment.

First investigation on cellulose nanocrystal (CNC) was reported by Ranby et al. in 1950 [9, 10]: after carrying out a sulfuric acid hydrolysis to wood cellulose fibers, he observed rodlike particles with two nanoscale dimensions. Indeed, by hydrolyzing cellulose fibers, most of the amorphous parts of the cellulose are disintegrated, and final nanomaterials are highly crystalline. Cellulose nanocrystals have a length between 100 and 500 nm and a width between 2 and 15 nm depending on the cellulose source and the chemical treatment applied. Indeed, even if the use of sulfuric acid for hydrolysis is the most common process, other research groups have investigated the use of other acids, leading to CNC with different properties. In any case, washing steps are essential to remove any chemicals and to well-disperse the

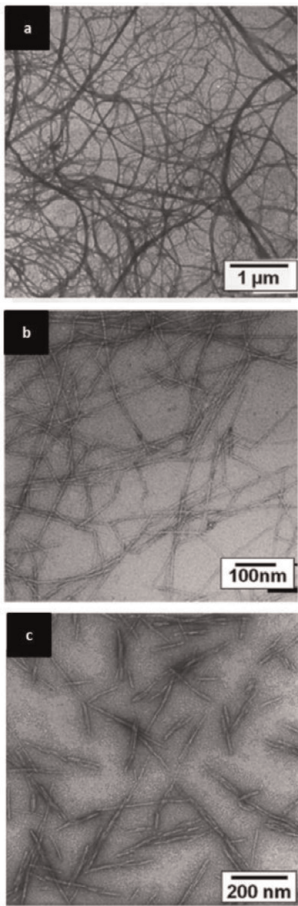


Figure 4.
TEM images of (a) microfibrillated cellulose (MFC), (b) TEMPO-oxidized nanofibrillated cellulose (NFC), and (c) wood cellulose nanocrystals (CNC) (extracted from [8]).

CNC. Concerning their industrialization, around 10 CNC producers can be recorded, with annual production up to 400 tons/year. These productions are significantly lower than those of CNF, but requirement of more chemicals and difficult industrial production steps (washing, dialysis, and sonication) can easily explain this difference. **Table 1** shows the non-exhaustive list of CNC producers

Company	Country	Annual production capacity (tons)
CelluForce Inc.	USA	400
America Process Inc. (GranBio)	USA	200
Alberta Pacific Forest Industries Inc.	Canada	180 (expected in 2021)
Anomera Inc.	Canada	11
Forest Products Laboratory (FPL)	USA	5
University of Maine	USA	4
Blue Goose Biorefineries Inc.	Canada	4
Cellulose Lab	Canada	4
Advanced Cellulosic Material Inc.	Canada	1
FPIInnovations	Canada	0.5
InnoTech Alberta	Canada	0.3
Embrapa/National Nanotechnology Laboratory for Agriculture	Brazil	Pilot
Melodea	Israel	Pilot

Table 1.
Main CNC producers and their location and annual production capacity (data extracted from Refs. [12, 13]).

and their annual production capacity. Note that the leader and pioneer CelluForce® has recently announced new strategy of efficient industrialization [11].

2.2 Cellulose nanocrystals: nanomaterials with interesting properties

2.2.1 Isolation of cellulose nanocrystals

Cellulose nanocrystals are obtained by applying a chemical treatment to cellulose fibers: mild acid hydrolysis. Typically employing strong sulfuric acid H_2SO_4 is going to penetrate into accessible amorphous domains of cellulosic chains and dissolve them to release crystalline parts. Amorphous domains are randomly oriented and arranged inducing a lower density of these domains which are thus more vulnerable to acid hydrolysis [14] and especially to the infiltration of hydronium ions H_3O^+ leading to hydrolytic cleavage of glycosidic bonds. In this sense, Ranby et al. were the first to prove the preparation and the presence of CNCs, the smallest cellulosic building blocks. **Figure 5** synthesizes the different steps of CNC isolation using sulfuric acid hydrolysis.

As previously mentioned, cellulose fibrils are exposed to a sulfuric acid hydrolysis, with defined concentration, temperature, and reaction time. Once amorphous domains are dissolved, a sonication step allows the separation between intact crystalline domains, leading to isolated CNC bearing half-sulfate ester groups on their surface. These charges come from the reaction between sulfuric acid and surface hydroxyl groups of cellulose and induce repulsive forces between negatively charged CNC leading to colloidal stability and dispersion in water [15]. While sulfuric acid is the most common acid used for cellulose fibers hydrolysis, other researches have focused on the use of other organic or mineral acids, like phosphoric acid, hydrobromic acid, or hydrochloric acid [16–19], generally leading to less stable suspension due to the lack of charges at the surface of the CNC. Moreover, the use of deep eutectic solvents is the subject of the next part of this chapter. When

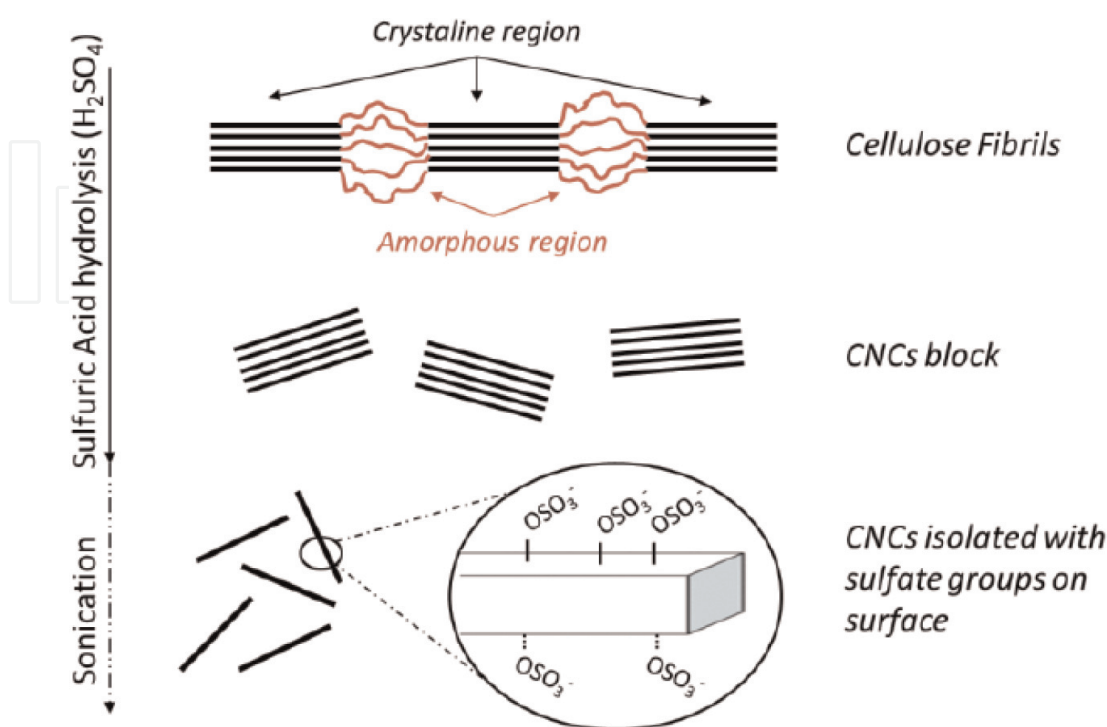


Figure 5. Schematic representation of sulfuric hydrolysis of cellulose fibers (This scheme was extracted from an unpublished work (PhD manuscript of E. Gicquel, 2017)).

cellulosic source is not totally pure, previous steps are required. Indeed, alkali treatment (generally NaOH) and bleaching steps (generally acetic acid, aqueous chlorite) are essential to remove impurities, especially lignin and hemicelluloses when starting directly from biomass or even biowaste. Cellulose content of raw material is thus drastically increased. Note that a lot of studies have investigated the production of CNC from less conventional sources like rice, soy, and others in order to valorize food and organic waste [20, 21]. Final yield and morphology of CNC are really dependent on the cellulosic source and on the hydrolysis conditions. Indeed, optimization and control of the acid hydrolysis have been the subject of several publications. If common parameters are the hydrolysis with 64 wt% sulfuric acid at 40–45°C during about 30 min, it has been proved that variation of one of the parameters can largely influence the reaction yield as well as CNC properties. For example, by increasing of 10 min the time of hydrolysis, it has been shown by Flauzino Neto et al. that crystalline parts are destructed inducing a significant decrease in length [20]. Beck et al. [22] have confirmed this point, admitting that too long times of reaction induce degradation of cellulose but that too short times induce only large and non-dispersible fibers and large aggregates. Only specific reaction times yield to a well-dispersed colloidal suspension of CNC. Chen et al. [17] have confirmed that best yield and CNC properties are obtained with previously mentioned standard conditions. Moreover, the importance of acid concentration relative to cellulose fibers is highlighted too, since a too high concentration could be too drastic and a too low concentration insufficient for the hydrolysis efficiency. At the end of the reaction, mixture media are first diluted with distilled water to quench the reaction, then submitting to several separation steps with centrifugation cycles and filtrations and washed by dialysis against distilled water for several days, in order to remove unreacted compounds and chemicals. In some cases, they use also NaOH to neutralize pH which can modify the crystallinity and the surface ions. After dialysis, a final centrifugation cycle or another filtration process aims to remove aggregates. CNC suspension is finally sonicated in order to well disperse the nanocrystal and obtain colloidal suspension thanks to dimensions and sulfate half ester groups bearing by CNC.

2.2.2 Properties of cellulose nanocrystals

In addition to their nanometric size, CNC are unique biodegradable and renewable nanomaterials. Moreover, they result from a previously described optimized acid hydrolysis applied on abundant sources of cellulose and exhibit many other interesting properties. **Figure 6** summarizes the main CNC properties as well as their applications. Regarding the surface properties of CNC, they generally exhibit half-sulfate ester groups (—SO_3^-) on their surface after being treated with sulfuric acid. Even if the amount of —SO_3^- is pretty low (about 50–200 $\mu\text{mol g}^{-1}$), these negative charges are sufficient to induce repulsive forces between nanomaterials and thus colloidal stability in aqueous media. Moreover, as presented in **Figure 6**, due to isolation process, other charged groups can be present on CNC surface, like carboxyl groups (—COO^-), aldehyde groups (—CHO), and others [23], leading to different charge properties inducing different CNC properties. Moreover, numerous hydroxyl groups (three groups in each AGU units) are at reactive surface sites for the introduction of new functional groups via hydroxyl groups' functionalization. Regarding the physical properties of CNC, they have a low density (1.606 g cm^{-3}), a high aspect ratio length/width (e.g., varying between 10 and 30 for CNC extracted from cotton and around 70 for those extracted from tunicate [15]), and a high surface area (between 150 and 800 $\text{m}^2 \text{g}^{-1}$). Note that all their morphological and surface properties are highly dependent on their source as well

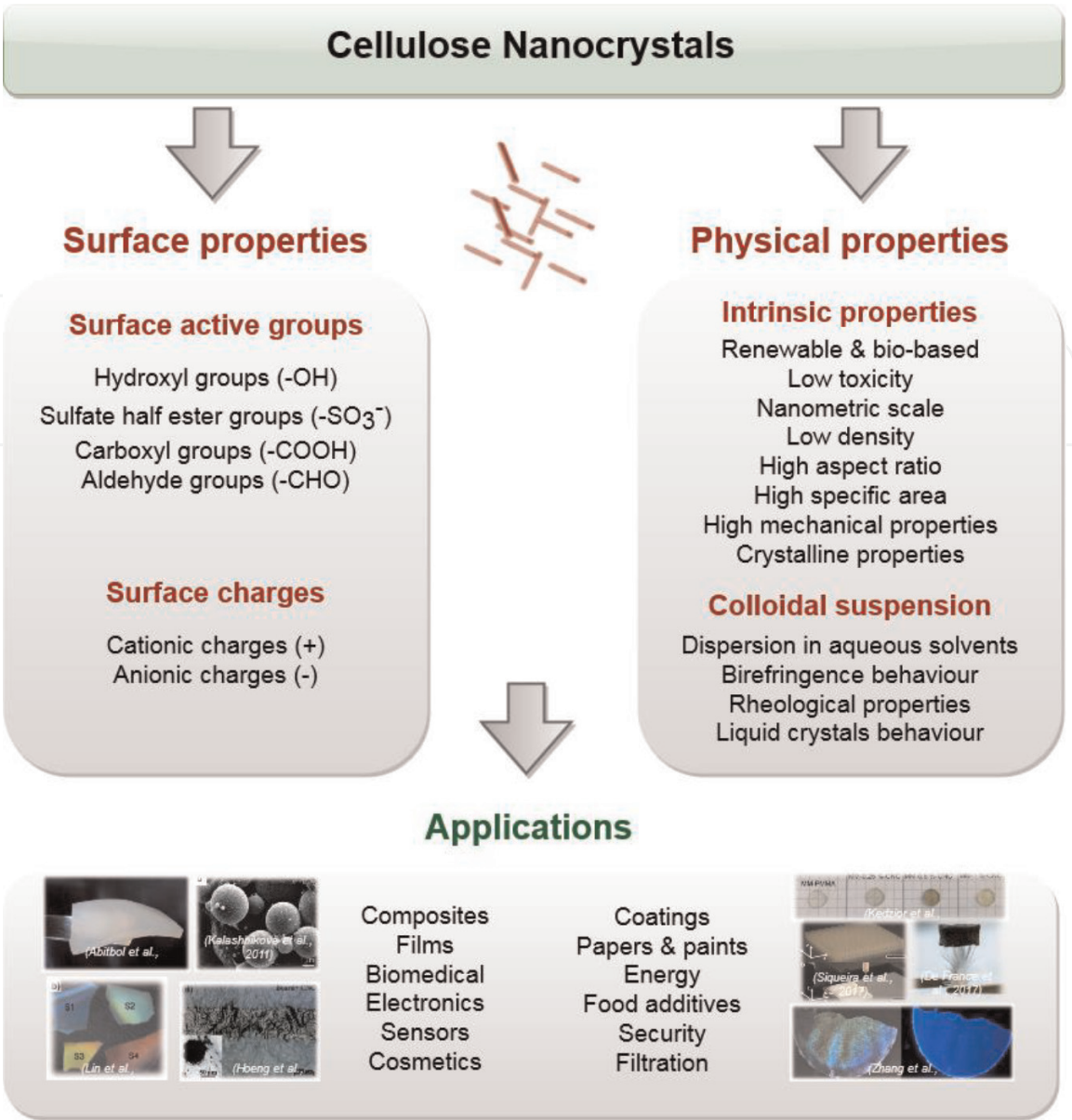


Figure 6.
Main surface and physical properties of cellulose nanocrystals and inherent main applications.

as their isolation process and conditions [8, 22]. Moreover, CNC exhibit highly interesting mechanical properties. Indeed, in addition to their high crystallinity (between 54 and 88% according to the source [24]), their high elastic modulus ($\approx 150 \pm 50$ GPa) and tensile strength ($\approx 7.5 \pm 0.5$ GPa) [25] make them interesting materials as mechanical reinforcement in polymer matrices, for example. For comparison, their mechanical properties are similar to Kevlar® fibers [26] widely used in composite field.

At low solid content (< 3 wt%), due to hydrogen bonds between cellulose chains and thus between each nanocrystals, CNC water suspension is in the form of a translucent gel. Rheological properties of CNC are outstanding and concentration dependent. Indeed, at low concentration (< 3 wt%), CNC suspension presents shear thinning behavior at high shear rate, and at higher concentration (> 3 wt%), the suspension presents shear thinning behavior explained by the nanocrystals alignment in the flow direction at a critical shear rate [27]. Source and isolation of CNC influence these rheological properties too. Besides all these properties, CNC self-organize in ordered structure, especially to form a nematic phase. Revol et al. [28] described in the 1990s this self-organization of CNC in water suspension into stable chiral nematic phases. These last exhibit liquid crystalline properties, which when

added to intrinsic birefringence of CNC induce interesting optical properties. Moreover, when ordered CNC suspension is solvent evaporated and thus solidified in a self-standing film, conserved chiral nematic structure (helicoidal structures) and iridescent behavior of films are observed and monitored by CNC concentration and surface charge as well as suspension sonication [27, 28]. **Figure 7** shows explicit pictures of these rheological and liquid crystalline properties.

All these outstanding surface and physical properties of CNC confirm their high and increasing interest in research and industrial field during the last decades. Although their isolation and characterization are currently well-advanced and optimized, application fields are at the center of ongoing researches, as described in the following part.

2.2.3 Various applications of cellulose nanocrystals and their industrialization

As exposed in **Figure 6**, CNC found applications in various fields. Indeed, thanks to their outstanding morphological, mechanical, and rheological properties as well as their colloidal stability and high surface reactivity. All these properties added to their biodegradability and renewability make them highly interesting and innovative materials with many potential applications. **Table 2** summarizes CNC applications and corresponding exploited properties, as well as some literature references.

Nanocomposite field is an emerging research area which finds applications in several domains like food packaging, medical devices, and building. Renewable aspect of CNC is particularly interesting since it correlates with the development of bio-based and biodegradable polymers as mentioned in the first part of this chapter. Moreover, these same properties are just as interesting in other application fields, from coatings, electronics, filtration, and biomedical devices to energy, cosmetics, and security. Note that for applications that may enter in contact with food or human body and for any industrialization, toxicity of CNC is a key challenge to investigate. Indeed, even if cellulose is known to be a nontoxic polymer, CNC are nanomaterials—and the “nano” prefix can be frightened for media and population

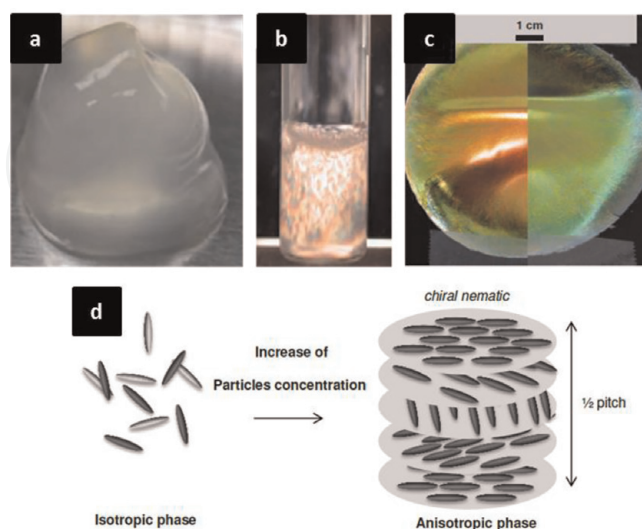


Figure 7. (a) Translucent gel-like CNC suspension at 15 wt% in water (extracted from [57]), (b) birefringence with shear-inducing observed for an aqueous CNC suspension at 0.6 wt% in cross-polarized light (extracted from [57]), (c) solvent-casted CNC film in diffuse light, normal to the surface (on the left part) and oblique to the surface (on the right part) (extracted from [29]), and (d) schematic representation of CNC orientation in isotropic and anisotropic phases (This scheme was extracted from an unpublished work (PhD manuscript of R. Bardet, 2014)).

Market	Applications	Exploited CNC properties	References
Composites/films	Nanocomposites Flexible packaging Optical films	High mechanical properties Filmogenic properties Morphology	[30, 31]
Coatings/paints/adhesives	Coatings for flexible packaging	Morphology Rheological properties	[32, 33]
Electronics/sensors	Flexible electronics E-paper Piezoelectric sensors	Electrical insulating Piezoelectric properties Surface area	[34–36]
Filtration	Mesoporous films and membranes	High specific surface area High mechanical properties Hydrophilicity	[37]
Biomedical	Biocomposites for bone/tooth replacement Drug delivery Protein immobilization Wound dressings Biosensors	Low toxicity Colloidal stability High mechanical properties Surface reactivity	[38, 39]
Energy	Supercapacitors Flexible batteries	Strength Large surface area	[40]
Cosmetics	Hydrogels and foams	Colloidal stability Emulsion interfacial stabilization	[41, 42]
Security	Security papers and inks	Iridescent properties Morphology	[43]

Table 2.
Main market applications of CNC and corresponding properties and literature references.

—with specific morphology and surface properties. A recent review of Roman et al. [44] explored CNC toxicity. Results of this study correlate with previous results of Lin et al. [39] and Kovacs et al. [45], demonstrating that CNC are not toxic by ingestion or dermal contact and for aquatic organisms. However, pulmonary and cytotoxicity are less ideal since their toxicity depends on CNC properties and form (especially if they are in powder form, since they are more volatile). In any case, toxicity of CNC is low, especially when they are in wet-state or in composites, films, or coatings, for example, not constraining development of new CNC-based products.

3. Deep eutectic solvent for cellulose nanocrystals preparation

As described in the first part of this chapter, the traditional methods used to obtain cellulose nanocrystal consist of strong acid hydrolysis, enzymatic hydrolysis, or oxidation reactions. These treatments allow to hydrolyzing the amorphous regions in cellulose chains, and they are often followed by mechanical or ultrasonic treatment to homogenize the suspension. However, these methods use toxic chemicals and are difficult to industrialize.

Type	Component 1	Component 2
I	Quaternary ammonium salt	Metal chloride
II	Quaternary ammonium salt	Metal chloride hydrate
III	Quaternary ammonium salt	Hydrogen bond donor
IV	Metal chloride hydrate	Hydrogen bond donor

Table 3.
The four DES families.

Deep eutectic solvents (DESs) are a new class of green organic solvents; they are in the continuity of molten salt and ionic liquid solvent, but they are less toxic and easier to use. A deep eutectic solvent is composed of at least two compounds, a Lewis or Brönsted acid and a base. According to its constituents, a DES can be classed in one of the four existing categories listed in **Table 3**.

The association of these compounds with a specific ratio forms an eutectic mixture with a melting temperature far below than of its constituents.

In the case of type III, it is accepted that the self-association occurs via hydrogen bonding interactions between the hydrogen bond donor and the hydrogen bond

Cellulose source	Pretreatment (DES, etc.)	Molar ratio	Time	Temp. (°C)	Yield (%)	Dimension (nm)	References
Dissolving pulp	ChCl:OAD	1:1	2 h	100	68	l = 390 ± 25 d = 13.6 ± 1.1	[49]
		1:1	2 h	120	73	l = 353 ± 16 d = 13.8 ± 0.7	
	ChCl:p-t	1:1	2 h	60	70		
	ChCl:levulinic acid	1:2	2 h	100	88		
Dissolving pulp	ChCl:OAD	1:1	30 min	100		l = 50–350 d = 3–8	[50]
Cotton fiber	ChCl:OAD	1:1	1 h	100	79.8	l = 194.1 d = 9.6 ± 2.9	[51]
	ChCl:OAD	1:2	1 h	100	80.0	l = 152.7 d = 6.1 ± 1.2	
	ChCl:OAD	1:3	1 h	100	81.6	l = 122.4 d = 4.7 ± 2.2	
Cotton fiber	ChCl:OAD Microwave assisted	1:1 800 W	3 min	80	74.2	l = 100–350 d = 3–25	[52]
		1:1 800 W	3 min	90	62.4		
		1:1 800 W	3 min	100	57.8	l ≈ 150 d < 17	
Bleached eucalyptus kraft pulp	ChCl: OAD + catalysis, FeCl ₃ .6H ₂ O (mmol/gDES)	1:4 0	7 h	80	86	l = 5152 ± 3328	[53]
		1:4 0.15	6 h	80	73	l = 270 ± 92	
		1:4 0.3	6 h	80	71	l = 258 ± 54	
		1:1 0.15	6 h	80	88	l = 5726 ± 3856	
Bleached birch Kraft pulp	AH:glycerol	1:2	10 min	70		d = 5.7 ± 1.3	[54]
Empty fruit bunch	ChCl:citric acid	1:2	6 h	85		l = 25–37	[55]
Dissolving pulp	GH:APA	1:2	24 h	Room T	80	d = 5.6 ± 1.4	[56]

ChCl, choline chloride; OAD, oxalic acid dihydrate; t, toluenesulfonic; AH, aminoguanidine hydrochloride; GH, guanidine hydrochloride; APA, anhydrous phosphoric acid.

Table 4.
Overview of the different DES pretreatments tested for cellulose nanocrystals obtention.

acceptor. The strong hydrogen bonds between the different compounds prevent the crystallization of each product and decrease the melting point of the mixture below room temperature [46]. Type III DESs are easy to obtain by simply mixing the compounds with the right ratio at a temperature higher than the melting point during 1 h. The mixture obtained is homogenous and transparent and has a low vapor pressure. However, the main drawback of deep eutectic solvents is their price. Nevertheless, some studies show that it is possible to recycle them between

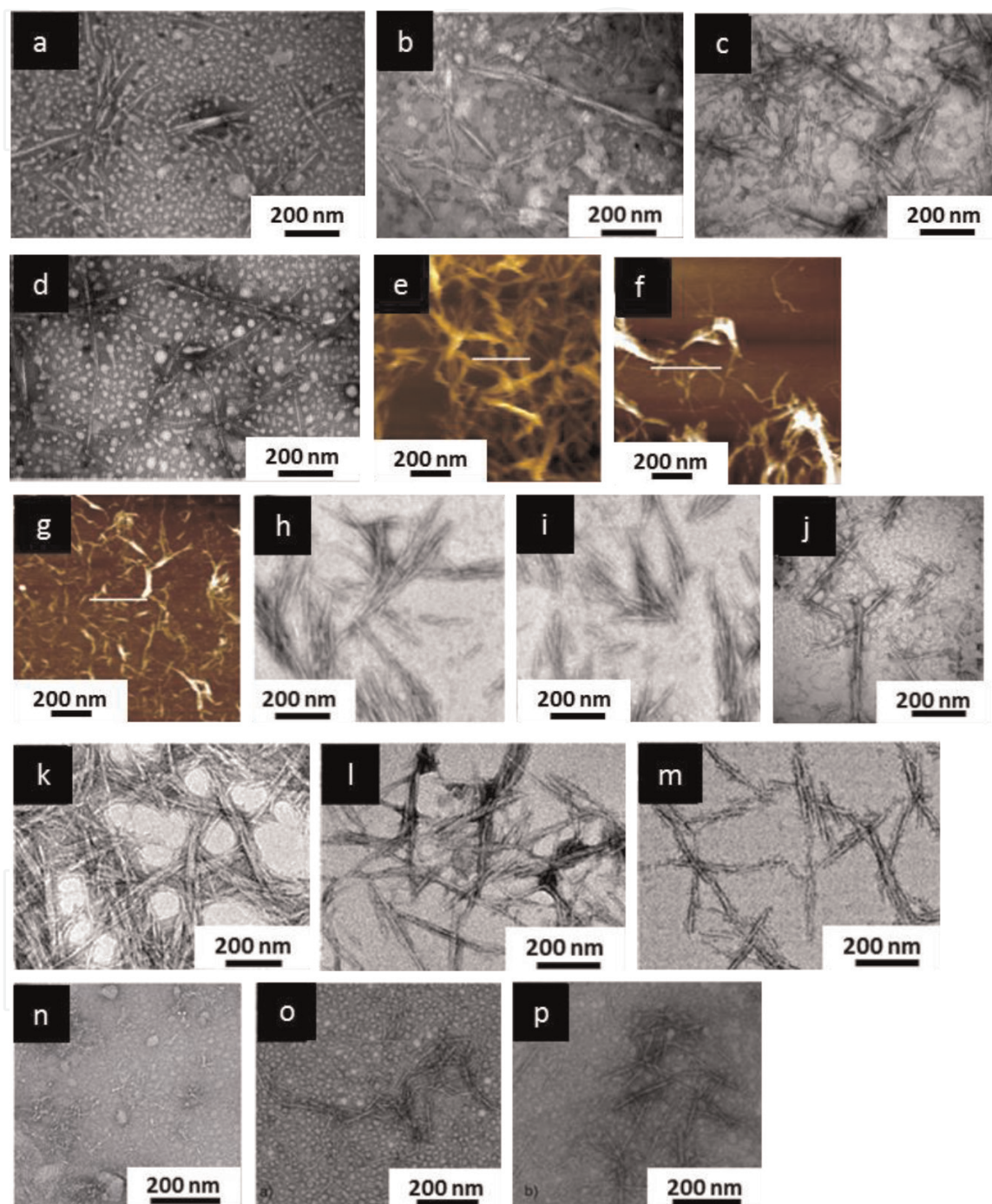


Figure 8.

Transmission electron micrographs of CNCs using DES pretreatment: (a) ChCl:OAD 1:1, 2 h–100°C [49]; (b) ChCl:OAD 1:1, 4 h–100°C [49]; (c) ChCl:OAD 1:1, 6 h–100°C [49]; (d) ChCl:OAD 1:1, 2 h–120°C [49]; (e) ChCl:OAD 1:1, 1 h–100°C [51]; (f) ChCl:OAD 1:2, 1 h–100°C [51]; (g) ChCl:OAD 1:3, 1 h–100°C [51]; (h) ChCl:OAD 1:4 + cat:FeCl₃·6H₂O (0.15 mmol/gDES), 6 h–80°C [53]; (i) ChCl:OAD 1:4 + cat:FeCl₃·6H₂O (0.3 mmol/gDES), 6 h–80°C [53]; (j) ChCl:OAD 1:1, 30 min–100°C [50]; (k) microwave-assisted ChCl:OAD 1:1, 3 min–80°C [52]; (l) microwave-assisted ChCl:OAD 1:1, 3 min–90°C [52]; (m) microwave-assisted ChCl:OAD 1:1, 3 min–100°C [52]; (n) guanidine hydrochloride:anhydrous phosphoric acid 1:2, 24 h room temperature [56]; (o) aminoguanidine hydrochloride:glycerol 1:2, 10 min–70°C [54]; (p) aminoguanidine hydrochloride:glycerol 1:2, 10 min–70°C [54].

three and five times depending on the DES components and the usage [47]. Moreover, a subclass of DESs, named natural deep eutectic solvents (NADES), is formulated using bio-based compounds; these solvents are environmentally friendly and their price can be lower.

DESs and NADES can be helpful in organic chemistry; indeed they can replace some toxic organic solvents; Zdanowicz summarized all their possible application domains for polysaccharide processing [48]. Among all these applications, one of them consists of the use of type III DESs as an acidic hydrolytic solvent for cellulose nanocrystal obtention.

This principle has been studied for the first time by Sirviö et al. [49]; they manage to extract individual nanocrystals using a choline chloride: oxalic acid dihydrate treatment from dissolving pulp. Different DESs had been prepared in different ratios and studied to hydrolyze the amorphous part of cellulose fibers from different sources: an overview of these treatments is summarized in **Table 4**.

In 2016, Sirviö tried three different DESs with choline chloride as hydrogen bond acceptor and oxalic acid (anhydrous or dihydrate), p-toluenesulfonic acid monohydrate, and levulinic acid as hydrogen bond donors [49]. Only DESs composed of choline chloride/oxalic acid dihydrate (ChCl:OAD) with a 1:1 molar ratio are allowed to obtain, after mechanical disintegration and CNC suspension. Different batches were prepared using different times and temperatures (**Figure 8(a–d)**). Cellulose nanocrystals obtained after 2 h of treatment at 120°C had the highest aspect ratio with a mean length of 353 ± 16 nm and diameter of 9.9 ± 0.7 nm (**Figure 8d**). The study showed that the final width of CNCs depends on the pretreatment temperature [57].

Ling et al. studied the effect of ChCl:OAD treatment on cellulose nanocrystal structure [51]; three molar ratios were chosen 1:1, 1:2, and 1:3, under two temperatures 80 and 100°C. Cellulose nanocrystals suspensions were obtained in every case (**Figure 8(e–g)**). Lower crystallinity and lamellar structures were observed for CNCs with lower acid content, and hydrogen bonds were more broken with higher acid ratio (ChCl:OAD = 1:3) during the DES treatment. Moreover, these CNCs obtained were better dispersed and had a higher aspect ratio.

In order to decrease the treatment temperature and increase the CNC yield, Yang et al. proposed to add a catalyst (FeCl_3) during the DES treatment [53]. They found out that the optimum conditions for the treatment were 80°C and 6 h using a deep eutectic solvent composed of choline chloride, oxalic acid dihydrate, and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ with a molar ratio of 1:4.43:0.1. Cellulose nanocrystals with a length between 50 and 300 nm and a diameter range of 5–20 nm were isolated from eucalyptus kraft pulp with a yield of 90% (**Figure 8(h–i)**).

Using ChCl:OAD (1:1) DES, Laitinen et al., in 2017, were able to obtain a CNC suspension after 30 min of pretreatment at 100°C and a microfluidizer treatment. The cellulose nanocrystals obtained had a low charged content and could be used as effective oil–water Pickering stabilizers (**Figure 8(j)**) [50].

In 2017, interesting work was published by Liu et al. [52]. They reported an ultrafast fabrication of CNCs using the DES ChCl:OAD (1:1) assisted by microwave pretreatment. In only 3 min, the CNCs obtained had diameters between 100 and 25 nm and lengths between 100 and 350 nm (**Figure 8(k–m)**). The yield was 74.2%, and the nanocrystals' crystallinity was higher than 82%.

Another DES composed of choline chloride and citric acid with a molar ratio of 2:1 allowed Ibrahim et al., in 2018, to hydrolyze lignocellulosic materials and to obtain cellulose nanocrystals [55].

Some deep eutectic solvents can dissolve cellulose; it is the case for the DESs composed of guanidine hydrochloride and anhydrous phosphoric acid (1:2). This

solvent was studied by Sirviö to treat dissolving pulp during 24 h and then regenerate it into cellulose nanoparticles [56] (**Figure 8n**)).

In addition to the hydrolyzation of cellulose amorphous part, some DESs can simultaneously chemically modify the CNC surface. For example, Li et al. obtained cationic nanocrystals using aminoguanidine hydrochloride and glycerol mixture with a molar ratio of 1:2 (**Figure 8(o-p)**) [54].

4. Conclusion

The aim of this chapter was to provide an overview of cellulose nanocrystals and their production by various hydrolysis procedure.

Traditionally extracted from multiple cellulose sources via sulfuric acid hydrolysis, these cellulosic nanomaterials are pioneering for a wide range of applications, briefly introduced in this chapter. Such hydrolysis process has allowed the industrialization of this cellulose nanocrystals since 2011. However, in current context, the development of green chemistry is crucial in this research field, and new alternative process are expected.

In order to support this sustainable strategy, the use of natural deep eutectic solvents for the production of cellulose nanocrystals in mild condition has been very recently developed with interesting and encouraging results.

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Conflict of interest

The authors declare no conflict of interest.

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