

Emerging green routes to nanocellulose

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1. Introduction

First isolated in 1977 in the form of a translucent hydrogel at a USA-based paper and pulp company by repeated treatment of a 3% slurry of chopped wood pulp fibers with a high-pressure milk homogenizer, the new biomaterial was called “microfibrillated cellulose” (MFC).¹ “At the high temperature the high forces (pressure/cavitation/shear/impact) of the homogenizer acting in tandem or sequentially” wrote Turbak in 2015 “had broken down the cell walls of the microfibers and liberated the desired nanofibrils”.²

Nanocellulose, namely cellulose fibrils with widths in the nanometer range,³ was born. Explicitly mentioning its “uses and commercial potential” in the early research reports,¹ chemists understood that the material had numerous potential applications, well beyond paper and paperboard making which was (and still is) the main industrial utilization of wood-derived cellulose.

In the subsequent four decades, nanocellulose has attracted the research attention of scientists from across the world who rapidly discovered its exceptional mechanical, optical, chemical, biological and thermal properties.^{3,4} Composites, furthermore, are easily obtained through the straightforward combination of highly hydrophilic nanocellulose with inorganic and organic substances.⁵ In principle, the aforementioned properties coupled to full recyclability, biodegradability, and lack of toxicity make nanocellulose and nanocellulose-based composites suitable for application in a vast array of industrial fields.

Numerous excellent books^{6,7,8} describe the structure and the preparation routes of different nanocelluloses, with recent monographs devoted to specific applications of nanocellulose for instance in electronics⁹ or in water treatment.¹⁰

From nanocellulose-based aerogels,¹¹ through energy storage systems,¹² applications in biomedicine,¹³ environmental remediation,¹⁴ and catalysis,¹⁵ numerous review articles on nanocellulose uses have been published and are continuously published on a routine basis. Hence, rather than adding a new review in a rapidly evolving research field, this study provides a critical outlook on the emerging green production routes of this “ageless bionanomaterial”.¹⁶

The study concludes suggesting new avenues to foster economic development and tackle environmental

issues using nanocelluloses sourced from cellulosic biowaste¹⁷ based on said new environmentally friendly production routes.

2. Current production routes

Nanocellulose is generally sourced by selected companies from wood pulp as cellulose nanofiber (CNF) or cellulose nanocrystal (CNC). In addition, highly pure and expensive bacterial nanocellulose (BNC) is industrially synthesized on small scale from glucose using *Gluconoacetobacter xylinus* bacteria. The latter methods, however, “are inefficient and the growth medium is expensive”¹⁸

A comprehensive review on nanocellulose including the main production routes and the history of nanocellulose has been lately published by Li, Yadav and co-workers.¹⁹ In general, harsh chemical conditions, high-energy costs and undesired production of large effluent amounts so far have intrinsically limited the large-scale production of nanocellulose.

Likewise to the process used in the paper and pulp industry, separation of cellulose from lignin is done either via acid-chlorite or alkaline treatment. Alone, this process generates large amounts of wastewater. After that, nanocellulose fibrils are extracted from wood pulp either via acid hydrolysis with sulfuric acid (further adding wastewater to the process), enzymatically (requiring long extraction times and with relatively low efficiency), or mechanically via high-pressure homogenization.²⁰ Steam explosion or ultrasonication, with high-energy consumption, are also suitable.²¹

Hydrolysis with aqueous H₂SO₄ affords nanocellulose in nanocrystal form. Comprised of cellulose I only, CNC has a low length/diameter “aspect” ratio (10-100), and a tensile strength similar to that of aramid-fiber (10 GPa). Its industrial production from has an estimated production cost ranging from \$3632/t to \$4420/t, with feedstock cost and capital investment being the major cost drivers.²² Remarkably, in the same year of these estimates (2017) for large scale production, CNC was reported to be actually sold at \$1,000/kg.²³

Chiefly manufactured using TEMPO-mediated oxidation of wood cellulose followed by mechanical dispersion of the oxidized fibers, CNF has a higher length/diameter ratio (100-150). Its structure includes both amorphous cellulose and crystalline cellulose I. The 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) used in according to de Nooy’s protocol for the selective oxidation of primary alcohol groups in polysaccharides (aqueous NaOCl as primary oxidant in the presence of a catalytic amount of bromide at pH 9-10)²⁴ partly oxidises the primary alcohol groups of water-insoluble cellulose to carboxylate groups.²⁵ It is enough to mechanically grind or sonicate the TEMPO-oxidized (wood pulp, cotton, tunicin, and bacterial cellulose) cellulose to fibrillate the oxidized cellulose fibers into an homogeneous, highly viscous suspension 3-5 nm cellulose nanofibrils.²⁵ The electrostatic repulsions between the cellulose fibrils bearing the COO⁻ groups ensures good dispersion and high stability of the nanofibrils in solution. Repulsion among the carboxylated fibers, furthermore, causes a decrease in the electricity consumed to power the mechanical fibrillation process.

Since 2017, the process is used by a large paper company in Japan to manufacture CNF in the form of nano-dispersed fibers with uniform fiber width of 3 to 4 nm starting from bleached wood pulp at two different paper mills.²⁶ The company supplies the ‘Cellenpia’ product series to different industrial customers producing CNF-reinforced tires, paper barrier cups for beverages, personal care, hygiene, and cosmetic products. In 2019, the same company successfully developed a CNF-reinforced composite subsequently used to produce a car whose weight was about 10% lower than a conventional car made in steel.²⁷

Currently CNF is sold at a cost of \$90-100/kg.²⁸ This high cost is due to the high cost of TEMPO and to the cost of processing the spent hypochlorite dilute solution containing the genotoxic TEMPO catalyst as well as corrosive NaBr.²⁸ Separating nitroxyl radicals in solution is a multi-step, expensive process,³⁰ whereas TEMPO concentration in any material suitable for biomedical use, must be lower than the threshold of toxicological concern (*i.e.* , 4 ppm).³¹

3. Emerging green routes

Recently reviewing research published between 2015 and 2020 concerning new CNF/CNC preparation routes, Li and co-workers identified 69 studies.¹⁹ All new processes included two or three pretreatment steps, followed by chemical and mechanical treatment. Amid the mechanical treatment processes, ultrasonication was found to be dominant. Another recent comprehensive review aimed to identify new extraction methods from cellulosic biowaste reported that sugarcane bagasse with its high lignocellulose content and loose structure and algae residues are the most suited biowastes to extract nanocellulose.³²

Poor in lignin and available in over 60 million tonnes yearly amount, citrus processing waste (CPW) obtained from the citrus juice industry is another ideal cellulose feedstock. The annual production of citrus fruits exceeds 120 million tons, and more than half of the fruit is non-edible and discarded as waste. Alone, the the global volume of citrus fruits squeezed at industrial juice plants every year exceed 31 million tonnes, 50-60% of which is waste.³³

Unfortunately, the routes to citrus nanocellulose starting from CPW based on enzymatic,³⁴ microwave-assisted hydrothermal treatment,³⁵ and acid hydrolysis,³⁶ all present significant technical limitations. For example, the nanocellulose fibrils obtained via multi-step microwave-assisted extraction of dried depectinated orange peel are deeply colored in brown due both to caramelized sugars and to the Maillard reaction between sugars and residual proteins at the high temperatures (120°C to 180°C) required for extraction.³⁵

One entirely green route to nanocellulose in CNC form was reported by Huang and co-workers in 2018.³⁷ The team used ball milling of cellulose in water only, followed by centrifugation. The process quickly affords cellulose disintegration down to elementary fibrils 3-10 nm wide and 120-400 nm long. To understand the relevance of this discovery, it is instructive to compare it to enzymatic hydrolysis with cellulase enzymes. Applied to eucalyptus cellulose pulp using a new commercial enzymatic complex at cellulose loading of 10% (w/v) and enzyme loading of 10 mg/g cellulose,³⁸ or even relying on a cellulolytic enzymatic complex produced on-site by *Aspergillus niger* followed by sonication,³⁹ the optimal enzymatic process affords a 24.6% yield in CNC (after 96 h of enzymatic hydrolysis of cellulose pulp, followed by 5 min sonication).

As mentioned above, the TEMPO-mediated carboxylation of cellulose and production of nanocellulose has already been commercialized.²⁶ Numerous practically relevant discoveries using heterogenized TEMPO catalysts showed evidence, on laboratory scale, how shifting the CNF production process from using TEMPO in solution to new generation heterogeneous TEMPO catalysts has substantial benefits in terms of enhanced CNF materials and reduced environmental impact.⁴⁰

Interestingly, Turbak recognized that cavitation was among the “high forces of the homogenizer”² responsible for cellulose fibrillation using the high pressure homogenizer. More than 40 years after Turbak and co-workers discovery, in 2010 Pandit and Pinjari in India were the first to report the outcomes of acoustic cavitation (AC) and hydrodynamic cavitation (HC) applied to a 1% w/v (0.5 kg in 50 L water) aqueous suspension of 63 µm cellulose microparticles.⁴¹

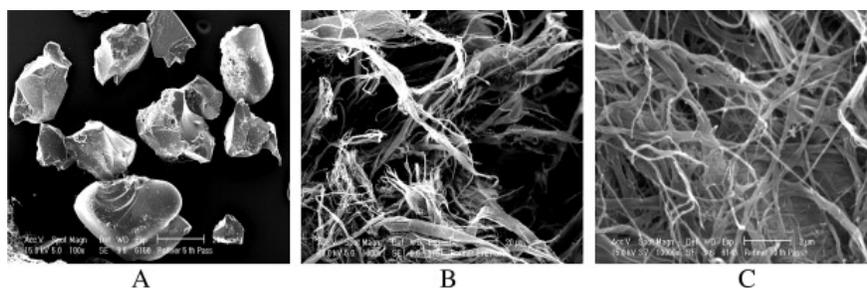


Figure 1: SEM images of (A) initial sample at 100×, (B) hydrodynamically processes sample at 5000×, and (C) ultrasonically processes sample at 10,000×. [Reproduced from Ref.41, Creative Commons Attribution (CC BY) license].

The team called “declumping” the fibrillation of the bulk cellulose driven by both AC and HC (Figure 1). Indeed, ultrasonically processed cellulose was completely fibrillated into individually separated fibrils less than 100 nm thick due to the more intense cavitation collapse and absence of fluid flow of acoustic cavitation, whereas hydrodynamic cavitation resulted into full cellulose fiber-fiber detachment with some fibers at nano level and most of the fibers of micrometer thickness.

Both forms of cavitation reduced cellulose crystallinity from 87% to 38%. Such dominant presence of amorphous domains enhances the flexibility and plasticity of the material, and lowers both stiffness and elasticity.⁴² The particle size decreased to 1.36 μm and 0.3 μm for the hydrodynamically and ultrasonically processed cellulose samples, respectively. whose thermal stability was significantly higher of the newly obtained nanocelluloses due to decrystallization.

We briefly remind that the cavitation bubbles generated in water via acoustic or hydrodynamic cavitation upon collapse locally release short-lived (μs duration) shockwaves of extreme pressures (1000-2000 atm) and temperatures (5000 K) that are ideally suited for the extraction of natural products.⁴³

Two years later, Paquin and co-workers in Quebec reported that by carrying out the aminoxyl-radical mediation oxidation of a diluted suspension (1 wt%) of bleached hardwood kraft pulp in a 45 L flow-through sonoreactor, a 87.5% decrease in energy consumption (in comparison to the process in batch reactor) and a 95% higher production rate of oxidized fibers (compared to reaction without any ultrasound in batch mode) are achieved. These results, the team concluded, suggest the possibility of scaling up the process on industrial scale directly in continuous mode.⁴⁴

The original discovery of Pandit and Pinjari using no added chemicals to fibrillate crystalline cellulose, however, remained without further investigation until the teams of Meneguzzo and Pagliaro demonstrated the process on semi-industrial scale by processing via HC more than 30 kg of citrus (lemon and grapefruit) processing waste in 120 L water.⁴⁵

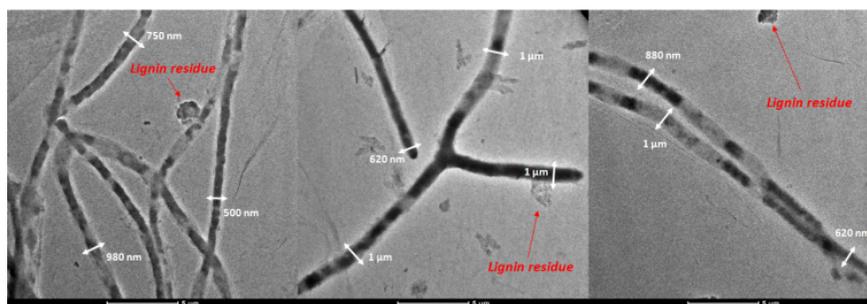


Figure 2: TEM images of grapefruit CythroCell focusing on selected single fibrils. [Reproduced from Ref.44, Creative Commons Attribution (CC BY) license].

Lemon CythroCell consists of 0.5-3 μm long microfibrils whose section varies between about 110 and 420 nm. Grapefruit CythroCell is comprised of ramified microfibrils whose diameter varies from 500 nm to 1 μm (Figure 2).⁴⁶ Both new “CythroCell” materials consist of cellulose of low crystallinity index (0.33 for lemon and 0.36 for grapefruit). The one-pot process requires no subsequent mechanical treatment of the fibrillated nanofibers. In brief, the highly efficient HC creates cavitation bubbles which fibrillate and promote decrystallization of the citrus peel microcrystalline cellulose fibers. The effect is intensified by the presence of the residual citric acid relatively abundant in the wet CPW used as biological source of nanocellulose, as it happens when acoustic cavitation is applied to microcrystalline cellulose in the presence of 0.2 M citric acid.⁴⁷

4. Outlook and perspectives

Comparing four routes to wood pulp-derived nanocellulose (TEMPO-oxidation followed by sonication or homogenization and chloroacetic etherification followed by sonication or homogenization), Rennecker and co-workers found that TEMPO oxidation followed by homogenization is the lowest impact nanocellulose process.⁴⁸ For comparison, the team found that the energy and environmental impact factors for nanocellulose industrial production using the latter optimal route are, respectively, 4 and 20 times larger than the kraft pulp production.

Whether using concentrated H_2SO_4 to hydrolyze the amorphous regions of cellulose and isolate CNC,²² or relying on the TEMPO-catalyzed process with bleach as primary oxidant and bromide as co-catalyst to afford CNF,^{25,26} current nanocellulose production methods are capital-intensive and have high operating costs. In the case of CNC, feedstock cost and capital investment are the major cost drivers, with sulfuric acid and lime consumption alone accounting for 25% of production costs for the lowest plant configuration without acid recovery.²²

In the case of CNF, high manufacturing costs are due to the large amount of electrical energy required for homogenization followed by the high cost of the TEMPO catalyst.⁴⁹ Furthermore, a large amount of solvent is needed to separate the CNF from genotoxic TEMPO, whereas the expensive TEMPO catalyst is lost amid the reaction effluents as the method to recover the TEMPO catalyst in a mixture of a water-miscible organic solvent and water,³⁰ could not be industrialized in the aqueous only cellulose oxidation process, likely due to high cost.⁵⁰

It is perhaps not surprising to find that the first large nanocellulose production plants are operated by paper and pulp companies, which are facing a dramatic fall in paper demand following the advent of the internet and other digital technologies.⁵¹ Beyond the aforementioned paper and pulp company producing CNF at two production sites in Japan,²⁶ for instance, another paper and pulp company based in Norway since late 2016 produces MFC at a production site with a 1,000 t/a capacity (on a dry basis). The ingredient is shipped to different industrial customers as 2% or 10% aqueous formulation.⁵²

Comparing CNC chiefly extracted from different producers via hydrolysis with concentrated H_2SO_4 and purified according to different procedures, Cranston and Reid found that all products share the same basic chemical structure and physicochemical properties of laboratory-made CNC.⁵³

Still, both main nanocellulose production methods need to be simplified, made less energy and capital intensive, and operating at lower cost. Beyond enzymatic extraction,³⁹ three methods are ready for optimization, scale up and commercialization: the heterogeneously catalyzed oxidation over new generation solid TEMPO catalysts,⁴⁰ (including magnetically recoverable Karimi's nanocatalyst),⁵⁴ ball-milling in the presence of water of cellulose,³⁷ and (for applications in need of nanocellulose of low crystallinity) acoustic and hydrodynamic cavitation.^{41,44,45} All are promising considering that many of the aforementioned catalysts are now commercial (Karimi's nanocatalyst in the form of 50 nm beads easily recovered with a magnet);⁵⁵ whereas the safe and robust hydrodynamic cavitation process for the extraction of natural products such as waste orange peel is easily scaled-up.⁵⁶

Enzymatic extraction, too, is an eminently clean nanocellulose production process.^{38,39} Dr Farinas in Brazil is one of the leading scholars in the field. Asked whether companies are using enzymatic extraction, she noted that:

“The use of enzymes to obtain nanocellulose is very challenging, but I believe it is a very promising alternative route. I believe that there are few companies using enzymes to obtain nanocellulose, but mostly to facilitate the production of nanofibrillated cellulose, as far as I know. One of them is VTT, using the *HefCel* concept in which enzymes facilitate the mechanical process”.⁵⁷

“HefCel” stands for high-consistency enzymatic fibrillation technology developed at VTT Technical Research Centre of Finland, in which cellulose fibrils are produced at high consistency (20-40%) by stirring concen-

trated cellulose pulp (20-40%) in the presence of a tailored cellulase enzyme mixture, resulting in 90% yield in fibrillated cellulose.⁵⁸ The low water content, furthermore, lowers the cost of drying.

Though not providing a timeline, market projections dating back to 2014 estimated a potential volume of nanocellulose exceeding 6.4 million tonnes/year only in the USA (5.9 million tons/year only in the high volume category, and 0.48 tonnes/year in the low volume category).⁵⁹ Four years later, however, the nanocellulose market did not reach 40,000 tonnes (39,600 tonnes), with the large majority of being produced at pulp mills in form of MFC used in their own paper and paperboard products.⁶⁰ In 2020, the market value amounted to about \$300 million globally, with dried bacterial nanocellulose selling at \$50/g,⁶¹ and the world's largest nanocellulose production plant having a capacity of 2.5 t/day.⁶⁰

It is instructive to learn that, besides use of MFC on paper and paperboard products, the main uses of nanocellulose concern low volume, and high value applications of CNF. For example, in Japan, the world's leading CNF manufacturing country, products using CNF include biodegradable cutlery of enhanced strength; foam materials for the midsole of sport shoes; CNF-coated diaphragm for speakers and television sets; coating agent to prevent concrete adhesion; and undercoat paint (sealer) preventing discoloration of the base material and cracks in the paint film.⁶²

For nanocellulose-enabled technologies⁵⁻¹⁰ to find practical utilization and industrial uptake there is a need for green production technologies through which scale up production, lower production costs and make nanocellulose available to industrial customers at affordable price. This, *inter alia*, requires to switch from expensive wood pulp (priced at \$907/tonne as of April 2021)⁶³ to low cost and abundant biowaste as cellulose source. Poor in lignin, and available in over 31 million tonnes/year, citrus biowaste whose other main component, pectin, is in high and increasing demand since more than a decade,⁶⁴ is an ideal nanocellulose source in a integrated biorefinery.⁶⁵

As put it by Jessop and Reyes, in scientific publications that use the “green chemistry” terminology, “there is an inversely proportional relationship between the number of papers published in an area and its associated environmental impact”.⁶⁶ This is true also for nanocellulose production where the raw material originates from agroforestry (paper and pulp, citrus, sugarcane, etc.) companies which are slowly, but inevitably, transforming into bioeconomy firms.^{26,52}

Though originating from apparently distant areas such as heterogeneous catalysis, enzymatic catalysis and acoustic or hydrodynamic cavitation, the new green chemistry technologies to manufacture nanocellulose are ready to be evaluated on scale and, if found technically and economically viable, uptaken by industry. To accelerate this progress, the new bioeconomy industry needs young researchers trained in the aforementioned chemical and physicochemical technologies, and with a critical knowledge of the field.

This study offers such critical outlook *en route* to mass uptake of this versatile, robust and safe bionanomaterial sustainably produced and preferably sourced from low cost cellulosic biowaste.

Conflict of interest

The Authors declare no conflict of interest.

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