

Recent progress in cellulose nanocrystals: sources and production

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Abstract:

Cellulose nanocrystals, a class of fascinating bio-based nanoscale materials, have received a tremendous amount of interest both in industry and academia owing to its unique structural features and impressive physicochemical properties such as biocompatibility, biodegradability, renewability, low density, adaptable surface chemistry, optical transparency, and improved mechanical properties. This nanomaterial is a promising candidate for applications in fields such as biomedical, pharmaceuticals, electronics, barrier films, nanocomposites, membranes, supercapacitors, etc. New resources, new extraction procedures, and new treatments are currently under development to satisfy the increasing demand of manufacturing new types of cellulose nanocrystals-based materials on an industrial scale. Therefore, this review addresses the recent progress in the production methodologies of cellulose nanocrystals, covering principal cellulose resources and the main processes used for its isolation. A critical and analytical examination of the shortcomings of various approaches employed so far is made. Additionally, structural organization of cellulose and nomenclature of cellulose nanomaterials have also been discussed for beginners in this field.

Keywords: cellulose nanocrystals, natural resources, pretreatments, isolation processes

30 **1. Introduction**

31 The emergence and development of nanotechnology, a field expected to revolutionize
32 several aspects of human life, offer a new approach to education, learning, innovation and
33 governance. Currently, the disciplines of nanoscience and nanotechnology have been
34 emphasized for exceptional focuses by various funding agencies and governments^{1,2}. In 2009,
35 the worldwide market for products incorporating nanotechnology was found to be attained a
36 value of about USD 254 billion and this number was expected to double each 3 years until
37 2020, when this value could reach USD 3 trillion^{3,4}. Ever since the successful production of
38 nanocrystalline materials by Gleiter in the 1980s⁵, nanomaterials have seen a rapid
39 development having wide range of applications in chemistry, physics, catalysis, material
40 science, biomedical science, etc.⁶. Seeing the current emphasis on green chemistry and
41 chemical processes, the application of the fundamental principles of green chemistry to
42 nanotechnology and nanomaterials may extend their appeal to consumers and open up new
43 markets for renewable materials for advanced applications. Indeed, materials from bio-based
44 resources have attracted immense research interest in recent years as a result of their very high
45 potentials for fabricating several high-value products with low impact on the environment⁷⁻¹⁴.
46 Effective utilization of various nature-based nanomaterials offers certain ecological
47 advantages, extraordinary physicochemical properties and high performance to name a few.
48 However, full employment of the intrinsic properties of starting nanoscale materials
49 necessitates continuous development of robust and versatile isolation, synthetic and
50 processing procedures to well control assembly over a variety of length scales.

51 Among various natural materials, cellulose holds a crucial position in abundant organic
52 raw materials. It is considered as a virtual inexhaustible source of feedstock meeting the
53 increasing demand for green and biocompatible products^{13, 15, 16}. Exploitation of cellulose has
54 been known since the beginning of civilization, from clothes and paper to use as construction

55 materials, yet over the last few decades, it has attracted much attention and growing interest
56 owing to its abundancy and versatility when processing on the nanoscale in the form of
57 cellulose nanomaterials^{3, 8, 17-25}. Employing various reaction strategies, different types of
58 nanomaterials can be extracted from cellulose owing to its hierarchical structure and
59 semicrystalline nature^{20, 21, 25}. One of the most recent robust trend, on an international scale, is
60 to extensively focus on the extraction of nanostructured materials and nanofibers of cellulose
61 with dimensions in tens of nanometer and to employ their improved properties to develop
62 innovative high value materials with new and advanced functionalities. Several forms of such
63 cellulose nanomaterials can be prepared using various routes and from different cellulose
64 sources^{3, 26-32}.

65 Recently, highly crystalline nanoscale material, namely cellulose nanocrystals (CNCs), has
66 garnered tremendous level of attention from many research communities^{3, 11, 22, 33-36}, which
67 can be confirmed by the increasing number of scientific publications in the field over the past
68 decade, as shown in Fig. 1. CNCs are broadly needle-shaped nanometric or rod like particles
69 having at least one dimension < 100 nm, and exhibit a highly crystalline nature. They can be
70 produced from diverse starting materials that include algal cellulose, bacterial cellulose, bast
71 fibers, cotton linters, microcrystalline cellulose, tunicin, and wood pulp^{3, 8, 11, 22, 33-42}. These
72 nanocrystals impart attractive combinations of biophysicochemical characteristics such as
73 biocompatibility, biodegradability, light weight, non-toxicity, stiffness, renewability,
74 sustainability, optical transparency, low thermal expansion, gas impermeability, adaptable
75 surface chemistry, and improved mechanical properties^{43, 44}. These nanocrystals can also
76 substitute some petrochemical-based products and are more economic than the similar high
77 performance nanomaterials. Variations in the CNCs extraction process lead mainly to
78 different CNCs properties. One of the main shortcomings concerning the employment of
79 CNCs in commercial applications is related to their efficient fabrication at affordable quantity

80 and quality. Acid hydrolysis is one of the most frequently used technique to prepare CNCs
81 from various cellulose based starting materials and employs strong acids namely sulfuric and
82 hydrochloric acids ^{11, 22, 23, 25, 35}. Recently, other mineral and organic acids have also been
83 utilized to produce CNCs ^{8, 38, 39, 45-47}. Several other preparations approaches have been
84 developed, such as enzymatic hydrolysis ⁴⁸⁻⁵¹, mechanical refining ⁵²⁻⁵⁴, ionic liquid treatment
85 ^{48-51, 55-58}, subcritical water hydrolysis ^{32, 59}, oxidation method ⁶⁰⁻⁶³ and combined processes ⁶⁴⁻
86 ⁶⁸. Keeping in mind the different synthesis strategies, one of the prime objectives of this
87 review is to summarize and emphasize the up-to-date procedures employed to extract CNCs
88 showing their advantages and drawbacks, that we believe will provide a strong base for the
89 future development in this emerging area of research.

90 Among various materials, functional nanomaterials are of particular importance as they
91 permit the formation of novel materials with new or enhanced properties by combining
92 multiple ingredients and exploiting synergistic effects, such as physicochemical, catalytic,
93 selective permeation, electronic, mechanical, optical, magnetic, or bioactivity, adsorption, etc.
94 With a special functionality or numerous remarkable functions, functional nanomaterials
95 present an imperative class of materials having high potential for advanced applications. To
96 expand the application fields of CNCs, various approaches have been used to improve the
97 interface properties ²³. Previously various covalent/ non-covalent chemical modification
98 techniques have been used to develop new surface modified CNCs with outstanding
99 properties⁶⁹⁻⁷¹. One of the procedure is to covalently graft hydrophobic molecules through
100 reactions with hydroxyl groups on the CNCs surface, such as esterification, acetylation,
101 silylation, and polymer grafting. Another approach is to utilize non-covalent interactions by
102 incorporating compatibilizing agents into composites, including surfactants, polymers, and
103 counter ion salts.

104 The production of CNCs and their surface modifications have become one of the most
105 intensely investigated areas of CNCs research on nanocomposites, since this nanoscale
106 material offers a unique combination of high physicochemical properties even at low filler
107 content, environmental benefits, and can surpass other candidates such as Kevlar, Boron
108 nanowhiskers, carbon nanotube, and carbon fibers, as shown in Table 1. However, most of
109 them are not biodegradable, and during the past couple of decades, the interest for
110 nanomaterials derived from renewable sources has increased ⁷². CNCs display intrinsically
111 high aspect ratios and large surface area owing to their nanoscale size that renders them ideal
112 candidates for nanocomposites. Specifically, greater interfacial area and strong interactions
113 among the reinforcing filler and the polymer matrix are known to give rise to nano-
114 confinement effects that enable substantial improvement of mechanical properties.
115 Nanocomposites reinforced with CNCs have reliably showed good properties including
116 multifold increase in the elastic modulus and significant shifts in glass transition, while at the
117 same time preserving excellent optical properties of the host polymer and contributing to
118 stimuli-responsive mechanical properties and shape memory behavior ^{22, 33, 44, 73}. Fig. 1
119 reveals that such investigations on CNCs are increasing rapidly with very high number of
120 research articles published on CNC-based composites. The next generation of nanocomposites
121 requires the manufacturing of products and materials that have the capability to surpass the
122 current academic and industrial expectations. Whether it is for automotive, medicine,
123 building, marine, or aerospace, such materials must possess advanced performances, lower
124 cost, reliable and adaptable properties. Other potential applications of CNCs include barrier
125 films, flexible displays, antimicrobial films, biomedical implants, transparent films,
126 pharmaceuticals, drug delivery, templates for electronic components, fibers and textiles,
127 separation membranes, supercapacitors, batteries, and electroactive polymers, among many
128 others ^{3, 11, 22, 23, 25, 33, 43, 44, 74}.

129 Several reviews^{3, 11, 13, 19, 22-25, 33-36, 43, 44, 69, 75-81}, books^{8, 12, 20, 42, 82, 83} and patents²¹ have
130 been published in the last two decades covering various aspects related to CNCs, including
131 isolation processes, characterization, chemical modification of surfaces, self-assembly of
132 suspensions, CNCs-containing nanocomposites and processing.

133 However, the focus of the current article is different from the published literature and
134 where appropriate, specific points covered in published literature are summarized and/or
135 referenced out to the corresponding paper/book/patent. This review firstly provides an
136 overview on the recent research developments on principal cellulose sources followed by the
137 main procedures used for its isolation in details. The extraction methodologies of CNCs are
138 considered and discussed as well. In addition, we have also provided a critical and analytical
139 examination of the shortcomings of various approaches employed so far.

140 **2. Structural organization of cellulose**

141 Cellulose (a carbohydrate polymer) is the most abundant renewable polymer in nature and
142 represents about fifty percent of natural biomass having an yearly production estimated
143 around 10 tons^{11, 71}. A number of review articles have already summarized the state of current
144 knowledge on this fascinating and innovative polymer^{8, 11, 15, 22, 25, 84}. Broadly, cellulose is a
145 fibrous, tough, water-insoluble substance that plays a crucial role in preserving the structure of
146 natural fibers. Cellulose ($(C_6H_{10}O_5)_n$; $n = 10\ 000$ to $15\ 000$, where n is depended on the
147 cellulose source material) is defined as long polymer chain of ringed glucose molecules and
148 has a flat ribbon-like conformation^{20, 85}. It is a linear natural polymer consisting of 1,4-
149 anhydro-D-glucopyranose units as depicted in Fig. 2. Through natural synthesis, the cellulose
150 does not exist as an individual entity but several chains of cellulose molecules (30 to 100
151 chains) could be packed together during extended chain conformation via van der Waals
152 forces and hydrogen bonds to form the basic unit of cellulose fibers, which are elementary
153 fibrils (protofibrils) at nano-scale^{22, 33, 86}. These protofibrils are further gathered by

154 intermolecular and intramolecular hydrogen bonding into the hierarchical microstructures,
155 which usually recognized as microfibrils that display cross dimensions ranging from 2 to 20
156 nm^{20, 25}. Depending on inter- and intramolecular interactions, molecular orientations, method
157 of extraction and treatment, cellulose can exist as various polymorphs or allomorphs^{15, 22, 25}.

158 As a result of the equatorial positions of hydroxyls, three hydroxyl groups (OH) that
159 protrude laterally along the cellulose chain have been reported to be easily available for H-
160 bonding^{11, 25, 33}. The complex and strong network of H-bonds between the hydroxyl groups of
161 cellulose chains can arrange and stabilize the cellulose molecules into a highly organized
162 structure through crystalline packing. It gives rise to the structures with slender and nearly
163 endless crystalline rods along the microfibril axis^{23, 87}. However, another part of cellulose
164 molecules that could not be stabilized laterally through H-bonding, would form disordered
165 and less organized segments which are linked with cellulose crystals³³. These amorphous
166 domains are characterized with lower density in comparison to the crystalline parts and are
167 easily available for bonding (e.g. hydrogen) with other molecules including water. On the
168 application of an appropriate combination of chemical, enzymatic and mechanical treatments
169 to these microfibrils, the highly crystalline domains of the cellulose microfibrils can be easily
170 isolated that results in the formation of the desired cellulose nanocrystals³⁴.

171 **3. Nomenclature of cellulose nanomaterials**

172 The development of cellulose nanomaterials has attracted great interest from both the
173 academic and industrial world along with the standards community during the last couple of
174 decades owing to the unique and potentially useful properties they endow such as high tensile
175 strength, high Young's modulus, high surface area-to-volume ration and low coefficient of
176 thermal expansion. This interest is well evident from the research papers published in this
177 field as well as extensive number of patents on the work containing cellulose nanomaterials,
178 as shown in Charreau review²¹. Cellulose nanomaterials (CNM) are considered as a type of

179 nano-objects where the term nano-object is defined according to ISO publications as material
180 with one, two or three external dimensions in the nanoscale^{88, 89}. CNM is a term often
181 employed to describe nanoscale of a cellulosic material, which is considered to be in the
182 nanoscale range if the fibril particle diameters or width is between 1 to 100 nm. Fig. 3
183 illustrates the diverse hierarchical structure of cellulose nanomaterials. It is worth noting that
184 anomalies still exist regarding the nomenclature and terminology applied to CNM^{11, 21, 22, 24,}
185^{35, 90}. Recently, the Technical Association of the Pulp and Paper Industry (TAPPI) has
186 established a Nanotechnology Division devoted to the standardization of cellulose
187 nanomaterials definitions. For the first nanomaterials standard (TAPPI WI 3021: Standard
188 Terms and Their Definition for Cellulose Nanomaterials) a draft version has been prepared
189 and comments on this standard are still under review⁹¹. The existing literature suggests that
190 various terminologies have been and are currently employed to designate cellulose
191 nanomaterials, which unfortunately leads to ambiguities and misunderstanding. Different
192 terms have been used to refer to cellulose nanomaterial elements including cellulose
193 nanofibers, nanoscale cellulose, cellulose microfibrils, cellulose nanofibrils, nanocellulose,
194 nanocellulosic fibrils, cellulose nanoparticles, and nano-sized cellulose fibrils^{11, 21, 23, 24, 90}. As
195 shown in Fig. 3, nanoscale cellulose can be divided into nanostructured materials and
196 nanofibers resulting from the use of various isolation processes^{3, 21, 90, 92}. These nanostructured
197 materials procured from cellulose are generally categorized into microcrystalline cellulose (or
198 cellulose microcrystals) and cellulose microfibrils (TAPPI WI 3021). The cellulose
199 nanofibers, however, are sub-grouped into: (1) cellulose nanofibrils with a variety of
200 terminologies that have been employed including mainly nanofibrillar cellulose,
201 nanofibrillated cellulose, nanoscale-fibrillated cellulose, cellulosic fibrillar fines, nanofibers,
202 nanofibrils, fibril aggregates and sometimes microfibrillated cellulose or microfibrils^{18, 19, 90, 92,}
203⁹³; and (2) cellulose nanocrystals with different names that have been received throughout the

204 years including cellulose whiskers, cellulose nanowhiskers, cellulose crystallites, nanorods,
205 nanocrystalline cellulose, rodlike cellulose crystals, and nanowires^{3, 21, 35, 90}. The nomenclature
206 that will be used further (cellulose nanocrystals) in the present paper is in agreement with the
207 TAPPI standard recommendation.

208 **4. Cellulose nanocrystals**

209 Cellulose fibrils have several highly crystalline regions owing to the linear and
210 conformationally homogeneous nature of the cellulose polymer and the extensive
211 intermolecular hydrogen bonding between adjacent cellulose chains. The degree of
212 crystallinity and size of the crystalline regions depend on the natural source of the cellulose
213 and the isolation process. For instance, the degree of crystallinity may vary from
214 approximately 50% in many plants to 60% in bacterial cellulose, 80% in tunicates and up to
215 90% in some algae⁹⁴. Regarding the isolation of crystalline cellulosic domains in the form of
216 CNCs, a facile process primarily focused on acid hydrolysis is generally employed. The idea
217 of employing acid hydrolysis process to isolate CNCs, from the disordered intercrystalline
218 regions of the networks of cellulose chains, was initiated by Nickerson and Habrle⁹⁵ and
219 confirmed by Rånby⁹⁶, when he produced colloidal suspensions of cellulose crystals. Later,
220 Marchessault⁹⁷ and coworkers in 1959 and Hermans⁹⁸ in 1963 showed that birefringent liquid
221 crystalline phases could be obtained and revealed that such colloidal suspensions of CNCs
222 exhibit the nematic liquid crystalline order. However, interest in CNCs only began to grow
223 after the publication of studies by Revol and coworkers⁹⁹ in 1992, who demonstrated that a
224 stable chiral nematic (cholesteric) liquid crystalline phase is formed in aqueous suspensions of
225 CNCs above a critical concentration, and by Favier et *al.* in 1995 on CNCs as composite
226 reinforcement¹⁰⁰.

227 CNCs consist of “rod-like” or “needle-like” particles with high crystallinity and high
228 specific surface area that can be derived from different natural sources. Fig. 4 represents the

229 transmission electron micrographs (TEM) of selected cellulose nanocrystals. The dimensions
230 and the crystallinity of these nanocrystals depend on the origin of the cellulose fibers as well
231 as the procedure employed to obtain them. Conventionally, highly crystalline CNCs with
232 spherical or shorter rod-shaped morphologies were typically produced from terrestrial woody
233 biomass using acid hydrolysis (aspect ratios between 10 and 30). However, higher aspect
234 ratios of CNCs with a length of several micrometers were commonly derived from bacteria
235 and tunicates (aspect ratio around 70)¹⁰¹. The size of CNCs can vary from 100 nm to several
236 micrometers in length and 4 to 70 nm in width ^{75, 102}. During the synthetic process, cellulose
237 chains primarily combined in fascicular microfibrils. The amorphous domains distributed as
238 chain dislocations on segments along the elementary fibril are more available to acid and
239 more disposed to hydrolytic action due to kinetic factors and reduced steric hindrance;
240 whereas crystalline domains present a higher resistance to acid attack^{20, 94, 103}. Thus, CNCs
241 can be afterward produced on the removal of the amorphous regions from microfibrils at the
242 defects.

243 Pristine cellulose has been found to have limited reactivity due to its functionalities;
244 however the three-dimensional hierarchical structures composed of cellulose nanocrystals
245 open up new opportunities for new fields, ranging from engineering to biomedical. CNCs
246 impart attractive combinations of physicochemical characteristics^{20, 30, 33, 43, 67}, such as
247 biocompatibility, biodegradability, optical transparency and anisotropy, low cost, high tensile
248 strength, elasticity, low density, large specific surface area, and adaptable surface chemistry.
249 Such unique CNCs' properties have promoted the progress of a wide range of new functional
250 biomaterials, transforming research in different academic disciplines of science and
251 engineering's. At laboratory scale, CNCs have been widely used as sustainable low-cost
252 environmental friendly materials in miscellaneous fields^{25, 33, 43, 103-105} including composites,
253 separation membranes, barrier films, specific enzyme immobilization, supercapacitors,

254 antimicrobial films, medical implants, green catalysts, emulsion stabilizers, biosensors, drug
255 delivery, batteries, and templates for electronic devices. However, in spite of the huge
256 potential of CNCs, for real life applications, the processing has some limitations. These
257 limitations must have to be overcome in order to effectively utilize these CNCs at large
258 scale^{35, 104}.

259 **4.1. Cellulose nanocrystals sources**

260 Sustainable materials from renewable resources have attracted immense research interest
261 during the last two decades owing to their potential for producing several high-values
262 products with environmental friendly advantages. Different types of sources such as plant cell
263 walls, cotton, microcrystalline cellulose, algae, animals and bacteria can be used to derive
264 CNCs. Several CNCs with variable structure, properties and applications could be obtained,
265 depending on the source, maturity, origin, processing methods and reaction parameters. A
266 detailed study on research employing different source materials for extraction of cellulose
267 particles has been beautifully compiled by Dufresne²⁰ in his book and review by Agbor¹⁰⁶. In
268 the following subsections, a concise overview of cellulose nanocrystals sources will be
269 presented.

270 **4.1.1. Lignocellulosic sources**

271 Lignocellulosic fibers (woody and non-woody plants) are considered as excellent feedstock
272 for production of various materials that has been proven by the high number of patents and
273 peer reviewed articles, besides the large number of products already marketed^{21, 22, 35, 79, 81, 102,}
274 ¹⁰⁶⁻¹¹⁰. Lignocellulosic natural fibers can be generally classified based upon the origin of the
275 plant: (1) bast or stem, (2) leaf, (3) seed or fruit, (4) grass, and (5) straw fibers⁶⁵. All over the
276 world, more than 2000 species of useful fiber plants have been reported⁷⁹. Woody and non-
277 woody plants can be referred as cellular hierarchical bio-composites created by nature in
278 which hemicellulose/lignin, waxes/ extractive and trace element serves as matrix materials

279 while semicrystalline cellulose microfibril act as reinforcement^{33, 81}. A number of factors such
280 as chemical composition and internal fiber structure significantly affect the properties of
281 natural fibers along with the change between various parts of a plant and among different
282 plants. An effective removal process of hemicellulose, lignin and other impurities gives rise to
283 pure cellulose. CNC is currently manufactured from various lignocellulosic sources using top-
284 down technologies. Wood is apparently the main source of cellulosic fibers, and is
285 consequently the most important raw material used in the production of CNCs^{11, 76, 111}.
286 Nevertheless, competition among numerous areas such as furniture, pulp and paper industries,
287 building products along with the combustion of wood for energy, renders it challenging to
288 offer all sectors with the necessary quantities of wood at a reasonable price. Moreover, wood
289 is not available in several regions, thus tuning its options to non-woody cellulose¹⁵. Hence,
290 interest in other sources such as herbaceous plants, grass, aquatic plants, agricultural crops
291 and their by-products has extensively stimulated significant interest. In their fibers, the
292 cellulosic microfibrils are less tightly wound in the primary cell wall than in the secondary
293 wall in wood, this fibrillation to made CNCs should be easiest¹⁶. These non-woody plants
294 usually encompass less lignin as compared to the quantity found in wood. Therefore,
295 bleaching methods are less chemical and energy demanding.

296 In recent years, wide variety of annual plants as well as agricultural residues have been
297 investigated for the isolation of CNCs, including sesame husk¹¹⁰, cotton¹¹²⁻¹¹⁴, rice husk¹¹⁵, oil
298 palm^{27, 116, 117}, Groundnut Shells¹¹⁸, macrophyte *Typha domingensis*⁸⁷, potato peel¹¹⁹, jute¹²⁰,
299 spruce bark¹²¹, *agave angustifolia* fibers¹²², mango seed¹²³, sugarcane bagasse^{39, 124, 125},
300 corncob¹²⁶, bamboo¹²⁷, straws³⁰, soy hulls¹²⁸, olive stones¹²⁹, *Miscanthus Giganteus*²⁸,
301 kapok¹³⁰, Flax Fibers¹³¹, pineapple leaf and coir¹³⁰, banana^{130, 132}, sisal¹³³, tomato peels¹³⁴,
302 *calotropis procera* fibers³¹, onion waste¹³⁵, citrus waste¹³⁶ and coconut^{137, 138}. Other recent
303 explored sources for CNCs preparation have been reviewed in Table 2 as well. CNCs

304 obtained from different types of cellulose sources of miscellaneous provenance using various
305 isolation processes and conditions commonly differ in their degree of polymerization,
306 morphology, surface charge, geometrical dimensions, crystallinity, surface area, porosity,
307 mechanical properties, thermal stability, etc.

308 **4.1.2. Animal, algae and bacterial sources**

309 Although lignocellulosic materials are considered as the most common sources of
310 cellulose, other living organisms including animals, bacteria and some types of algae can also
311 be employed to produce cellulose microfibrils.

312 Tunicates, which live in the oceans, are revealed as the only animal source for cellulose.
313 The name “Tunicata” has been derived from its unique integumentary tissue the “tunic”,
314 which covers the entire epidermis of the animal. In the tunic tissues, the cellulose microfibrils
315 act as a skeletal structure. Cellulose-synthesizing enzyme complexes that exist in the plasma
316 membrane of their epidermal cells are responsible for cellulose synthesis. Tunicates include
317 three classes, and only two classes (*Asciacea* and *Thaliacea*) contain tunics. There are over
318 2300 species in *Asciacea* alone²². To extract and utilize the cellulose from tunicates, the
319 quantity or production yield is crucial. Historically, the tunic has been reported to contain
320 approximately 60% cellulose and 27% nitrogen-containing components by dry weight¹³⁹. It
321 was confirmed that the cellulose present in tunics is chemically identical with plant cellulose.
322 However, tunicate cellulose shows different functions in various tunicates families and
323 species, giving rise to difference in the structure. It was reported that more than 40 species of
324 ascidian have been investigated for their structural diversity¹⁴⁰. Typically, tunicate cellulose is
325 composed of nearly pure cellulose I β . Hundreds of cellulose microfibrils are bundled in the
326 tunic; the shape and dimensions of the microfibril bundle vary depending on the species.
327 Noticeably, the *Ciona intestinalis* tunicate species could be farmed at very high densities in
328 the ocean, allowing tunicate cellulose fabrication at a large scale¹⁴¹. Therefore, tunicates

329 should be excellent candidate for CNCs preparation. The most frequently investigated species
330 have been *Ciona intestinalis*⁴¹, *Ascidia* sp.¹³⁹, *Halocynthia roretzi*¹⁴², *Metandrocarpa uedai*²²,
331 *Styela plicata*¹³⁹ and *Halocynthia papillosa*¹⁴³.

332 Although cellulose feedstock is generally associated with lignocellulosic materials, it is
333 now well-known that cellulose microfibrils are also produced by algae (green, gray, red,
334 yellow-green, etc.)²². Many studies have demonstrated that red algae such as *Gelidium*,
335 mainly composed of cellulose and agar, are a viable resource for numerous applications due to
336 its high carbohydrate content^{144, 145}. In 2010, Seo and coworker have first described the use of
337 two different species of red algae, namely *Gelidium amansii* and *Gelidium corneum* for the
338 production of bleached pulp in papermaking industry¹⁴⁶. *Gelidium elegans* was also utilized to
339 produce cellulose nanomaterials⁴⁰. The production of red algae has increasing exponentially
340 from 5.3 million tons in 2006 to 10.8 million tons in 2011¹⁴⁴. Therefore, the *Gelidium* red
341 algae appear to be a new promising candidate for cellulose nanomaterials production than
342 terrestrial biomass because of their abundance and availability. Besides, green algae are
343 reported to be appropriate for cellulose extraction as well. Cellulose-producing algae belong
344 generally to the orders Cladophorales (*Cladophora*, *Chaetomorpha*, *Rhizoclonium*, and
345 *Microdyction*) and Siphonocladales (*Valonia*, *Dictyosphaeria*, *Siphonocladus*, and
346 *Boergesenia*)¹⁴⁷. The cellulose obtained from *Valonia* or *Cladophora* presents a high degree
347 of crystallinity, which can exceed 95%⁷⁷. Because of the biosynthesis process, cellulose
348 microfibril structures have been found to be different for the different algae species.

349 The bacteria-derived cellulose is of prime concern owing to its high mechanical
350 properties, good chemical stability, highly crystalline network structure, high chemical purity,
351 an ultrafine and large water-holding capacity, light weight, renewability, biodegradability and
352 non-toxicity which avoids chemical treatments employed in plant-derived celluloses for the
353 elimination of lignin and hemicellulose²¹. Several excellent reviews and papers concerning

354 the characterization and properties of bacterial cellulose (BC) and its possible applications
355 have recently appeared^{20, 80, 148-150}. As a result to its special properties, cellulose produced by
356 bacteria has grown in popularity since its discovery in 1886. That strain was called
357 *Acetobacter xylinus*, but there are other bacteria able to produce cellulose, such as
358 *Agrobacterium*, *seudomonas*, *Rhizobium* and *Sarcina*¹⁴⁸. The most efficient producers are
359 gram-negative acetic acid bacteria *Acetobacter xylinum* (also called *genus*
360 *Gluconacetobacter*) which has been reclassified and included within the novel
361 *Komagataeibacter* as *K. xylinus*¹⁵¹. It has continued to be the highest producer of bacterial
362 cellulose so far. It is stringently aerobic, non-photosynthetic and able to convert glucose and
363 other organic substrates into cellulose in a few days¹⁴⁹.

364 **4.2. Cellulose isolation methods**

365 Two main steps that are used to isolate CNCs from a raw cellulose sample include (i)
366 homogenization pretreatment/ purification and (ii) the separation of the purified cellulose into
367 its nanocrystals components. Thus, to prepare cellulose nanocrystals, cellulose can be directly
368 hydrolyzed. Apart from pure cellulosic sources such as cotton, bleached wood pulp, and
369 MCC, other cellulose sources are generally first submitted to different pretreatments. Detailed
370 descriptions of several of these isolation methods are given below.

371 **4.2.1. Isolation of cellulose from lignocellulosic sources**

372 The amount of cellulose in various natural sources can vary depending on the species and
373 life time of the plants. In nature, lignocellulosic is a bio-composite which results from a
374 combination between nanoscale domains of cellulose, hemicellulose, lignin, extractives and
375 contaminants. From technological point of view, lignin content evaluation is a crucial
376 parameter to well optimize the pretreatment process needed to extract a pure cellulose pulp.
377 Indeed, lignin is considered the hardest chemical component to be removed from
378 lignocellulosic materials¹⁵. However, there are several procedures to isolate cellulose from

379 lignocellulosic sources using chemical, mechanical, biological and combined processes^{42, 86, 93,}
380 ¹⁰⁶. These processes have often been used as a pretreatment to simplify the hydrolysis process
381 for the production of CNCs. The pristine cellulose fibers are commonly boiled in toluene/
382 ethanol (volume ration of 2:1) mixture after water-washing process to remove the dirt/
383 impurities, water soluble extractives, wax and pectin, respectively. An example of cellulose
384 extraction procedure from tomato peels is shown in Fig. 5.

385 In chemical pulping process, some chemical agents are used to dissolve the lignin as well
386 as hemicellulose (both surrounds the cellulose fibers). The most common methods for
387 dissolving lignin and hemicellulose are either based on the Kraft process which uses sodium
388 hydroxide (NaOH) and sodium sulfide (Na₂S), followed by a bleaching step usually involving
389 chlorine dioxide (ClO₂), hydrogen peroxide (H₂O₂), ozone (O₃), or peracetic acid. Many
390 chlorine and/or sulfide-free treatments have been developed in order to decrease the
391 environment impact of the pulping process. The preliminary steps to obtain pure cellulose
392 fibers are crucial and must be performed carefully. The kraft extraction is done to solubilize
393 most of the lignin and hemicelluloses and the bleaching treatment is made to break down
394 phenolic compounds /molecules with chromophoric groups (in lignin) and to eliminate the by-
395 products of such breakdown, to whiten the material. However there are some serious
396 environmental concerns related to the chemical pulping especially the by-products and
397 residues of the process.

398 Mechanical methods are energy consuming, generally demanding high levels of pressure
399 or kinetic energy. The product, derived from the mechanical pulping, presents commonly
400 similar composition than that of the original feeding. A number of mechanical processes have
401 been frequently employed for the extraction cellulose fibrils from a wide range of cellulose
402 sources. Some of the most mechanical methods include comminution, high pressure
403 homogenization, microfluidization, cryocrushing, high intensity ultrasonication.

404 Along with the commonly used traditional pulping processes, biological or enzymatic
405 pulping has received much attention. This method depends on the ability of certain
406 microorganisms and their secreted enzymes (i.e., xylanase) to directly attack hemicellulose
407 and change the interface among lignin and cellulose, subsequently easing the removal of the
408 lignin-associated hemicellulose fraction. This process indeed simplifies the extraction of
409 purified cellulose with less degradation and superior quality pulps.

410 Combinatorial pretreatment strategies are usually more effective in increasing the biomass
411 digestibility and improving the cellulose isolation, and often used in designing leading
412 pretreatment technologies. The well-known physicochemical process involves is the
413 combination of a mechanical method to decrease the reaction times by enhancing chemical
414 accessibility. The tight intertwined fiber architecture is loosened by mechanical interactions,
415 and the region exposed to the chemical action is enlarged^{152, 153}.

416 **4.2.2. Isolation of cellulose from animal, algae and bacterial sources**

417 Tunicates are marine invertebrate sea animals that have been recently known for producing
418 cellulose in large amounts. The common process used for the extraction of cellulose is the
419 prehydrolysis-kraft cooking-bleaching sequence, which is originated from Koo et al.¹⁵⁴. The
420 isolation procedure from *Halocynthia roretzi* is depicted in Fig. 6. Similar method can applied
421 for the cellulose isolation from other tunicates species¹³⁹. Basically, tunicate tunic can be
422 obtained by eliminating the interior organs of the animal with a knife; the wet tunicate tunic
423 will be then freeze-dried and milled into powders. A simple prehydrolysis procedure can be
424 performed using an aqueous H₂SO₄ solution at 180 °C for 2 h with occasionally shaking in
425 order to remove all lipids, ash and other sugars than glucose. The derived insoluble residue
426 was recovered by filtration, washed thoroughly with acetone/water and freeze dried. A kraft
427 cooking step can be subsequently conducted using an aqueous solution of NaOH/Na₂S at 180
428 °C for 2 h with occasionally shaking to eliminate proteins and some residual sugars other than

429 glucose, followed by filtration, washing and drying. Finally, a bleaching process can be
430 performed using aqueous NaClO solution with agitation at 75 °C for 1 h to remove the
431 residual proteins and some chromophoric structures initially present in the tunics or generated
432 from the previous steps. This process can be repeated several times until the product becomes
433 completely white. This sequence is considered to be a more suitable method than those
434 mentioned in the literature¹⁵⁵⁻¹⁵⁷, since the original dissolving pulp process has proven very
435 effective and specific for cellulose preservation, resulting in limited damage to cellulose,
436 particularly crystalline cellulose¹³⁹.

437 To prepare high quality cellulose pulp from algae more efficiently, non-cellulosic
438 components need to be eliminated from the algae during the isolation process. Some
439 researchers have reported that the biomass should be washed with distilled water in so as to
440 ensure the removal of dirt/ contaminations on the fibers' surface⁴⁰. Subsequently, the fibers
441 are dried and these dried fibers are then grounded into powder form. A standard dewaxing
442 process is then applied in a soxhlet apparatus system by using toluene/ethanol, followed by an
443 alkalization treatment with NaOH to solubilize the agar (mucilaginous materials) from the
444 marine algae plant at 80 °C for 2 h. An efficient bleaching procedure is crucial to eliminate
445 the natural pigment and chlorophyll to produce a highly purified, whiteness isolated cellulose
446 pulp from the algae biomass. Two main oxidizing bleaching agents namely sodium chlorite
447 (NaClO₂) and hydrogen peroxide (H₂O₂) are commonly employed to bleach the algae biomass
448 fiber to obtain bleached algae pulp^{40, 158-160}.

449 Cellulose can also be synthesized in pure and highly crystalline microfibrillar form by
450 bacteria²⁰. For instance, *K. xylinus* can produce cellulose microfibrils in the form of flat, clear,
451 and thick pellicles that floats on the surface of the growth medium. The obtained cellulose
452 pellicles contain pure cellulose as well as a large proportion of water and some other
453 ingredients of the medium. Dilute alkaline solution are capable of hydrolyzing and removing

454 the impurities which exist in the cellulose pellicle. The washed cellulose pellicles can also be
455 dried and cellulose membranes can be then easily processed from these pellicles⁷⁷.
456 Furthermore, BC is commonly considered as a highly hydrated and pure cellulose membrane
457 and hence no chemical actions are required to eliminate hemicelluloses and lignin, as is the
458 case for lignocellulosics¹⁶. A number of studies have resulted in the development of BC on an
459 industrial scale, with a continuous/ semi-continuous process, economic raw materials and
460 small production of by-products^{102, 149}. Some detailed studies concerning the mechanism of
461 BC production using the fermentation process have been previously elaborated^{148, 149}.

462 **5. Extraction processes of cellulose nanocrystals**

463 Some significant research programs have been recently started on the production of
464 cellulose nanocrystals at the industrial scale. As far as we know, four commercial entities
465 producing CNCs at capacities beyond pilot plant scale: CelluForce (Canada, 1000 kg/day),
466 American Process (U.S., 500 kg/day), Melodea (Israel, 100 kg/day), Melodea/Holmen
467 (Sweden, 100 kg/day) and Alberta Innovates (Canada, 20 kg/day)^{35, 161}. Furthermore, various
468 research facilities are currently producing CNCs, and several new lab and pilot scale have
469 been announced such as US Forest Products Lab (U.S., 10 kg/day), Blue Goose Biorefineries
470 (Canada, 10 kg/day), India Council for Agricultural Research (India, 10 kg/day) and
471 FPIInnovation (Canada, 3 kg/day)¹⁶¹.

472 It is well known that the morphology, physicochemical properties and mechanical
473 characteristics of CNCs exhibit variations according to the origin of the raw material and the
474 extraction process. The latter step is crucial for further processing and developing CNCs into
475 functional, high-value added products, and, as such, efforts to face the shortcomings in the
476 conventional methodology, to increase the production with a reduced cost are continuously
477 reported in the literature. As shown above, CNCs can be extracted from various raw materials
478 on earth that firstly need to follow a pretreatment procedure for complete/ partial removal of

479 the matrix materials (e.g. lignin/ hemicelluloses/ fats/ waxes/ proteins, etc.) resulting in the
480 extraction of the individual cellulose fibers. Depending on the source of the cellulose, the
481 naturally occurring bulk cellulose primarily consists of highly ordered crystalline domains and
482 some disordered (amorphous) regions in varying proportions⁷⁷. When these microfibrils are
483 subjected to a proper combination of chemical, mechanical, oxidation and/or enzymatic
484 treatments, the crystalline domains of the cellulose microfibrils can be isolated, giving rise to
485 the formation of cellulose nanocrystals. The production of CNCs in an economic and
486 sustainable way and further exploration of its functional products are currently the major tasks
487 for the researchers both from the academia and industry. Several methods are reported for
488 isolation of CNCs (Table 3), namely, chemical acid hydrolysis, enzymatic hydrolysis,
489 mechanical refining, ionic liquid treatment, subcritical water hydrolysis, oxidation method
490 and combined processes.

491 **5.1. Acid hydrolysis**

492 In this method, a given concentration of desired acid and deionized water is mixed with
493 the purified starting material. This process is the most commonly used technique for the
494 separation of CNCs from cellulose fibers^{11, 20, 22, 23, 102}. The procedure involves an acid-
495 induced destructuring process, during the course of which the heterogeneous acid hydrolysis
496 involves the diffusion of acid molecules into cellulose microfibrils. It results in the cleavage
497 of glycosidic bonds within cellulose molecular chains in the amorphous domains along the
498 cellulose fibrils, thus leading to the breaking of the hierarchical structure of the fibril bundles
499 into CNCs^{3, 33}. The difference in the kinetics of hydrolysis between paracrystalline and
500 crystalline regions led to the selective cleavage of cellulosic chains²⁰. The mostly common
501 chemical function of the employed acids is their ability to release hydronium ions that tend to
502 penetrate the cellulosic material in the amorphous domains and react with the oxygen
503 elements on the glycosidic bonds between two anhydroglucose moieties to initiate protonation

504 of oxygen elements, and hence hydrolytic cleavage of glycosidic bonds of amorphous
505 regions^{15, 33}. The acidic treatment could hydrolyze the residual pectin and hemicellulose by
506 breaking down the polysaccharides into simple sugar as well. The literature mentioned that
507 these crystallites can grow in size owing to the large freedom of motion after hydrolytic
508 cleavage, and consequently the crystallites will be larger in dimension than the original
509 microfibrils²⁰. Acid hydrolysis results in a rapid decrease in the degree of polymerization of
510 cellulose nanocrystals. At the end of the process, the mixture undergoes a series of separation
511 and washing/rinsing steps that is followed by dialysis against deionized water to eliminate
512 residual acid and neutralized salts (Fig.7). To get the better and homogeneous dispersion of
513 CNCs in aqueous media, sonication treatment is generally applied^{8, 11, 22, 26, 102, 158}. A
514 schematic presentation of the acid hydrolysis process is shown in Fig. 7c.

515 Various acids such as sulfuric acid, hydrobromic acid, hydrochloric acid, phosphoric
516 acid, maleic acid, and hydrogen peroxide have been assayed to extract CNCs from different
517 resources. However, sulfuric and hydrochloric acids are frequently employed for the acid
518 hydrolysis of corresponding cellulose^{8, 20, 42, 102}. Numerous researchers had analyzed the effect
519 of processing conditions on the physicochemical, thermal and mechanical properties. The
520 temperature and time of hydrolysis procedure, nature and concentration of acid as well as the
521 fiber-to acid ratio play an important role in the particle size, morphology, crystallinity,
522 thermal stability and mechanical properties of CNCs^{20, 162-165}. Increment in the hydrolysis time
523 has been reported to reduce the length of the nanocrystals as well as increase the acid/fiber
524 ratio and reduce the crystals dimensions^{102, 166}.

525 The selection of an acid affects the properties of the resulting cellulose nanocrystals.
526 Those isolated using hydrochloric acid present low-density surface charges with limited
527 dispersibility and tend to promote flocculation in aqueous suspensions^{11, 26}. This issue can be
528 solved by surface functionalization. In contrasts, when sulfuric acid is employed, a highly

529 stable colloidal suspension is produced owing to the high negative surface charge promoted
530 by sulfonation of CNCs surface^{22, 33, 84, 90}. However, one disadvantage of this method is that
531 sulfate groups catalyze and initiate the degradation of cellulose, particularly at high
532 temperatures. Hence the CNCs have been found to have limited thermal stability, which
533 certainly restricts the processing of CNCs based nanocomposites at high temperature⁴⁶.
534 Several other approaches have been suggested to address the thermal stability problem^{113, 167,}
535 ¹⁶⁸. For instance, the use of mixtures of hydrochloric acid and sulfuric acid generated CNCs
536 with high thermal stability, unfortunately at the expense of lower dispersibility. Recently,
537 highly thermally stable CNCs have been prepared via mild acid hydrolysis (phosphoric acid)
538 and hydrothermal treatment (hydrochloric acid)^{46, 53}. However, these procedures are severely
539 restricted by low yields and poor scalability because of the high consumption of solvents and
540 time, respectively.

541 Although the previous acid-hydrolysis procedures are simple, some drawbacks are
542 needed to be addressed. Some of such drawbacks include serious large water usage,
543 equipment corrosion, and generation of huge amount of waste. Also, the prolonged exposure
544 of cellulosic materials to harsh conditions (mineral acids) can decrease crystallinity as the
545 crystalline regions are potentially subjected to hydrolysis and structure structural change¹⁶⁹. In
546 2011, Tang *et al.* have investigated the substitution of strong liquid acids by solid acids for
547 environmental and sustainable reasons⁴⁷. Their work reported the use of a cation exchange
548 resin hydrolysis method to produce CNCs with a yield of 50% and high crystallinity of 84%.
549 The authors have demonstrated that cation exchange resin catalyst is easiest to handle than
550 liquid acids. Also it does not present hazards to personnel or causes severe equipment
551 corrosion and can also be easily separated from the reaction products, can be regenerated and
552 causes less waste. In another work, Liu *et al.* have demonstrated that phosphotungstic acid can
553 be a potential candidate to produce CNCs through controlling hydrolysis parameters¹⁷⁰. This

554 green and sustainable method leads to prepare CNCs with relatively good dispersibility in
555 aqueous phase and high thermal stability. The method of producing CNCs from bleached
556 eucalyptus kraft pulp via FeCl₃-catalyzed formic acid hydrolysis was developed by Du et
557 *al.*³⁸. They proved that the obtained CNCs present high crystallinity and excellent thermal
558 stability with a high yield of 70-80%.

559 More recently, attention has turned towards other methodologies to produce CNCs based
560 on acid hydrolysis principle. Yu et *al.* reported the preparation of CNCs with carboxylic
561 groups from microcrystalline cellulose using single-step extraction based on
562 citric/hydrochloric acid hydrolysis²⁹. A schematic route for fabricating carboxylated CNCs is
563 shown in Fig. 8. The authors mentioned that the optimal CNCs samples with increased
564 crystallinity, best suspension stability and better thermal stability were achieved at the
565 hydrolysis time of 4 hours. Kontturi et *al.* described the preparation of cellulose nanocrystals
566 in high yields with minimal water consumption using hydrogen chloride (HCl) vapor⁴⁵. They
567 demonstrated that the use of HCl vapor gives rise to a rapid hydrolysis of cotton-based
568 cellulose fibers. An increase in crystallinity was deduced without any mass loss in the
569 cellulose substrate during hydrolysis and a minimal impact on the morphology of the cellulose
570 substrate was seen. The degree of polymerization was quickly reduced to the leveling off
571 degree of polymerization (LODP) of around 170, which corresponds to the LODP determined
572 by the conventional method with liquid-phase HCl as well as literature values⁸³. The yield
573 achieved by the authors was 97.4% instead of 20-50% with a liquid/solid system¹⁷¹. The
574 authors indicated that only the yield of 11% was reached when liquid HCl was employed.
575 Another approach was also developed by Chen et *al.* to produce high thermal-stable
576 functional CNCs using recyclable organic acid (oxalic, maleic, and p-toluenesulfonic
577 acids)¹⁷². They produced CNCs from a bleached eucalyptus kraft pulp exhibited good
578 dispersion, high crystallinity index and better thermal stability with a higher yield. They

579 revealed that the solid organic acids used can be easily recovered after hydrolysis reactions
580 through crystallization at a lower or ambient temperature, due to their low water solubility.

581 **5.2. Mechanical treatment**

582 Mechanical methods have also been widely investigated for the production of nanoscale
583 cellulose particles, either as part of the fabricating process employing combinations of acid
584 hydrolytic, oxidative, and enzymatic treatment, or directly^{42, 52, 173}. They include
585 microfluidization, ultrasonication, high pressure homogenization or ball milling. These
586 procedures are commonly employed to produce cellulose nanofibers which are characterized
587 with a diameter in nanometers or tens of nanometers and a length of up to several microns^{21,}
588 ²². More recently, Amine *et al.* have developed a scalable mechanical method using a high
589 energy bead milling (HEBM)⁵². The authors isolated CNCs from an aqueous dispersion or
590 dilute acid (phosphoric acid) dispersion of commercially available microcrystalline cellulose
591 (MCC) micronized through a HEBM process. They revealed that the morphology and the
592 aspect ratio values were quite similar to that of the CNCs prepared via acid hydrolysis. The
593 production yields of CNCs ranged between 57–76%. The resulted rod-like CNCs present a
594 crystallinity index of 85-95% with high thermal stability suitable to withstand the melt
595 processing temperature of most common thermoplastics. Another mechanical method also
596 reported the isolation of CNCs via ultrasonication^{52, 54}. Rod shaped CNCs were produced
597 from an aqueous dispersion of MCC using a purely physical method of high-intensity
598 ultrasonication. The CNC presented diameters between 10 and 20 nm and lengths between 50
599 and 250 nm. However, the production yield of CNC using this method does not exceed 10%.
600 The ultrasonication effect was found to be non-selective, meaning that it can eliminate both
601 the amorphous and crystalline cellulose.

602 **5.3. Oxidation method**

603 In 2006, Saito et *al.* reported a new method to introduce charged carboxylate groups into
604 cellulosic materials which helped disintegration into nanofibrils with smaller widths, by
605 utilizing a much lower energy input in comparison to that of the traditional pure mechanical
606 treatment¹⁷⁴. This process involves oxidation of never-dried native celluloses mediated by the
607 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) radical and subsequent homogenization by the
608 mechanical treatment. The mechanism of the TEMPO-mediated oxidation of cellulose, which
609 is a one of the regioselective chemical modifications of primary hydroxyl groups, is well
610 explained elsewhere⁹⁰. The reaction occurs on the surface of cellulose fibers and in
611 amorphous domains. As the carboxyl content is increased to a certain amount, cellulose starts
612 to disperse in aqueous solution but the crystalline regions remain intact and can therefore be
613 released²⁰. Surface carboxylated NCC has been prepared by oxidation. A direct ultrasonic-
614 assisted TEMPO–NaBr–NaClO system was employed to produce carboxylic cellulose
615 nanocrystals from cotton linter pulp¹⁷⁵. Some of the amorphous domains of the cellulose were
616 found to be gradually hydrolyzed during the oxidation process, and a stable and well
617 dispersed aqueous suspension was subsequently obtained in one step. Microscopic
618 observations revealed the presence of cellulose nanocrystals 5–10 nm in width and 200–400
619 nm in length. Cao et *al.* have extracted cellulose nanocrystals using TEMPO–NaBr–NaClO
620 system⁶². They reported that a stable and transparent dispersion of CNCs (80% yield) was
621 obtained with high crystallinity and high surface area. CNCs produced by TEMPO oxidation
622 were able to be completely dispersed at the individual nanofibril level in water by electrostatic
623 repulsion and/or osmotic effects. This behavior was attributed to the anionically charged
624 sodium carboxylate groups that were densely present on the fiber surfaces¹⁷⁶. However,
625 TEMPO-mediated oxidation method still exhibits some serious drawbacks, such as toxic
626 TEMPO reagents (leading to environmental issues), oxidation time, and limited oxidation at
627 C6 primary hydroxyl groups in CNCs. Another oxidation method using periodate-chlorite was

628 developed^{60, 177}. Generally, periodate is firstly utilized to oxidize the C2 and C3 hydroxyl
629 groups using chrolite. However, this two-step oxidation method requires the expensive and
630 toxic periodate along with the disintegration process having very high energy consumption⁶³.
631 Moreover, the glycosidic rings will be successively split after the oxidation reaction, which
632 may reduce molecular chain lengths/rigidity of the CNCs. Very recently, carboxylated CNCs
633 presenting a similar mean particle length along with length polydispersity with yields in the
634 range of 14–81% were successfully isolated from numerous cellulosic sources by one-step
635 ammonium persulfate hydrolysis, but this method necessitates time-consuming alkaline
636 pretreatments and long reaction times of 16-24h^{61, 63}.

637 **5.4. Enzymatic hydrolysis**

638 The concentrated acid employed in the common acid hydrolysis procedures is hazardous,
639 toxic, and corrosive; hence highly corrosion-resistant reactor and extreme precaution in
640 material handling are needed in the process. This makes acid treatment an expensive route.
641 Furthermore, the concentrated acid should be recovered after treatment to make the method
642 economically and environmentally feasible. As compared with acid hydrolysis method,
643 enzymatic fabricating of CNCs is a less expensive alternative preparation technique that
644 removes the need for harsh chemicals and necessitates much less energy for mechanical
645 fibrillation and heating⁴⁸. Furthermore, enzymes that selectively degrade the amorphous
646 domains of cellulose fibers, and do not considerably digest the crystalline areas, result in
647 CNCs that preserve a hydroxyl group surface chemistry which allows for easier chemical
648 manipulation, and thus an expanded commercial potential. Cellulases (mixtures of
649 endoglucanases, exoglucanases, and cellobiohydrolases) are one such interesting class of
650 enzymes having ability to act as a catalyst for the hydrolysis of the cellulose. These enzymes
651 act synergistically in the hydrolysis of cellulose. Endoglucanase randomly attacks and
652 hydrolyzes the amorphous domains while exoglucanase reacts with the cellulosic chain from

653 either the reducing or nonreducing ends. Cellobiohydrolases hydrolyze cellulose from either
654 the C₁ or the C₄ ends employing a protein in each case, into cellobiose sub-units²⁰.
655 Consequently, the cellulose not only gets into amorphous parts of cellulose fibers, but also
656 affects the crystalline regions because of the function of Cellobiohydrolases (CBH).
657 Nevertheless, the cellulose that can be formed in the reaction process can adsorb on the
658 activity center of CBH and avoid the thorough enzymolysis. This favorable effect presents an
659 advantage for the controlled enzymolysis production of CNCs⁵⁰. Satyamurthy et al. have
660 produced CNCs using a controlled microbial hydrolysis of MCC with the cellulolytic fungus
661 *Trichoderma reesei*⁵¹. The production yield reported was 22%. The authors concluded that the
662 penetration of fungus into the crystalline domain of MCC during incubation resulted in
663 reduced crystallinity of CNCs produced by microbial hydrolysis compared to that of acid
664 hydrolysis. In order to overcome some of the problems caused by the use of enzymatic
665 hydrolysis process, some authors utilized different pretreatments before enzymolysis to
666 produce CNCs. Chen et al. pretreated natural cotton with DMSO, NaOH or ultrasonic waves
667 and applied enzymatic treatment to prepare CNCs⁵⁰. A highest yield of 32.4% was reached.
668 Recently, Xu et al. employed a cloned endoglucanase derived from *Aspergillus oryzae* to
669 hydrolyze pretreated hemp and flax fibers⁴⁹. They demonstrated that a pretreatment of fibers
670 with sonication-microwave in 2% NaOH solution leads to NCCs of better quality and higher
671 yield. The methods of Xu et al. effectively eliminate the need for acids to fabricate CNCs, but
672 the mechanical pretreatment is still costly, taking into account the processing required and the
673 preprocessing performed before enzyme digestion. More recently, Anderson et al. examined
674 the ability of enzymes with endoglucanase activity to produce CNCs⁴⁸. They showed that
675 cellulase from *Aspergillus niger* was capable of fabricating CNCs with minimal processing
676 from feedstock of well-solubilized kraft pulp. The estimated yield in this case was 10%.

677 Enzymatic routes for the synthesis of CNCs have been found to offer the potential for
678 acceptable yields, advanced selectivity, and milder operating conditions in comparison to the
679 chemical processes. However, this technique is also still hindered by economical (i.e., high
680 cost of cellulose enzyme) and technical (rate limiting step of cellulose degradation with a long
681 processing period) constraints. The slow rate of enzymatic hydrolysis has been found to be
682 affected by numerous factors that also comprise structural features resulting from
683 pretreatment and enzyme mechanism¹⁷⁸.

684 **5.5. Ionic liquid treatment**

685 Ionic liquids (ILs) have received increasing attention from the scientific community
686 specifically as recyclable, highly stable, low melting point and low vapor pressure reagents,
687 leading to innovative and sustainable solutions. They exhibit unique solvating properties and
688 are considered as emerging environmentally friendly solvents for lignocellulosic materials
689 pretreatment and processing. In spite of their unique advantages, their embodied energy and
690 cost, the recyclability and the reuse of ILs undoubtedly appear to be indispensable for the
691 conception of any environmentally and economically viable CNCs isolation process. Some
692 research works attested that the recovery rate of ILs can be reached as high as 99.5% by
693 evaporating the anti-solvents⁵⁶. Currently, imidazolium-based acidic ILs, such as 1-butyl-3-
694 methylimidazolium chloride ([BMIM]Cl), 1-ethyl-3-methylimidazolium diethylphosphonate
695 ([EMIM]DEP), 1-butyl-3-methylimidazolium acetate ([BMIM]OAc) and 1-butyl-3-
696 methylimidazolium hydrogen sulfate ([BMIM]HSO₄), are considered as the most interesting
697 and the most investigated solvents for cellulose. Moreover, numerous recent studies clearly
698 demonstrated that ILs could be efficiently employed as alternative reaction media for
699 selective and controlled cellulose hydrolysis leading to nanoscale particles isolation. Man et
700 *al.* utilized [BMIM]HSO₄ to produce rod-like CNCs from MCC¹⁷⁹. According to the authors,
701 the hydrolysis mechanism with the [BMIM]HSO₄ would be quite similar to the acid

702 hydrolysis with H₂SO₄. The potential of [BMIM]HSO₄ was fruitfully emphasized, both dry
703 and in aqueous medium, for isolation of rod-like CNCs from microcrystalline cellulose (yield
704 of 48%). A preferential dissolution of amorphous domains lead to the increase of crystallinity
705 during the treatment, while the native conformation of cellulose type I was conserved¹⁸⁰. Mao
706 *al.* have developed a two-step hydrolysis approach (24-h swelling at ordinary temperature and
707 12-h hydrolysis at 100 °C) employing [BMIM]HSO₄⁵⁷. This procedure gives rise to good
708 CNC surface properties (sulfur content as low as 0.2%) with high production yields (up to
709 76%). Another work of Tan et *al.* can be highlighted as well, where [BMIM]HSO₄ was
710 investigated both as solvent and acid catalyst⁵⁶. A treatment of MCC in [BMIM]HSO₄ at 70–
711 100 °C 1h30 was utilized to prepare rod-like cellulose nanocrystals. The authors mentioned
712 that the basic cellulose I structure was preserved in CNCs during the catalytic conversion
713 process and the degree of crystallinity of 95.8% was found to be higher compared to the
714 MCC. Recently, Abushammala et *al.* have reported for the first time a direct extraction of
715 CNCs from wood by means of [BMIM]OAc treatment⁵⁸. They demonstrated that the obtained
716 CNCs present high crystallinity of 75% and high aspect ratio of 65 with a yield of 44%. They
717 attributed the direct production of CNCs to the simultaneous capability of [BMIM] OAc to
718 dissolve lignin in situ and at the same time resulting in the swelling of cellulose only. More
719 recently, researchers have reported a facile one-pot preparation of hydrophobic CNCs from
720 wood pulpboard using the solvent system tetrabutylammonium acetate/dimethylacetamide in
721 conjunction with acetic acid, in which both the dissolution of amorphous cellulose and the
722 acetylation of hydroxyl groups takes place¹⁸¹. A typical procedure has been shown in Fig.
723 9. The authors mentioned that the CNCs were found to be hydrophobic with a rod-like
724 morphology, a good thermal stability and high crystallinity index. The yields of extraction
725 were unfortunately not mentioned in this study. Lazko et *al.* have reported the combination of
726 ILs to produce CNCs⁵⁵. They have extracted CNCs from cotton fibers using Brønsted acid-

727 type ionic liquids (ILs) via a two-step swelling/hydrolysis route. Water addition was used as a
728 medium to switch between these two stages. This complete process was accomplished in a
729 single reaction medium predominantly based on [BMIM]Cl and 1-(4-sulfobutyl)-3-
730 methylimidazolium hydrogen sulfate ([SBMIM]HSO₄). [BMIM]Cl and [SBMIM]HSO₄ are
731 known for their capacity of dissolving cellulose in function of water and promoting hydrolytic
732 processes, respectively^{55, 182}. Both swelling and hydrolysis of the cellulosic substrate were
733 successively achieved in a single [BMIM]Cl/[SBMIM]HSO₄ reaction medium; the switch
734 between the two swelling and hydrolysis steps being merely induced by water content
735 variation.

736 **5.6. Subcritical water hydrolysis**

737 The aptitude of water to hydrolyze polysaccharides is well known, as seen in hydrothermal
738 processes of hemicelluloses elimination¹⁸³. The main characteristics for a prevalent hydrolysis
739 rate are both the presence of water molecules and the availability of H₃O⁺ species and water.
740 Sub- and supercritical water has lower values of K_w and, therefore, higher concentrations of
741 ionized species¹⁸⁴. Consequently, their utilization could be efficient for the hydrolysis
742 reactions. Some study has previously employed water at high temperature and pressure to
743 hydrolyze lignocellulosic materials. Very few investigations have been reported concerning
744 the production of CNCs by subcritical water hydrolysis method^{32, 59}. The exclusive utilization
745 of water as reagent is a promising procedure not only for its green characteristics but for its
746 low and cleaner effluent, low corrosion, and low cost of reagents as well⁵⁹. Novo *et al.*
747 produced CNCs from commercial microcrystalline cellulose using this process⁵⁹. The authors
748 reported that optimization of reaction conditions leads certainly to a good quality of CNCs
749 with a higher yield³². They used subcritical water (120 °C and 20.3 MPa for 60 minutes) to
750 hydrolyze cellulose. The experimental conditions allow higher diffusion, activity and
751 ionization of water. With that, partial hydrolysis of cellulose was reached with a yield of

752 21.9%. The obtained CNCs showed high crystallinity index (79.0%), rod-like shape with
753 similar aspect ratio as those reported for conventional cellulose nanocrystals. These CNCs in
754 addition exhibited a higher thermal stability also in comparison with the original cellulosic
755 source (onset around 300°C).

756 **5.7. Combined processes**

757 There are several key factors such as CNC properties and yields that are affected by the
758 source of cellulosic materials as well as different applied process¹⁰³. Many efforts have been
759 devoted to improve the properties and increase the yield in CNCs isolation, what play a
760 crucial role in final application and cost. In this regards, the improvement of extraction
761 technologies and development of combined processes using a combination of two or several
762 of the aforementioned methods could be one of the most effective ways to enhance CNCs
763 properties and address the yield restriction issue. Furthermore, numerous limitations still need
764 to be considered, such as the pollution of the environment, the corrosion of equipment's and
765 the difficulty in controlling the hydrolysis degree of cellulose³⁵. A number of combined
766 approaches for isolation of nanocrystals from cellulose have been reported. For instance, Tang
767 *et al.* have examined the individualization of cellulose nanocrystals from commercial MCC
768 employing a low-intensity sonication concept to improve the yield of CNCs based on sulfuric
769 acid hydrolysis. The obtained results showed that the overall yield of CNCs was increased
770 from 33% to 40% as a result of the supplement of sonication at 100 W for 30 min compared
771 to the traditional sulfuric acid hydrolysis method¹⁸⁵. Same research group has recently
772 proposed a method of for isolating CNCs from old corrugated contained fibers employing a
773 combined process that consists of enzymatic hydrolysis, phosphoric acid hydrolysis, and
774 sonication. It was revealed that the obtained CNCs present high crystallinity, good thermal
775 stability and improved dispersion with a higher yield of 28.98% with respect to CNCs derived
776 from a single phosphoric acid hydrolysis process⁶⁷. Another investigation by Beltramino *et al.*

777 allowed the optimization of the experimental condition to prepare CNCs using a combined
778 process using acid hydrolysis assisted with enzymatic treatment⁶⁶. Optimal conditions (10 U/g
779 odp cellulase, 25 min hydrolysis, 47 °C, 62 wt.% H₂SO₄) generated nanosized particles of
780 around ~200 nm with decreased surface charge and sulfur content. The optimization allowed
781 reduction of hydrolysis time by 44 % and increase of yield (>80%). More recently, Rohaizu &
782 Wanrosli reported the use of sono-assisted TEMPO oxidation of oil palm lignocellulosic
783 biomass to produce CNCs⁶⁴. They demonstrated that the sono-assisted treatment has a
784 remarkable effect, resulting in an increase of more than 100% in the carboxylate content and a
785 significant increase of approximately 39% in yield compared with the non-assisted process.
786 The obtained CNC displayed high crystallinity index of 72% and good thermal stability with a
787 yield production of 93%.

788 Ultrasonication wave and microwave techniques have also been used as assisting
789 technologies in physicochemical treatments of plant fiber materials to attain high efficiency.
790 Simultaneous ultrasonic wave microwave assisted method was first applied by Lu *et al.* to
791 produce CNCs from filter paper using sulfuric acid hydrolysis. Under the optimal conditions,
792 the yield and the crystallinity of CNCs with the crystal form of cellulose I α are 85.75% and
793 80%, respectively⁶⁸. Recently, Chowdhury & Abd Hamid have reported the preparation of
794 CNC from stalk of *Corchorus olitorius* employing the combination of ultrasonication and
795 microwave⁶⁵. They pretreated the jute stalk powder with sodium hydroxide under microwave
796 irradiation, followed by a bleaching with hydrogen peroxide. The obtained crude product was
797 hydrolyzed by ultrasonication in the presence of various hydrolyzing mediums (ionic liquid or
798 sulfuric acid). The derived rod-like CNCs exhibited high crystallinity index (>83%). The
799 yield percentage obtained using ionic liquid process (48%) was higher than that obtained
800 using sulfuric acid (43%).

801 **5.8. Purification and fractionation CNCs**

802 Since the common process used to produce CNCs is based on either pure acid hydrolysis
803 or combined with another process, the resulting aqueous suspension is usually quenched by
804 diluting with water at room temperature (eventually diluted with ice cubes) and in sometimes
805 filtered over a small-pore fritted glass filter. This hydrolysis procedure, however, presents
806 some post-treatment drawbacks, such as prolonged time and cost to eliminate free acid in the
807 cellulose nanofibers, for their utilization in industrial scale. Part of the excess acid and water-
808 soluble fragments can be removed during the centrifugations steps. The remaining free acid
809 molecules from the dispersion can further be eliminated by dialysis against water until they
810 achieve neutral pH. This step is costly and takes long time (more than two or three days) as
811 well^{20, 22}. To address such issues, CNCs prepared from acid hydrolysis can be adjusted to pH
812 about 9 using sodium hydroxide and washed with distilled water until to reach the
813 neutrality¹⁸⁶. Although this latter also took a long time, the chemical neutralization procedure
814 remains simple with less processing steps to produce CNCs. Recently, it was demonstrated
815 that CNCs neutralization method using NaOH was a simple, economic, and efficient with
816 respect to the dialysis method¹⁸⁷. The neutralization procedure can be followed by a
817 disintegration of aggregates to generate a complete dispersion of the nanocrystals using a
818 sonication step. The final aqueous suspension can be stored in a refrigerator after possible
819 filtration to eliminate any residual aggregates and adding few drops of chloroform to avoid
820 bacterial growth. The dialysis step in the acid hydrolysis extraction of CNCs procedure is not
821 necessary when enzymatic, ionic liquid, subcritical water, oxidation and mechanical methods
822 are employed. The main steps in this case consist of different treatments by washing,
823 neutralization, centrifugation and sonication. Supplementary steps of post-treatment of the
824 produced CNCs can be performed. For instance, the aqueous suspensions of CNC could be
825 separated into isotropic and anisotropic phases by increasing the concentration (by water

826 evaporation). Hirai et *al.* showed that the smaller nanoparticles lie in the isotropic phase
827 whereas the longer ones are found in the anisotropic phase¹⁸⁸.

828 To mitigate transportation costs during the processing of CNCs, drying of the final aqueous
829 suspensions has been reported to be an imperative step. In most cases CNCs is treated as
830 aqueous suspension because of its hydrophilic nature and tendency to agglomerate during
831 drying³⁵. The well established procedures are supercritical drying, freeze drying, and spray
832 drying¹⁸⁹. Results displayed that both the freeze and supercritical drying approaches generate
833 highly networked structures of agglomerates having multi-scalar dimensions (e.g. nanoscale).
834 Han et *al.* have reported on the self-assembling behavior of CNCs during freeze drying¹⁹⁰.
835 Fig. 10 depicts the formation mechanism of the lamellar geometry along with the alignment of
836 ultrafine fibers during the freeze-drying process. On the other hand, the spray drying has been
837 suggested as a technically suitable production procedure to dry CNCs suspensions¹⁸⁹.

838 **6. Conclusions**

839 Environmental friendly bio-renewable materials form different natural resources has
840 resulted in a great interesting in exploring new materials for advanced applications. Among
841 different renewable materials, cellulose is the most important and common polymer available
842 on the mother earth. Cellulose can be processed into different forms such as fibers; micro and
843 nanocellulose. Very recently the cellulose nanocrystals (CNCs) are being explored for a
844 number of advanced applications especially because of their crystalline structure and the
845 properties resulting from the crystalline structure. However, in spite of the huge advantages of
846 the cellulose nanocrystals, the energy consumption and production costs have limited their
847 wide spread applications. Hence, the first part of this review article has focused on the
848 different sources of cellulose and later has focused on the production methods for CNCs. In
849 addition structural organization of cellulose and nomenclature of cellulose nanomaterials has
850 also been discussed for beginners in this field. We believe that the studies presented in this

851 article will increase the interest of researchers on cellulose based nanomaterials as well as the
852 basic understanding of the cellulose nanocrystals.

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- 1210 **Fig. 1** Illustration of the annual number of scientific publications since 2006, using the search
1211 terms “Cellulose nanocrystals/cellulose nanowhisker and composite”. Data analysis
1212 completed using Scopus search system on 22 November, 2016.
- 1213 **Fig. 2** Schematic representation of the chemical structure and intra-, inter-molecular hydrogen
1214 bonds in cellulose (reprinted with permission from ref.¹⁹, Copyright © Elsevier
1215 Limited).
- 1216 **Fig. 3** Hierarchical structure of cellulose and its nanomaterials types. The combined figure is
1217 reproduced from several figures appearing in ref.^{19, 92, 191, 192} with permission.
- 1218 **Fig. 4** Transmission electron microscope (TEM) images of cellulose nanocrystals derived
1219 from (a) softwood¹⁹³, (b) hardwood¹⁹⁴, (c) tomato peel¹³⁴, (d) *Calotropis procera*³¹, (e)
1220 oil palm⁶⁴, (f) red algae⁴⁰, (g) sea plant¹⁵⁸, (h) tunicate¹⁰³, (i) bacterial cellulose¹⁹⁵.
1221 (reprinted with permission from ref.¹⁰³, Copyright © The American Chemical Society;
1222 ref.^{193, 194}, Copyright © The Royal Society of Chemistry; ref.^{31, 40, 64, 134, 158, 195},
1223 Copyright © Elsevier Limited).
- 1224 **Fig. 5** Scheme for cellulose isolation from tomato peels. All yield values were based on
1225 original TP in %. Reprinted with permission from ref.¹³⁴, Copyright © 2015, Elsevier
1226 Limited.
- 1227 **Fig. 6** Scheme of the tunicate cellulose isolation from *Halocynthia roretzi*. Reprinted from
1228 ref.¹³⁹ with permission. Copyright © 2014, Springer Science.
- 1229 **Fig. 7** (a) Schematic representation of the different steps used to produce CNCs (or NCC)
1230 from bleached cotton fabric. Reprinted from ref.¹⁹⁶ with permission. Copyright ©
1231 2015, Elsevier Limited; (b) The overall procedure for the preparation of CNCs (or
1232 NCC) by using phosphotungstic acid (HPW). Reprinted from ref.¹⁷⁰ with permission.
1233 Copyright © 2014, Elsevier Limited; (c) Simplified structure of a cellulose microfibril
1234 with crystalline segments irregularly interrupted by disordered segments. Disordered
1235 segments can be selectively targeted with controlled acid hydrolysis, leading to the
1236 isolation of cellulose nanocrystals. Adapted from ref.²² with permission. Copyright ©
1237 2016, The Royal Society of Chemistry.
- 1238 **Fig. 8** Schematic route for fabricating carboxylated CNCs. Reprinted from ref.²⁹ with
1239 permission. Copyright © The American Chemical Society.
- 1240 **Fig. 9** One-pot preparation of hydrophobic CNCs in TBAA/DMAc with acetic hydride
1241 (upper), and the more typical route (lower) with permission. Reprinted from ref.¹⁸¹
1242 Copyright © Springer Science.
- 1243 **Fig. 10** Schematic of possible formation mechanism of the lamellar geometry and the
1244 alignment of ultrafine fibers during the freeze-drying process. Reprinted from ref.¹⁹⁰
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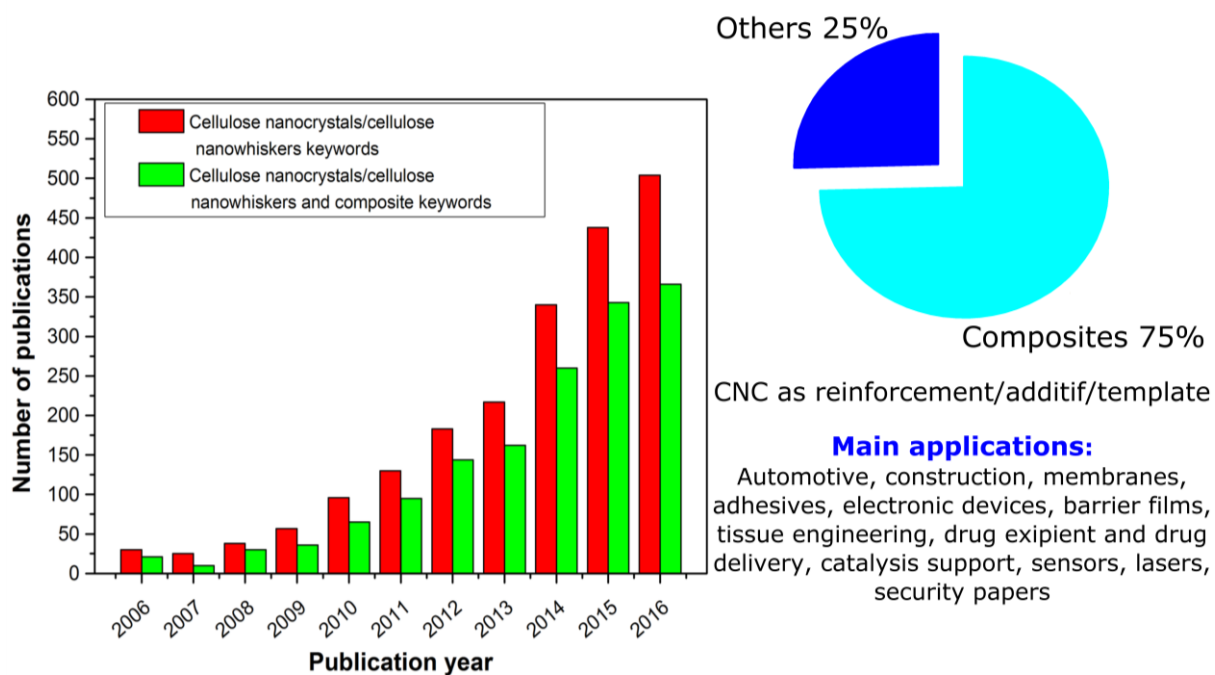


Fig. 1

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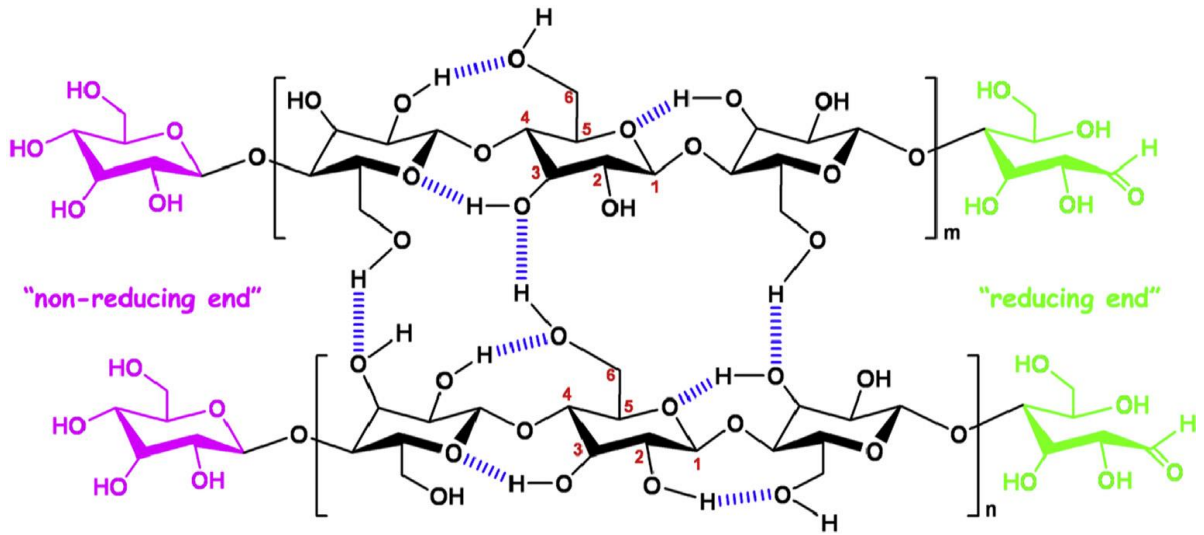


Fig. 2

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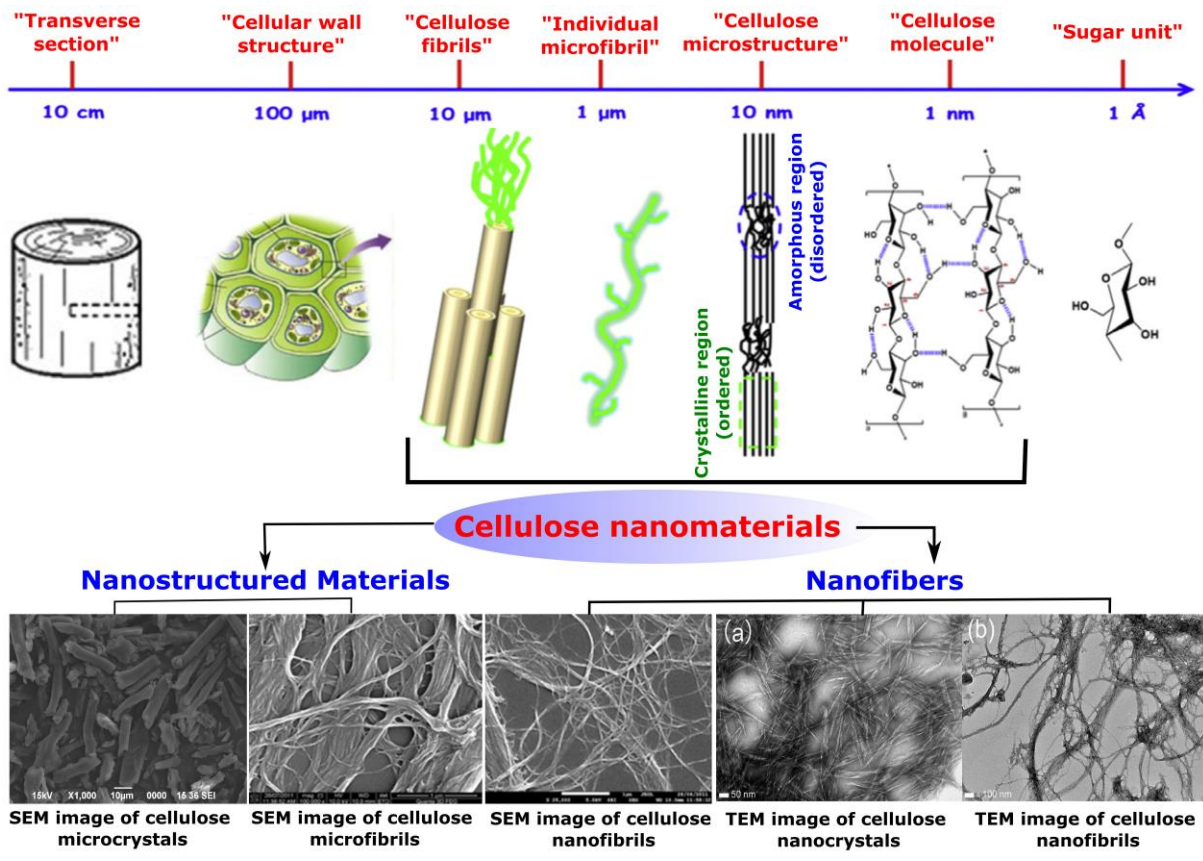


Fig. 3

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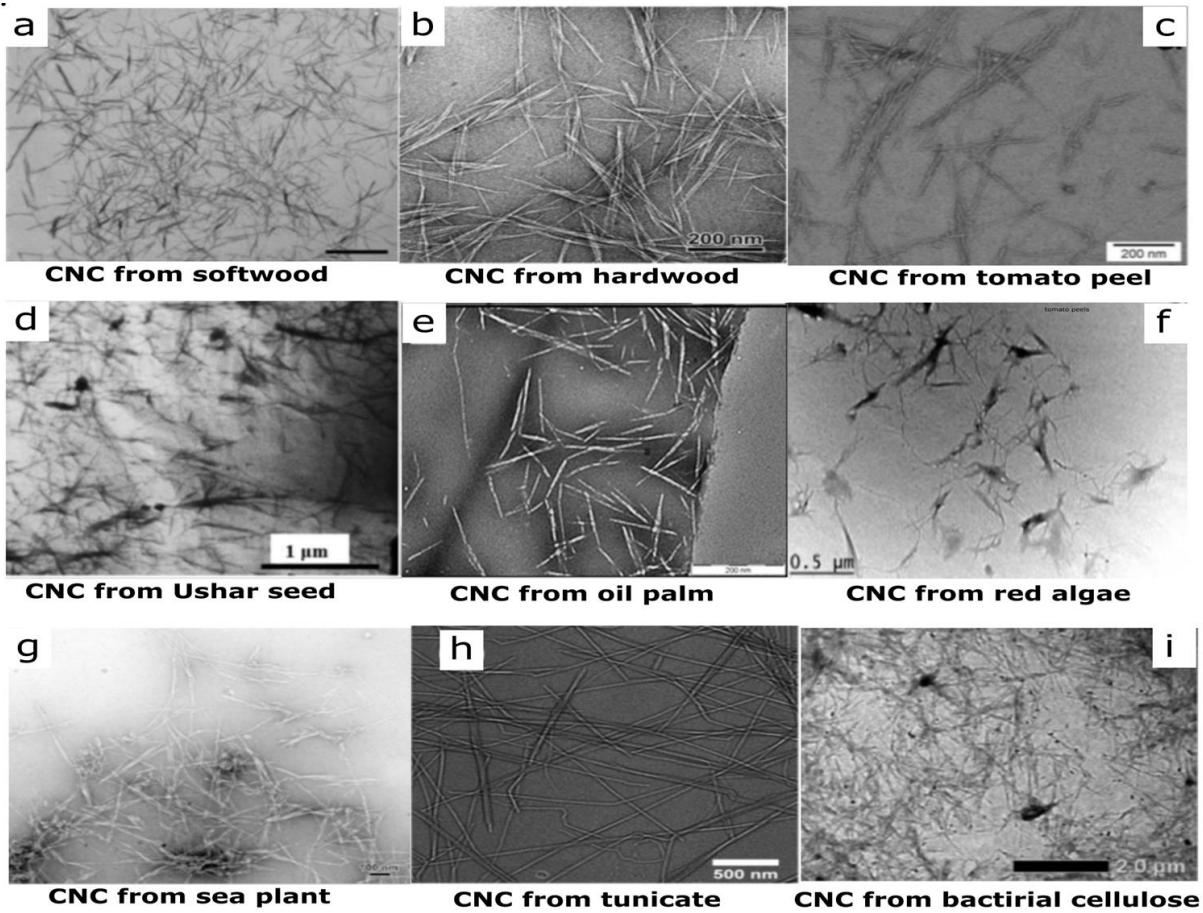


Fig. 4

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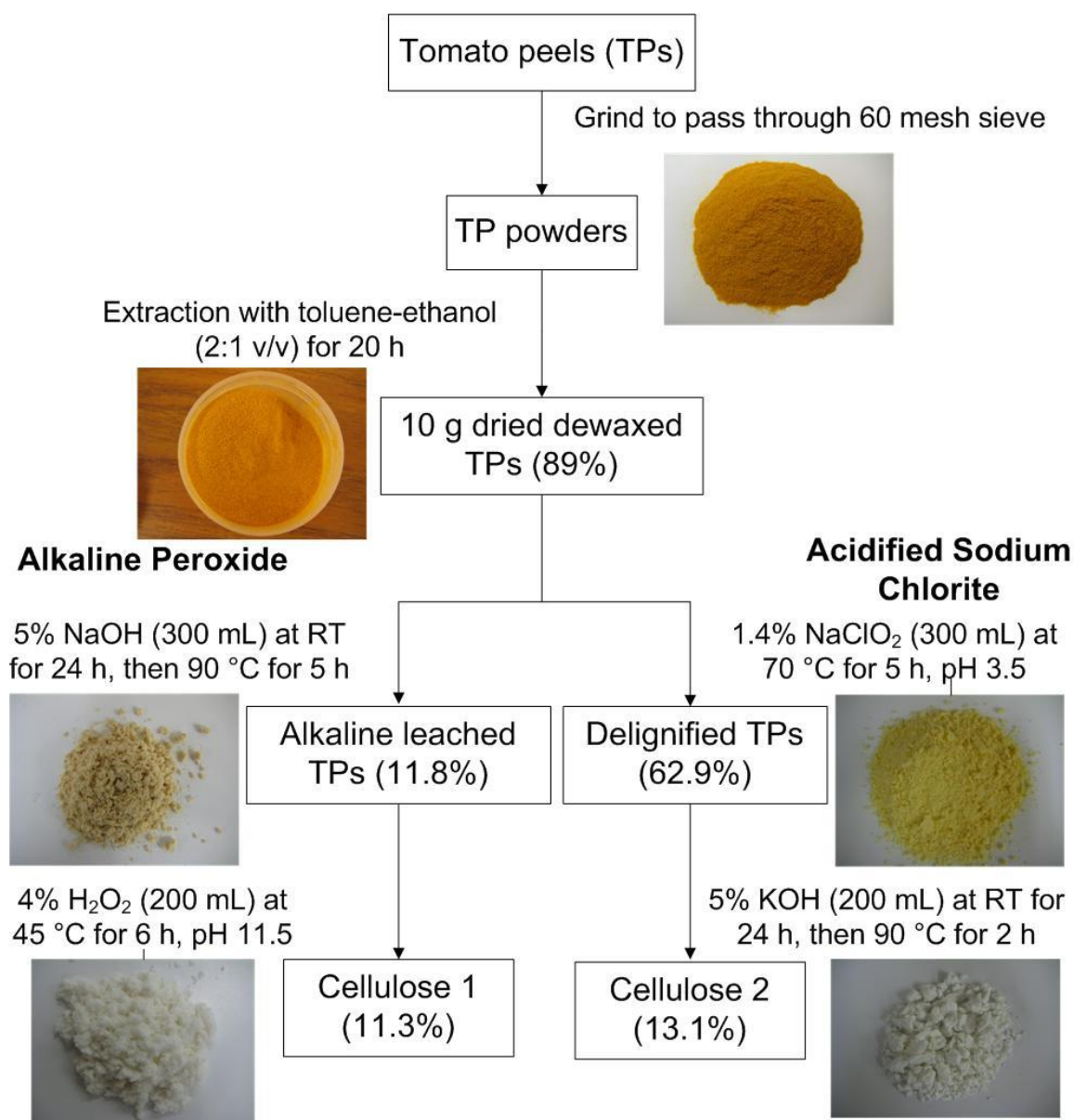


Fig. 5

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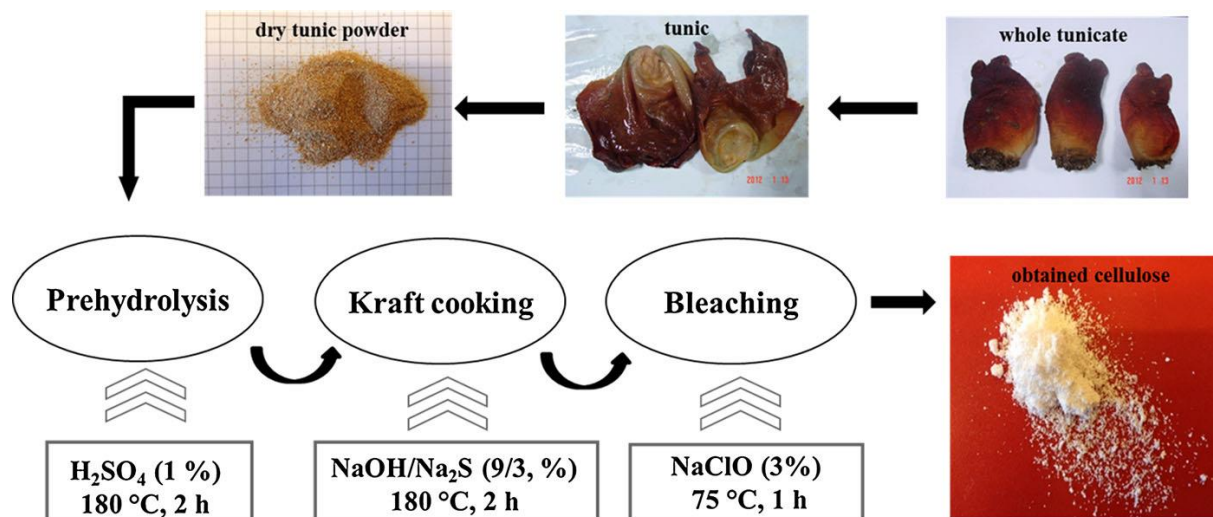


Fig. 6

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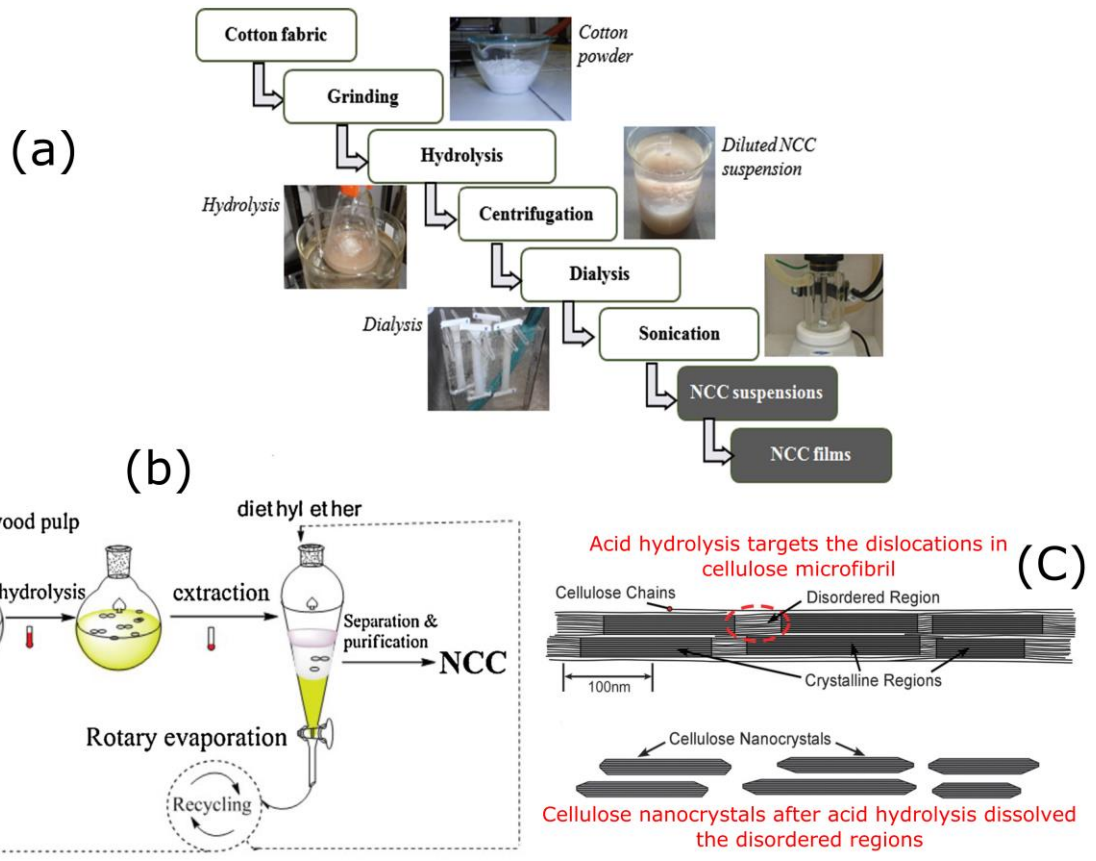
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Fig. 7

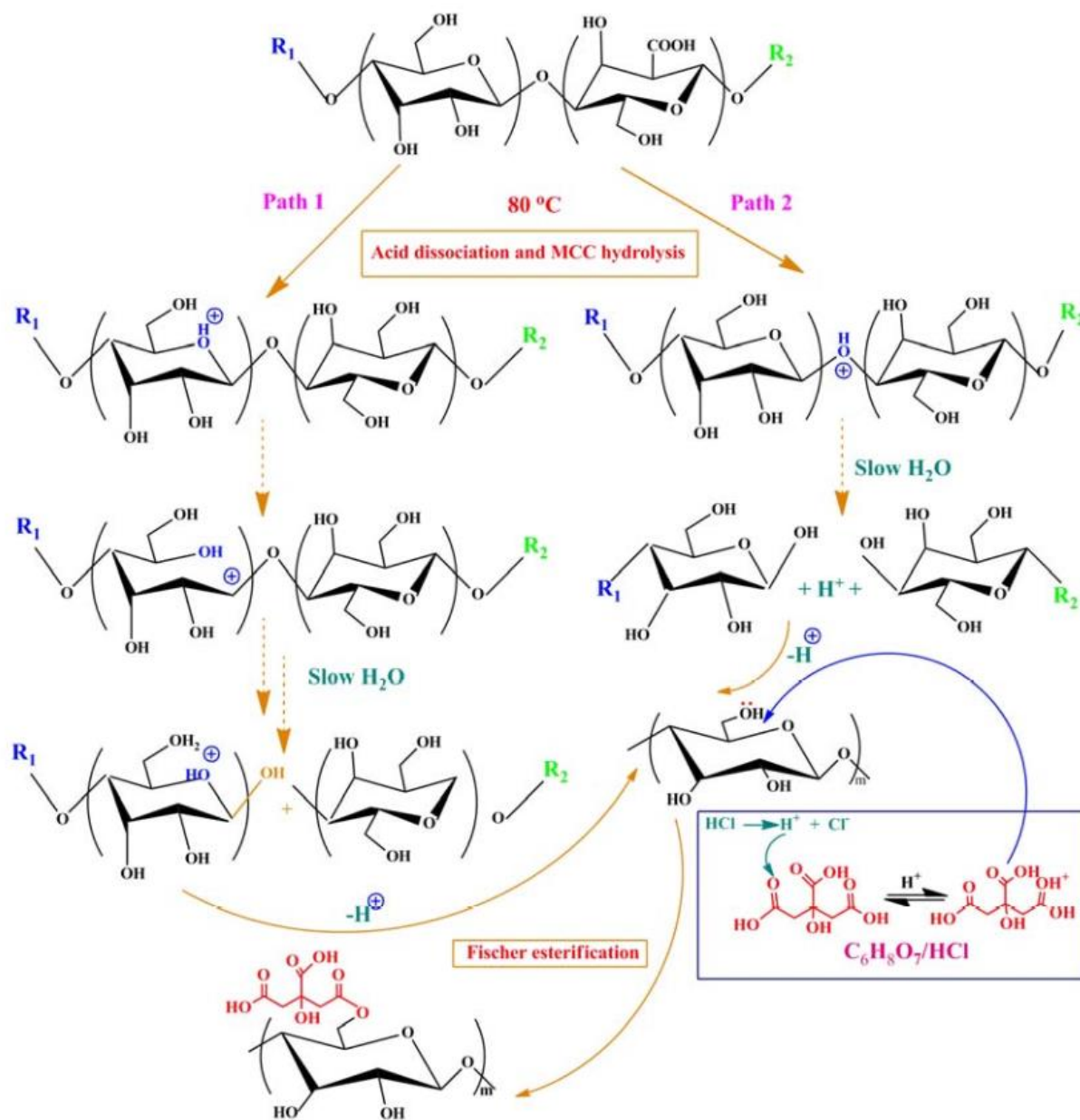
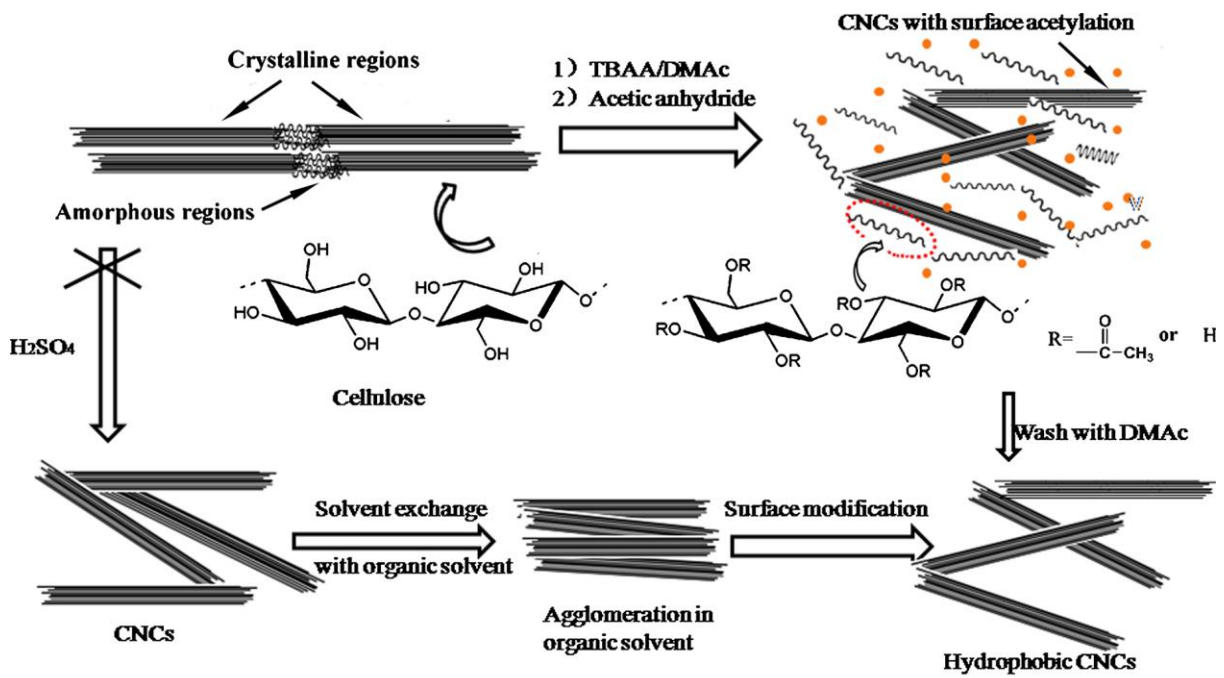


Fig. 8

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1345 • TBAA/DMAc, released carboxylic acid and the excess of use anhydride

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Fig. 9

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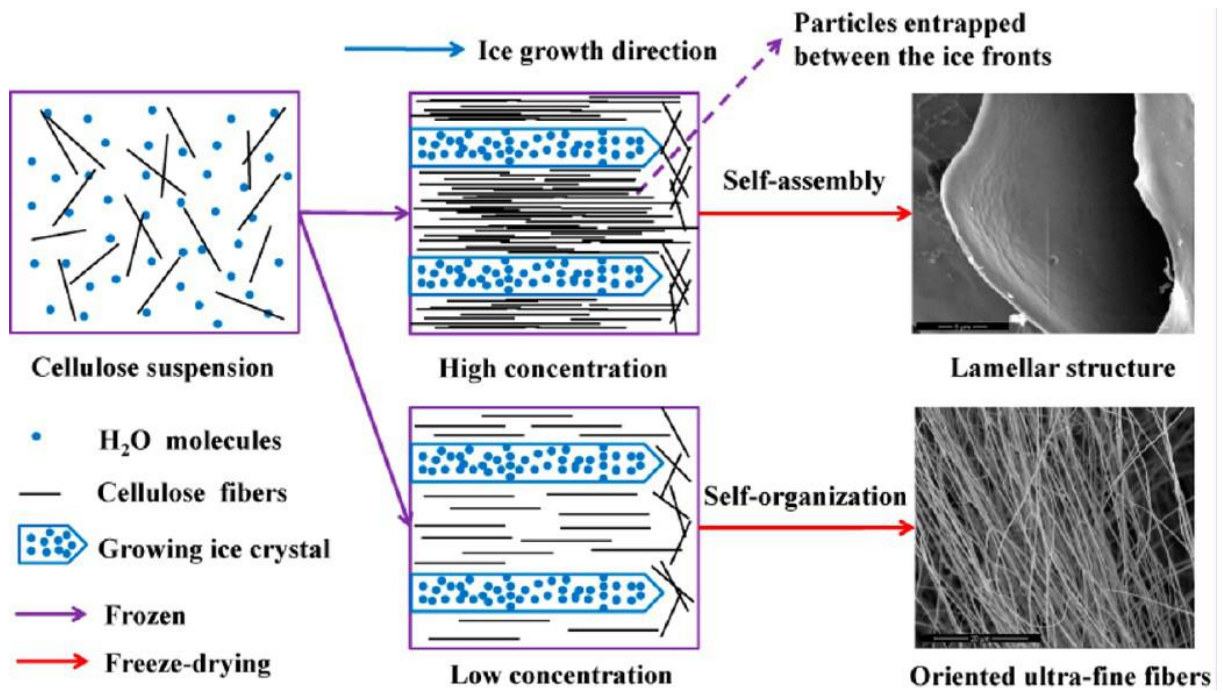


Fig. 10

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1371 **Table 1** Mechanical properties of cellulose nanocrystals and other reinforcement materials.

Material	σ (MPa)	E (GPa)	ρ (g cm ⁻³)	References
CNC	7500–7700	110–220	1.6	Moon et al. (2011) ²²
Glass fiber	4800	86	2.5	Kim et al. (2015) ⁷⁶
302 Stainless steel	1280	210	7.8	Hamad (2006) ¹⁹⁷
Softwood kraft pulp	700	20	1.5	Hamad (2006) ¹⁹⁷
Carbon fiber	4100	210	1.8	Moon et al. (2011) ²²
Boron nanowhiskers	2000-8000	250-360	—	Ding et al. (2006) ¹⁹⁸
Aluminum	330	71	2.7	Brinchi et al. (2013) ³⁵
Carbon nanotubes	11000-63000	270-950	—	Moon et al. (2011) ²²
Kevlar KM2 Fiber	3880	88	1.4	Brinchi et al. (2013) ³⁵

σ =tensile strength, E = *elastic modulus in axial direction*, ρ =*density*

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1387 **Table 2** Various lignocellulosic sources of cellulose nanocrystals fibers.

Source		References
Woody plants	Softwood	Hosseinidoust et al. (2015) ¹⁹⁹ , Moriana et al.(2016) ²⁰⁰ , An et al. (2016) ²⁰¹
	Hardwood	Du et al. (2016) ³⁸ , Mao et al. (2015) ⁵⁷ , Liu et al. (2014) ¹⁷⁰ , Chen et al. (2016) ¹⁷²
	Sawdust wastes	Kalita et al. (2015) ²⁰²
Non-woody plants and agricultural residues	Flax Fibers	Mtibe et al. (2015) ¹³¹ , Barbosa et al. (2016) ²⁰³
	Oil palm	Haafiz et al. (2014) ¹¹⁶ , Dungani et al. (2016) ¹¹⁷ , Lamaming et al. (2017) ²⁷
	Peanut Shells	Liu et al. (2015) ²⁰⁴
	Potato peel	Chen et al. (2012) ¹¹⁹ , Jiang and Hsieh (2015) ¹³⁴
	Jute	Cao et al. (2012) ⁶² , Kasyapi et al. (2013) ¹²⁰
	Kenaf	Kargarzadeh et al. (2012) ²⁰⁵ , Zainuddin et al. (2013) ²⁰⁶
	Hemp	Luzi et al. (2016) ²⁰⁷ , Abraham et al. (2016) ²⁰⁸ , Pacaphol et al. (2017) ²⁰⁹
	Bagasse	Camargo et al. (2016) ²¹⁰ , de Oliveira et al. (2016) ³⁹
	Corn	Silvério et al. (2013) ¹²⁶ , Kampeerappun (2015) ²¹¹ , Costa et al. (2015) ²¹²
	Pineapple leaf and coir	dos Santos et al. (2013) ²¹³ , Deepa et al. (2015)
	Alfa	Hammiche et al. (2016) ²¹⁴
	Bamboo	Chen et al. (2011) ¹²⁷ , Lu et al. (2015) ²¹⁵
	Sunflower	Fortunati et al. (2016) ²¹⁶
Garlic straw residues	Kallel et al. (2016) ²¹⁷	

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Table 3 Different processing conditions used for the production of CNCs.

Main process	Raw material	Purification	Treatment Procedure	Post-treatment	Reference
Acid hydrolysis	Microcrystalline cellulose	No	Dilution, cation exchange resin hydrolysis, ultrasonication	Filtration, rinsing, centrifugation	Tang et al. (2011) ⁴⁷
	Pineapple leaf	Grinding, Sodium hydroxide, acetic acid, sodium chlorite treatments	Grinding, H ₂ SO ₄ 64% at 45 °C hydrolysis, dilution	Centrifugation, dialysis, ultrasonication	dos Santos et al. (2013) ²¹³
	Whatman filter paper	Blending	4N HCl solution at 100 °C for 120 min	Centrifugation, dialysis, ultrasonication	Camarero Espinosa et al. (2013) ⁴⁶
		Blending	H ₃ PO ₄ 85% at 60 °C hydrolysis, dilution	Centrifugation, dialysis, ultrasonication, lyophilization	
	White coir	Organosolv process, alkaline-peroxide bleaching	H ₂ SO ₄ 30% at 60 °C hydrolysis, dilution	Centrifugation, dialysis, ultrasonication	Nascimento et al. (2014) ¹³⁸
	Pseudostems of banana plants	Soxhlet extraction, alkali treatment, bleaching with H ₂ O ₂ and acetic acid	Dilution, blending, H ₂ SO ₄ at 50 °C hydrolysis	Centrifugation, dialysis, lyophilization	Mueller et al. (2014) ¹³²
	Bleached hardwood pulp	No	Phosphotungstic acid (H ₃ PW ₁₂ O ₄₀) hydrolysis at 0 °C, extraction with diethyl ether	Decantation, ethanol precipitation, washing/centrifugation cycles	Liu et al. (2014) ¹⁷⁰
	Recycled Newspaper	Grinding, Sodium hydroxide, sodium chlorite treatments at 125 °C	H ₂ SO ₄ 65% at 45 °C hydrolysis, dilution	Centrifugation, dialysis, sonication	Mohamed et al. (2015) ²¹⁸
	<i>Posidonia</i>	Sodium hydroxide, acetic acid,	H ₂ SO ₄ at 55 °C hydrolysis	Centrifugation, dialysis,	Bettaieb et al.

	<i>oceanica</i>	sodium chlorite treatments		ultrasonication	(2015) ¹⁵⁸
	Bleached kraft eucalyptus dry lap pulp	Soaking in water, disintegrating, drying	Anhydrous organic acid hydrolysis at 90-120 °C, dilution, filtration	Washing, centrifugation, dialysis	Chen et al. (2016) ¹⁷²
	Sisal fibers	Grinding, bleaching	Grinding, H ₂ SO ₄ 60% at 55 °C hydrolysis, dilution	Centrifugation, dialysis	Mariano et al. (2016) ¹³³
	Bleached eucalyptus kraft pulp	No	Anhydrous ferric chloride -catalyzed formic acid hydrolysis at 95 °C	Centrifugation, dilution, distillation, dissolution in water, precipitation	Du et al. (2016) ³⁸
	Commercial microcrystalline cellulose	No	Citric/hydrochloric acid hydrolysis	Washing, centrifugation, freeze drying	Yu et al. (2016) ²⁹
	Bacterial cellulose	Washing, homogenization, drying, grinding	H ₂ SO ₄ /HCl mixture at 45 °C, dilution	Centrifugation, dialysis, ultrasonication	Vasconcelos et al. (2017) ²⁶
Mechanical treatment	Microcrystalline cellulose	No	Swilling in water, ultrasonication at power of 1500 W	centrifugation, freeze drying	Li et al. (2012) ⁵⁴
	Microcrystalline cellulose	No	Dispersion in water, ultrasonication for 50 minutes at an output of 500 W, frequency of 20 kHz Dispersion in water, high-energy bead milling	Decantation, freeze drying	Amin et al. (2015) ⁵²
	Wood	Ethanol solvothermal treatment, alkaline hydrogen peroxide treatment	Soaking in distilled water, ultrasonication	Washing, drying	Li et al. (2016) ²¹⁹
Oxidation method	Jute fibers	Grinding, Sodium hydroxide, washing, dimethylsulfoxide treatments	Treatment with TEMPO/NaClO/NaBr system	Centrifugation, sonication, drying	Cao et al. (2012) ⁶²

	Bleached kraft hardwood pulp	No	lithium chloride-assisted sodium metaperiodate oxidation at 75 °C	Washing, dispersion, homogenization	Visanko et al. (2014) ¹⁷⁷
Enzymatic hydrolysis	Cotton fibers	Hydrochloric acid hydrolysis (4N HCl)	Fermentation	Centrifugation, ultrafiltration, freeze drying	Satyamurthy et al. (2011) ⁵¹
	Cotton fibers	DMSO and NaOH, ultrasonic treatments	Treatment with buffer solution of cellulose at 45 °C	Centrifugation	Chen et al. (2012) ⁵⁰
	Flax and Hemp fibers	Washing, drying, chemical/ultrasonic/microwave pretreatment	Treatment in acetate buffer supplemented with endoglucanase and incubated in a shaker at 50 °C	Centrifugation, rinsing, ultrafiltration, freeze drying	Xu et al. (2013) ⁴⁹
	Bleached kraft pulp	Pre-soaking in water, grinding, centrifugation	Treatment with commercial enzymes or termite cellulose and incubated at intervals from 6-72 h at 35°C.	Washing, lyophilization	Anderson et al. (2014) ⁴⁸
Ionic liquid treatment	Cotton cellulose fibers	Drying at 105 °C during 24 h	Treatment with 1-butyl-3-methylimidazolium chloride in presence H ₂ SO ₄ of at 80 °C, dilution	Washing, centrifugation, freeze drying	Lazko et al. (2014) ¹⁸²
	Bleached wood kraft pulp	Oven drying	Swelling in pure 1-butyl-3-methylimidazoliumhydrogen sulfate at room temperature followed by the incorporation of deionized water	Centrifugation, dialysis, freeze drying	Mao et al. (2015) ⁵⁷
	Angelim vermelho wood	Grinding, dewaxing, washing, drying	Treatment with 1-Ethyl-3-methylimidazolium acetate at 60 °C, centrifugation	Washing, DMSO treatment, dissolving, drying	Abushammala et al. (2015) ⁵⁸
	Pure cotton	No	Swelling in 1-butyl-3-methylimidazolium chloride and 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate followed by quenching by adding cold water.	Washing/centrifugation cycles, freeze drying	Lazko et al. (2016) ⁵⁵

	Hardwood pulpboard	No	Treatment with solvent system tetrabutylammonium acetate/dimethylacetamide in conjunction with acetic acid at 65 °C	Washing, centrifugation, drying	Miao <i>et al.</i> (2016) ¹⁸¹
Subcritical water hydrolysis	Commercial microcrystalline cellulose	No	Water hydrolysis at 120 °C and pressure of 20.3 MPa	Filtration with a Pyrex® Buchner funnel with glass fritted disc, dialysis, ultrasonication	Novo <i>et al.</i> (2015 & 2016) ^{32, 59}
Combined processes	Filter paper	Cut into pieces	Treatment with sulfuric acid solution assisted by simultaneously ultrasonic wave and microwave	Dilution, centrifugation, drying	Lu <i>et al.</i> (2013) ⁶⁸
	Bamboo pulp sheet	Cut into pieces, pulping	Ultrasonication-assisted Ferric chloride -catalyzed hydrolysis, dilution	Washing, centrifugation	Lu <i>et al.</i> (2014) ²²⁰
	Old corrugated container material	Disintegration, soaking in water, pulping, sodium hydroxide pretreatment	Phosphoric acid hydrolysis, washing, enzymatic hydrolysis,	Ultrasonication , centrifugation, dialysis, freeze drying	Tang <i>et al.</i> (2015) ⁶⁷
	Cotton linters	No	Acid hydrolysis and subsequent processing in a high-pressure homogenizer.	Washing, filtration, drying, dispersion	Savadekar <i>et al.</i> (2015) ²²¹
	Commercial microcrystalline cellulose	No	Dispersion in water, ultrasonication combined with tungstophosphoric acid	Extraction with diethyl ether, drying	Hamid <i>et al.</i> (2016) ²²²
	Oil palm empty fruit bunch microcrystalline cellulose	No	Sono-assisted TEMPO-oxidation, followed by sonication (mechanical treatment)	Washing, centrifugation, drying	Rohaizo and Wanrosli (2017) ⁶⁴

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Cellulose nanocrystals, an emergent nanomaterial, can be produced from various natural sources using different procedures such as acid hydrolysis, mechanical, enzymatic, oxidation, ionic liquid, subcritical water or combined processes.

