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Sherin Peter, Nathalie Lyczko, Deepu Gopakumar, Hanna Maria, Ange Nzihou, et al.. Nanocellulose and its derivative materials for energy and environmental applications. *Journal of Materials Science*, 2022, 57 (13), pp.6835-6880. 10.1007/s10853-022-07070-6 . hal-03637175

HAL Id: hal-03637175


<https://imt-mines-albi.hal.science/hal-03637175v1>

Submitted on 11 Apr 2022

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Nanocellulose and its derivative materials for energy and environmental applications

Sherin Peter^{1,4,*} , Nathalie Lyczko¹, Deepu Gopakumar⁴, Hanna J. Maria⁴, Ange Nzihou^{1,2,3}, and Sabu Thomas⁴

¹ *Université de Toulouse, IMT Mines Albi, RAPSODEE CNRS UMR-5302, Campus Jarlard, 81013 Albi Cedex 09, France*

² *Department of Civil and Environmental Engineering, Princeton University, Princeton, NJ 08544, USA*

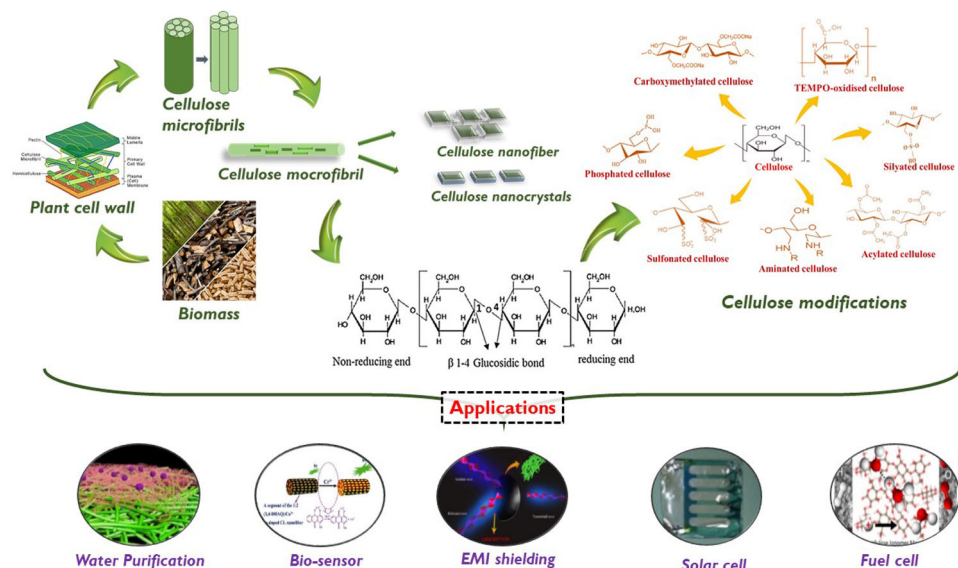
³ *Andlinger Center for Energy and the Environment, Princeton University, Princeton, NJ 08544, USA*

⁴ *International and Inter-University Centre for Nanoscience and Nanotechnology, School of Energy Studies, Mahatma Gandhi University, Kottayam 686 560, India*

ABSTRACT

The application of biomass-derived renewable materials has generated great interest in recent research works. Among many such biopolymers, nanocellulose has become the leading topic in the sphere of sustainable material owing to the outstanding mechanical, chemical and thermal properties along with non-toxicity, surface functionality, ease of modification and sustainability. Nanocellulose is often considered to be a second-generation renewable resource and a better replacement for conventional petroleum-based products with or without any modifications. Even though some reviews have reported on some of the applications of nanocellulose, so far there is no comprehensive report gathering the extraction, properties, functionalization towards energy and environmental applications. This review aims to present the use of nanocellulose based materials for energy and environmental challenges. Important characteristics such as crystallinity, hydrophilicity, thermal decomposition and surface charge are described as a function of the targeted applications. In the latter part of this review, we have looked into the recent studies in the area of applications such as air pollution, heavy metal sorption, dye adsorption, biosensors, EMI shielding, fuel cell, solar cell, lithium-ion batteries and biofuels etc. However, a green, sustainable and scalable nanocellulose extraction is yet to be fulfilled. In our view, the bacterial nanocellulose based approach can address all these issues with the added advantage of producing a very high purity of nanocellulose. Hence this review is intended to provide new insights into the field of eco-friendly functional materials with included in-depth perspectives about nanocellulose and its future based on the current research trends.

GRAPHICAL ABSTRACT



Introduction

The modern industrial and technological advancement resulted in high energy demands for daily operations and further developments. This high energy demand was met mostly by the exploitation of conventional natural fossil fuels such as petroleum and its derivatives. The never-ending energy demands and uncontrolled exploitations have resulted in the introduction of new pollutants to the environment, which resulted in more environmental pollution and thus forced to drive the attention towards eco-friendly and sustainable resources [1]. To counter the emerging uncontrolled pollution and also to maintain a sustainable futuristic approach, biomass-derived nano-materials have been vastly studied in recent years. Compared to the conventional alternatives, the multidimensional properties of the nano-materials and their derivatives exhibit certain advantages such as ease of processing, increased productivity, tunability, versatility and high surface to volume ratio all together have managed to attract the attention of many researchers to these materials[2]. The nano-size range contributed to

a very high surface area which is suitable for pollutant adsorption and modification, making the nanocomposite an attractive material for energy and environmental applications.

The lignocellulose-based sector has emerged as the green and sustainable alternative to conventional fossil resources to meet the increasing energy demands. It is estimated that the global nanocellulose market is forecasted to grow at a rate of 20.4% in terms of value, from USD 247.2 Million in 2019 to reach USD 1.08 Billion by 2027 as per the Reports and Data analysis. The major sources include; energy crops, food wastes, agricultural residues, forest residues, municipal and industrial wastes etc. Nanocellulose is found to be the most suitable material for preparing sustainable nano/micro composites for both energy and environmental applications where there is an increasing need for performance and sustainable new materials[3]. On an industrial scale, it is one of the most viable, dominant, sustainable and eco-friendly materials with outstanding inherent properties such as biodegradability, biocompatibility, outstanding mechanical properties, availability, low cytotoxicity, low density, high specific surface area, high aspect ratio [4]. The recent advancement shows

that nanocellulose can be isolated with different extraction methods, which could help in scaling up it for a larger application sector. There are numerous functionalisation techniques applicable to nanocellulose which could make it suitable for a broader range of applications [5]. The presence of a large number of hydroxyl groups on the surface of cellulose could be tailor-made for specific applications. Thus, nanocellulose-based composite materials have been synthesised in various forms in both energy production devices such as solar cells, biofuels, lithium-ion battery binders, separators in supercapacitors and energy storage devices like batteries [6]. Similarly, the non-toxicity, excellent mechanical properties, inherent hydrophilicity, ease of functionalisability and reactive surface hydroxyl groups make nanocellulose a very adaptable material for various environmental applications as well [7].

Some research articles have been published regarding the specific applications of nanocellulose from a wide range of potential areas such as Abdelhamid et al. reviewed several metal-organic frameworks (MOFs) composites in combination/based on cellulose. The review article has addressed a wide range of MOFs which are employed in water remediation, air purification, gas storage, sensing/biosensing, and biomedicine. Along with the various scientific publications the authors have also provided an in-depth view of future perspectives and limitations based on the current research trends [8]. Another approach was seen by Chen et al. where they have published a review article based on the specific characteristics exhibited by cellulosic composite materials ie, stretchable composite. This article aimed to discuss cellulose based on specific novel properties. Considering the increased sustainable approach, more cellulose-based articles can be expected [9]. Owing to these characteristics, many research articles have been published about cellulose and nanocellulose in years. The below-illustrated diagram (Fig. 1) demonstrates the increasing scientific potential of this material. However, an article that exclusively deals with nanocellulose, its extraction, functionalization and specific applications in energy and environmental areas are not published in recent years. By this review, we are trying to address this specific vacuum and to provide new insights into the field of eco-friendly functional materials.

Nanocellulose: structure, extraction, functionalization techniques and properties

Nanocellulose is a tough, linear, fibrous, homopolysaccharide with high molecular weight having β -1,4-anhydroglucopyranose part as the repeating unit. Biomass such as trees are the rich sources of these uniquely ordered cellulosic hierarchical structures which have aligned in the tree-growth direction, this is schematically represented in Fig. 2 [10]. During the biosynthesis of cellulose in plants, the cellulose is arranged with interspersed amorphous regions to long continuous crystallite regions. These units are assumed to be in chair conformation with successive repeating units rotated in 180° about the molecular axis and hydroxyl groups being in the equatorial plane. The surface consists of three alcoholic hydroxyl groups, which include one primary alcoholic, and two secondary alcoholic hydroxyl groups. Due to the strong interacting nature of hydroxyl groups, cellulose has a strong tendency to form an extended network by self-association via both intramolecular and intermolecular hydrogen bonds. These intramolecular and intermolecular interactions are present between cellulose chains and/or the suspended solvents [11]. The interactions are the major reason for the hydrophilic and higher crystalline nature of the cellulose material. Thus, the interaction of the hydroxyl groups in the amorphous region plays a significant role in the overall properties of the fibre. The extent of crystallinity, source of origin, part of biomass and polymerization etc. influences the morphology, surface chemistry, degree of crystallinity, aspect ratio and crystal structure of the nanocellulose obtained [12]. Table 1 illustrated below clearly demonstrate that different plant source exhibits different cellulose composition as mentioned in the previous statement. However, some studies propose that cellulose could be amphiphilic instead of hydrophilic which also needed to be discussed. These arguments were mainly used to explain the non-dissolution of cellulose in the water even though both are polar. Many researchers initially attributed the non-dissolution characteristics of cellulose to the formation of stable inter and intramolecular hydrogen bonds and their higher crystallinity values [13]. However, similar molecules like dextran and glucose are soluble in many solvents including water. This anomaly was addressed by the explanation using hydrophobic parts/pockets in the cellular structure

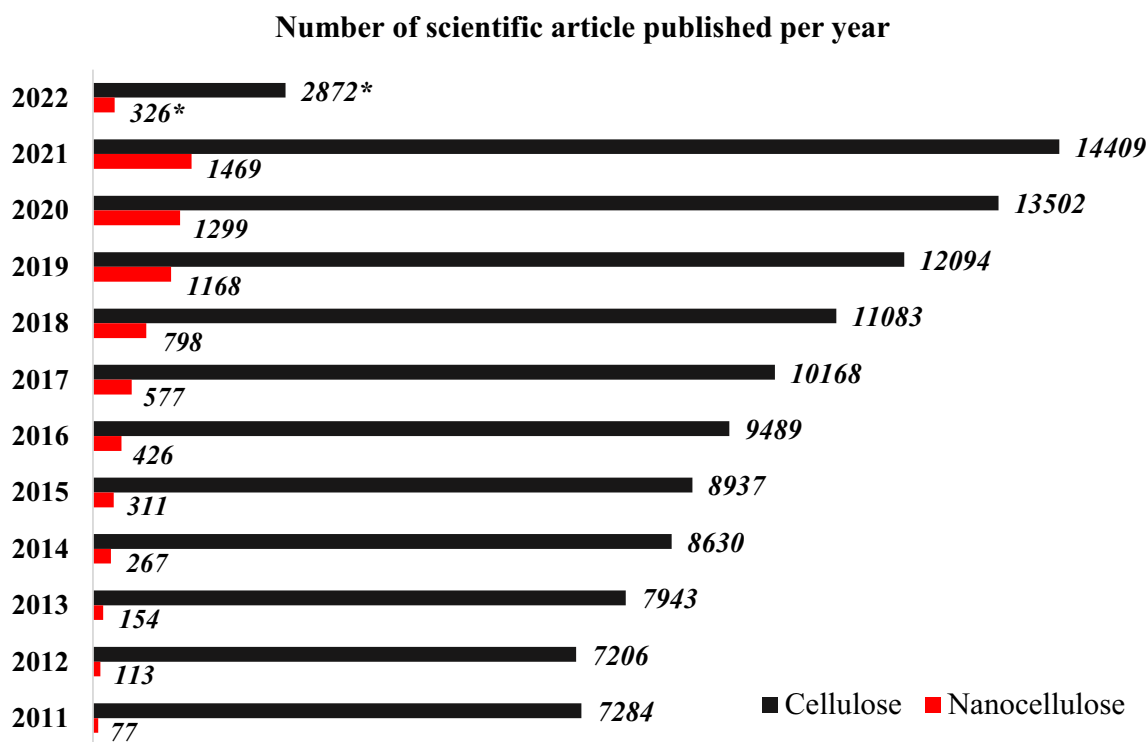


Figure 1 Number of scientific articles about cellulose and nanocellulose published per year (data obtained from Scopus using keywords “cellulose” and “nanocellulose”).

at spacial arrangements. This was initially demonstrated in the case of a single helix amylose molecule that has hydrophobic pockets and is insoluble in water [14]. Computer simulation and cellulose crystals derived studies have shown that along the long cellulose polymer chains at certain special arrangements all three hydroxyl groups are located at the equatorial direction of the glucopyranose ring, whereas the C–H bonds are located on the axial positions having hydrophobic characteristics. This also favours close stacking due to low hindrance which results in crystalline characteristics leading to inhibition of dissolution [15]. This can be further verified with the current applications of NaOH and urea mixture which are widely employed as cellulose solvents. It is established that urea can suppress the hydrophobic interactions at the same time this also results in dissolution is a clear shred of evidence to the influences of hydrophobic interaction, van der walls interaction in non-dissolution of cellulose, not just hydrogen bonding[16]. The use of polyethene glycol in combination with NaOH was also found to exhibit superior dissolution which can further support the influences of hydrophobic interactions[17]. This native variation in composition combined with

the fact that nanocellulose content is influenced heavily by the extraction technique justifies the ongoing research works aimed towards a higher concentration of nanocellulose extraction.

Based on the biosynthesis, crystallography and polymorphs, cellulose can be classified into two types: cellulose I and cellulose II. Cellulose I which is typically present in the plant cells and confirmed by the nuclear magnetic resonance (NMR) data and cellulose II is precipitated from solutions like alkali solutions. The structure of cellulose I constitute parallel chains whereas the structure of cellulose II is constituted of antiparallel arrangements. This arrangement in cellulose II provides an additional hydrogen bond per glucose unit hence this allomorph is more thermodynamically stable among the two. Cellulose II exhibit single hydrogen bonds between O5 and O3 and between O6 and O2. The presence of two different hydrogen-bonding interactions in the cellulose II also results in constraint to the structure which results in a shorter hydrogen bond between O6 and O2 compared to O5 and O3 [26]. Cellulose I has two different crystalline forms in existence, namely I α and I β . These two crystalline forms can be identified using Fourier transform infrared spectroscopy (FTIR)

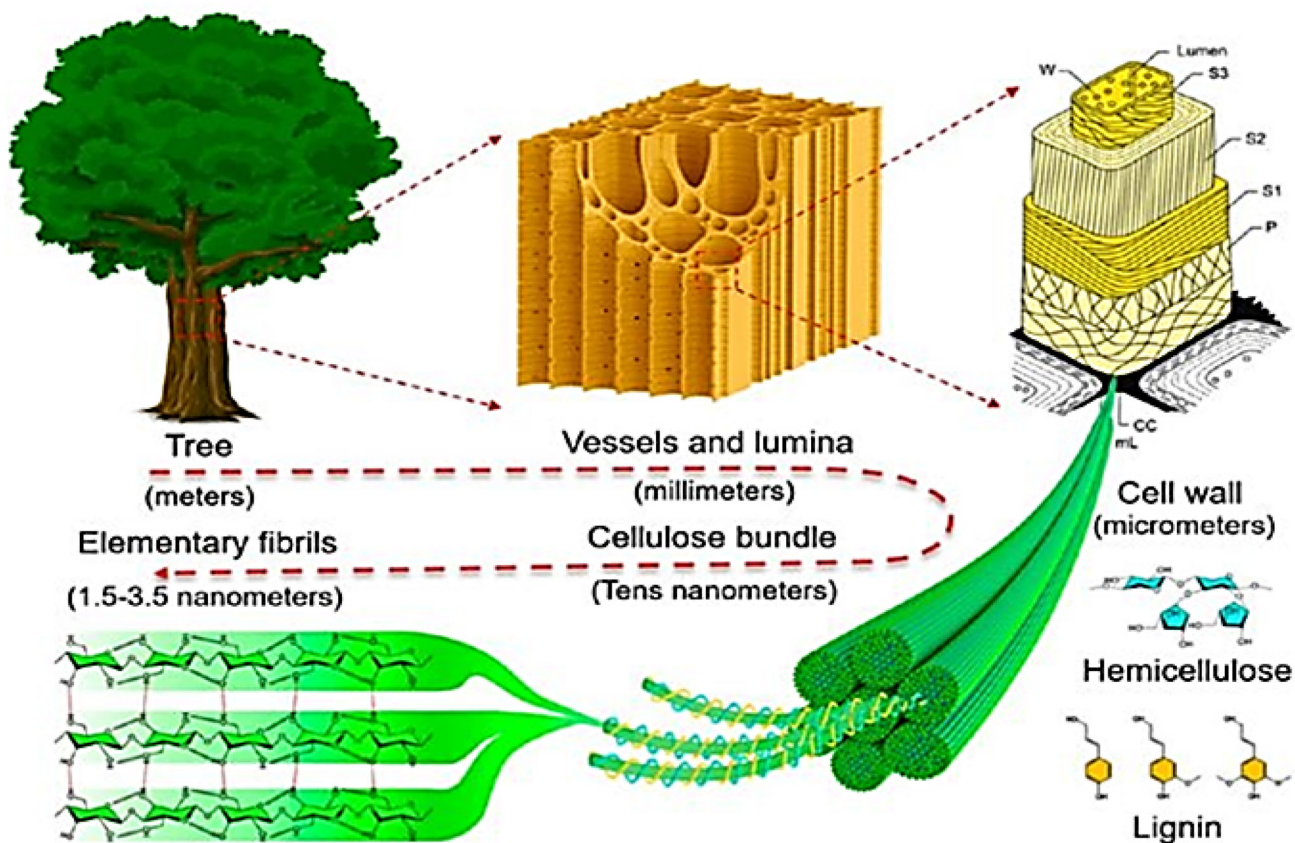


Figure 2 Graphical illustrations of the hierarchical structure nanocellulose. Adapted with permission from [10]. Copyright ACS Publications, 2018.

and electron diffraction during the study of the polymorphism of algal cellulose. Using NMR signalling, it was observed that the $I\alpha$ is identified by the P1 triclinic structure having one chain per unit cell and $I\beta$ is identified by the monoclinic P21 structure with two chains per unit cell [27]. Many studies have proposed that the majority of cellulose I is a mixture of cellulose $I\alpha$ and $I\beta$. Other important characteristics are the various cellulose conformations in dissolution where a two-fold conformation of the cellulose chain complex was reported for cellulose I and III at low concentrated NaOH solution. Whereas a three-fold conformation of cellulose chain was observed at a higher concentrated NaOH solution. The highest of them was reported was a five-fold conformation in the case of cellulose-sulfuric acid complex and other cellulose derivative crystals namely cellulose trinitrate. These sheds light into the complexity of the cellulose molecule and its dissolution characteristics [28, 29]. Owing to its nano-size range, nanocellulose exhibits inherent properties along with ease of tunability making it the perfect novel sustainable

future material to meet tomorrow's challenges in various domains. In this regard, we review the latest advancement in nanocellulose and its nanocellulose based materials energy and environmental applications. Generally, two types of nanocellulose are isolated from plant biomass: cellulose nanofibers (CNFs) and cellulose nanocrystals (CNCs). Similarly, there is one more nanocellulose is being widely synthesised from a non-biomass source called bacterial cellulose (BC). CNF is a flexible form of nanocellulose having an entangled network structure with amorphous and crystalline components coexisting in alternative order which has arisen due to the isolation method employed. The main isolation methods include high-pressure homogenization, grinding, ultrasonication, acid hydrolysis using mild acids or acids in low concentration [19]. On the other hand, CNC is prepared by acidic hydrolysis using strong acids like sulphuric acid, hydrochloric acid, phosphoric acid and it possesses has a more crystalline structure and better mechanical properties. On the other hand, the bacterial cellulose is being synthesised using various

Table 1 Chemical composition and mechanical characteristics of the typical cellulose source material by different authors

Source	Cellulose content (%)	Hemicellulose content (%)	Lignin content (%)	Density (g/cm ³)	Elongation at break (%)	Tensile strength (Mpa)	Youngs modulus (GPa)	Author(s)
Abaca	69.2–70.6	21.2–21.9	5.2–5.8	1.42–1.65	9–11	38–45	38–45	Leao et al. [18]
Banana	60.3–65.2	48.2–59.2	5.6–10.4	1.3	7	500	1.4	Abraham et al. [19]
Coconut (coir)	36.6–43.2	0.6–0.3	41.2–45.3	1.2	27.21–32.32	175	4.0–6.0	Satyanrayana et al. [20]
Corn stalks	38.3–40.3	25.2–32.2	7.3–21.4	1.27–1.55	1.90–2.30	33.4–34.8	4.10–4.5	Reddy et al. [21]
Flax	69.2–71.7	18.3–18.7	3.1–2.6	1.5	2.70–3.6	345–1035	27.6	Bismarck et al. [22]
Jute	69.2–72.4	12.6–13.7	12.7–13.2	1.3	1.5–1.8	393–773	26.5	Abraham et al. [19]
Oil palm	44.2–49.6	18.3–33.5	17.3–26.5	0.7–1.5	2.13–5.00	227.5–278.4	2.7–3.2	Abdul et al. [23]
Pineapple	70.6–82.3	18.7–21.9	5.3–12.3	1.25–1.6	2.27–3.34	166–175	5.5–6.7	Abraham et al. [19]
Rice straw	28.4–48.3	23.2–28.5	12.7–16.7	0.86–0.87	2.11–2.25	435–450	24–26	Reddy et al. [24]
Sisal	43.9–56.6	21.1–24.5	7.2–9.2	1.5	2.0–2.5	511–635	9.4–22.0	Favaro et al. [25]

bacterias such as *Pseudomonas*, *Acetobacter*, *Alcaligenes*, *Acetobacter xylinum* etc. which has higher purity and are mostly used in biomedical and food industries[30]. Illustrated below (Fig. 3) is a general schematic diagram of the different types of nanocellulose. Nanocellulose extraction is an area of scientific research where significant development occurs in a very short period. Hence the below illustration is a simplified general diagram demonstrating different classes of nanocellulose.

Cellulose nanofibers (CNFs)

The first isolation of CNF was reported by Gaulin laboratory homogenizer in the year 1983, which was initially termed as micro-fibrillated cellulose (MFC). The isolated gel showed a clear increase in viscosity when softwood pulp from cellulose passed through the homogenizer several times, the high shear forces yielded individualized cellulose microfibrils. Similar to this, many studies have been carried out on the isolation and characterization of CNFs from various sources which leads to the development of different methods for nanocellulose fibre extraction from the

cell walls of biomass, which include simple mechanical methods, chemical methods and the combination of both chemical and mechanical methods [31]. Some of which include high-pressure homogenization, grinding, cryo crushing and high-intensity ultrasonic treatments which led to the transverse cleavage of the cellulose fibres. Typically, a CNF has dimensions of 10–40 nm in diameter and lengths up to several micrometres. It is very difficult to find out the length of CNF due to a large number of entanglements. Also, many parameters can influence the characteristics of the final extracted fibre which makes influence the dimensions. For instance, if we consider the source of cellulose isolated, the degree of polymerisation of native cellulose from wood is around 10000 whereas the native cellulose from cotton has a higher degree of polymerisation of 15000. surprisingly, even the different part of the plant is also significant in influencing the degree of polymerisation. The next major influencing factor is the purification/extraction procedure. It has a depreciating effect on the degree of polymerisation and an increasing effect on crystallinity to a significant extent. It has been shown that the degree of

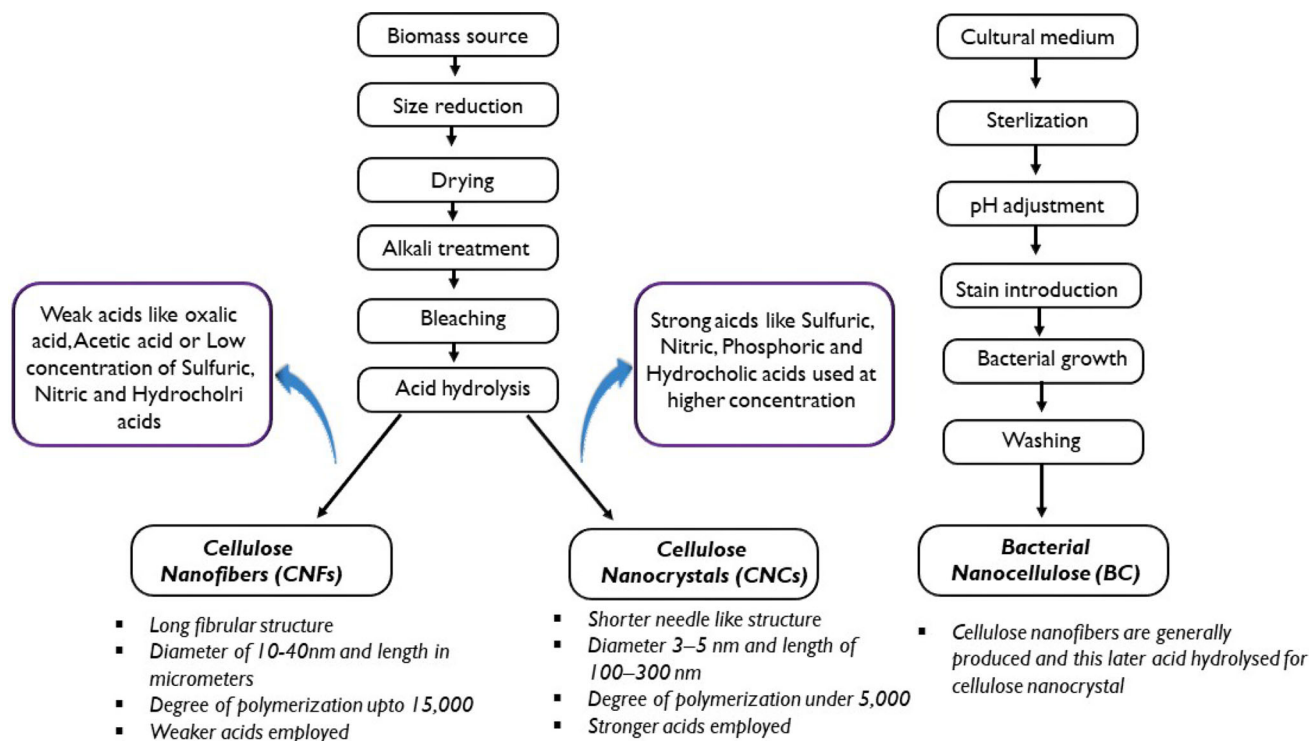


Figure 3 Generalized schematic diagram of classification of nanocellulose from the sources.

polymerisation can differ from 14000 to 2500 by the method of purification/extraction alone [24]. A typical CNF extraction by steam explosion consists of 3 major steps, namely; (1) alkali treatment with steam explosion, (2) bleaching and (3) mild acid hydrolysis coupled with the steam explosion. During the alkali treatment, the pre-washed and ground biomass is treated with 5% wt NaOH solution in an autoclave where it was steam exploded at a temperature around 180 °C and pressure around 137 Pa for 90 min. This is followed by multiple bleaching using a 5 wt% sodium hypochlorite solution with each step consisting of 90 min until the residue becomes white. The white residue after the washing process is steam-exploded in 5% oxalic acid under a pressure of 137 Pa in an autoclave for 20 min. The aforementioned conditions can be varied to optimize the nanocellulose extracted [32].

Cellulose nanocrystals (CNCs)

Cellulose nanocrystals are generally extracted by employing strong acidic hydrolysis of the CNFs. Some of the commonly used acids include hydrochloric acid, nitric acid, sulphuric acid, oxalic acid and hydrobromic acid etc. Among the different

acids available for the choice of hydrolysis treatment, sulphuric acid was used most commonly. The use of strong acids for the isolation resulted in the degradation of most of the amorphous region of the fibre chain, which resulted in a higher crystallinity compared to the CNFs. A typical CNC has diameters in nano and length in a few submicrometer. The removal of amorphous content from the CNFs have resulted in a long rod-like structure, which is different from the entangled structures of CNFs. Similar to CNF, the feedstock plays an important role in the property of the extracted CNCs. The thermal stability varies from material to material. Similarly, thermal stability varies based on the different steps involved in the isolation process[33]. The CNCs extracted using H₂SO₄ were less thermally stable than those extracted using HCl. Another influencing parameter includes the duration of extraction. The crystallinity and length of nanocrystals were found to be decreasing with the increase in the duration of extraction[34]. A typical CNC extraction procedure follows the order where the washed and ground biomass source is steam exploded at 195 °C in a very short period followed by multiple bleaching with 1.4% (w/v) sodium chlorite until the colour of treated fibres became white. This residue is then transferred

into a 60% (v/v) sulfuric acid solution and agitated for 75 min at 45 °C at a speed of 700 rpm. Coldwater is added after the reaction before the CNC separation by centrifugation [35]. While comparing cellulose nanofibres and cellulose nanowhiskers based on the reinforcing effect, it was found that even though both fillers led to an increase in tensile modulus and tensile strength, incorporation of CNFs led to significantly higher values due to the entanglements between the fibrils which resulted in a more rigid network of CNFs [36]. Recent advancements in the area of nanocellulose include extraction using deep eutectic solvents (DESs) which addressed the disadvantages of ionic liquids (ILs). These solvents share similar properties to a certain extent where the DESs considered to be a subclass of ILs. Liu et al. fabricated CNCs having high purity with a diameter ranging from 3 to 25 nm in DESs. They have used chlorine chloride and oxalic acid dehydrate at an equal ratio to prepare the DESs [37]. Owing to the wider liquid range, the ability to dissolve both inorganic and organic compounds, less expensive and hazardous while being mostly biodegradable has contributed DESs based extraction more attractive compared to the hazardous, non-biodegradable and expensive ILs based nanocellulose extraction methods.

Bacterial cellulose (BC)

Bacterial cellulose has the unique advantage of being lignin and other foreign substance-free. The nanocellulose extracted from bacteria are usually in the form of ribbon-shaped fibrils with a length less than 100 nm and width up to 2–4 nm nanofibrils. These nanofibrils have a degree of polymerisation roughly between 4000 to 8000 with 75–80% crystallinity[38]. A typical bacterial cellulose preparation comprises of culture medium that contains 1 L of distilled water, 4 g of monopotassium phosphate, 5 g of ammonium phosphate, 50 g of glucose, 5 g of yeast and 0.1 g magnesium sulfate heptahydrate. This medium was sterilized at 120 °C for 2 h. After cooling down to ambient temperature, vitamin B is introduced into the medium. Acidity is adjusted to pH 4 using glacial acetic acid. Later a stain of *G. xylinus* was then incubated into the culture medium for 21 days at a temperature of 28 °C. After this harvesting process, it was washed under tap water followed by rinsing with distilled water until it becomes neutral. The yield in optimum conditions

was around 30–40% of the weight of glucose. Other than glucose, some of the other reducing sugars such as fructose, galactose, xylose etc. could be used for biological nanocellulose production. The yield depends upon the growth rates which reflects in smaller yields of galactose and xylose compared with glucose. The common genera of bacteria include *Agrobacterium*, *Pseudomonas*, *Acetobacter*, *Alcaligenes* and *Rhizobium* [39].

Summary

Generally, nanocellulose can be classified into two namely plant cellulose and bacterial cellulose which is green and naturally occurring. Over the last decade, several research groups worldwide have reported the extraction and use of CNFs, CNCs and BC with varying dimensions and characteristics. Predominantly, the selection of the nanocellulose mainly corresponds to the end application. However, the development of new types of nanocellulose could bring greater futuristic potential. The nanocellulose type plays an important role in determining its suitable application. For instance, cellulose nanofibers can form better films compared to cellulose nanocrystals that enabling them to be used as a matrix for nanocomposites. Whereas, the cellulose nanocrystals have better crystallinity enabling them to use as binders in the battery (low water penetration based application). However, new types of nanocellulose have been developed in recent times. The most notable types are cellulose hollow structures, hairy cellulose nanocrystalloids (HCNC) and regenerated celluloses. The cellulose hollow structures (CHS) are a derivative of cellulose acetate having a hollow structure. This hollow structure enables it for better conductivity in battery devices and supercapacitors, increased surface areas for adsorption studies, better efficiency in infiltration performance and drug delivery studies (biomedical application)[40, 41]. Hairy cellulose nanocrystalloids is physically an intermediate of CNF and CNC while having more similarity with CNC. But unlike the CNC or CNF, the polymer chain end has different groups that enable it for different applications such as water solubility, pollution removal and many more [42]. Regenerated cellulose is another material that is not physically different from CNF, CNC, HCNC or CHS. Regenerated nanocellulose is a class

of materials manufactured by the conversion of natural cellulose (or biomass) to a soluble cellulosic derivative and subsequent regeneration, typically forming either a fibre or a film. This type of nanocellulose extraction can be both a green and approach with great control over the characteristics of the nanocellulose extracted [43, 44]. Electrospun nanocellulose, nanocellulose prepared from ionic liquids and deep eutectic solvents can be considered regenerated cellulose.

Extraction of nanocellulose from biomass

In general, nanocellulose extraction consists of pretreatment of biomass followed by extraction. Before the extraction, some pretreatments are given to the lignocellulosic biomass namely, alkali treatment and acid chlorite treatment. The main extraction process consists of mainly 3 steps which include acid hydrolysis, enzymatic hydrolysis and mechanical processing. Besides this, extracellular biosynthesis is employed in some bacteria for nanocellulose extraction [3]. Alkali treatment and acid-chlorite treatment are two main methods employed as biomass pretreatment. These treatments help to remove hemicelluloses and lignin from the cellulosic component. Sodium or potassium hydroxide is used as alkali for the removal of amorphous portions like hemicelluloses and lignin from the cellulosic fibres. The remaining filtrate was washed with water to neutrality. The resulting biomass contains mainly cellulosic components. This is the most commonly employed pretreatment in cellulose extraction. This pretreatment helps to reduce power consumption to a greater extent [7]. This process is then followed by a bleaching or delignification process in which the lignin from biomass is removed. This process includes mixing sodium hypochlorite, acetic acid and distilled water with lignocellulosic biomass at elevated temperature and pressure. The processing time depends upon the type of biomass used. The remaining filtrate is then washed until neutral [45]. After pretreatment, nanocellulose can be extracted via three techniques such as mechanical treatments, acid hydrolysis and enzymatic hydrolysis. Figure 4 is a generalized schematic diagram of different nanocellulose extraction methods along with their major characteristic. Even though the names of the method indicate complete independence from one

another, in practice, no method combination is employed. The naming is an indication of the principle employed in the extraction of CNF.

Mechanical methods

Mechanical methods are the most commonly used extraction techniques for nanocellulose isolation. This includes mechanical grinding using a mass collider, ultrasonication, ball milling, cryo crushing, microfluidization and high-pressure homogenization. These processes generally require very high energy to carry out. Mechanical stirring/homogenisation at several thousand revolutions per minute for several minutes to several hours are often required. Major concerns in these methods are the high maintenance cost of the equipment which is mainly operated in acidic environments, high cost of production, wastewater effluent management of acidic and chemical waste etc.[46]. Cellulose from various sources such as wood, wheat straw, flax and bamboo are reported to be isolated using ultrasonication in combination with acid hydrolysis. The process is used as an energy-efficient method and offers higher yielding. Steam explosion is also another method that is widely reported. Here the sudden drop of pressure from elevated pressure is utilized to defibrillate the cellulose fibres. The rapid drop of pressure results in generating shear force causing hydrolysis of hydrogen bonds as well as glycosidic linkages. Electrospinning is another method that uses electrical forces for the extraction of cellulose fibres. During the process, nanofibers are formed between the electrodes of different polarities. The insolubility in common solvents and the tendency for agglomeration makes electrospinning a less favourable method than others [47].

Acid hydrolysis

Acid hydrolysis is one of the commonly used extraction techniques for the preparation of CNCs. This is also known as chemical isolation where strong acids like sulfuric acid, phosphoric acid, hydrochloric acid and mild acids like formic acid, acetic acid, oxalic acid etc. are employed. The selection of acid depends upon the reaction parameters and the specificity of the product required. Reaction time, temperature, and concentration of acid are some of the major parameters which can influence the

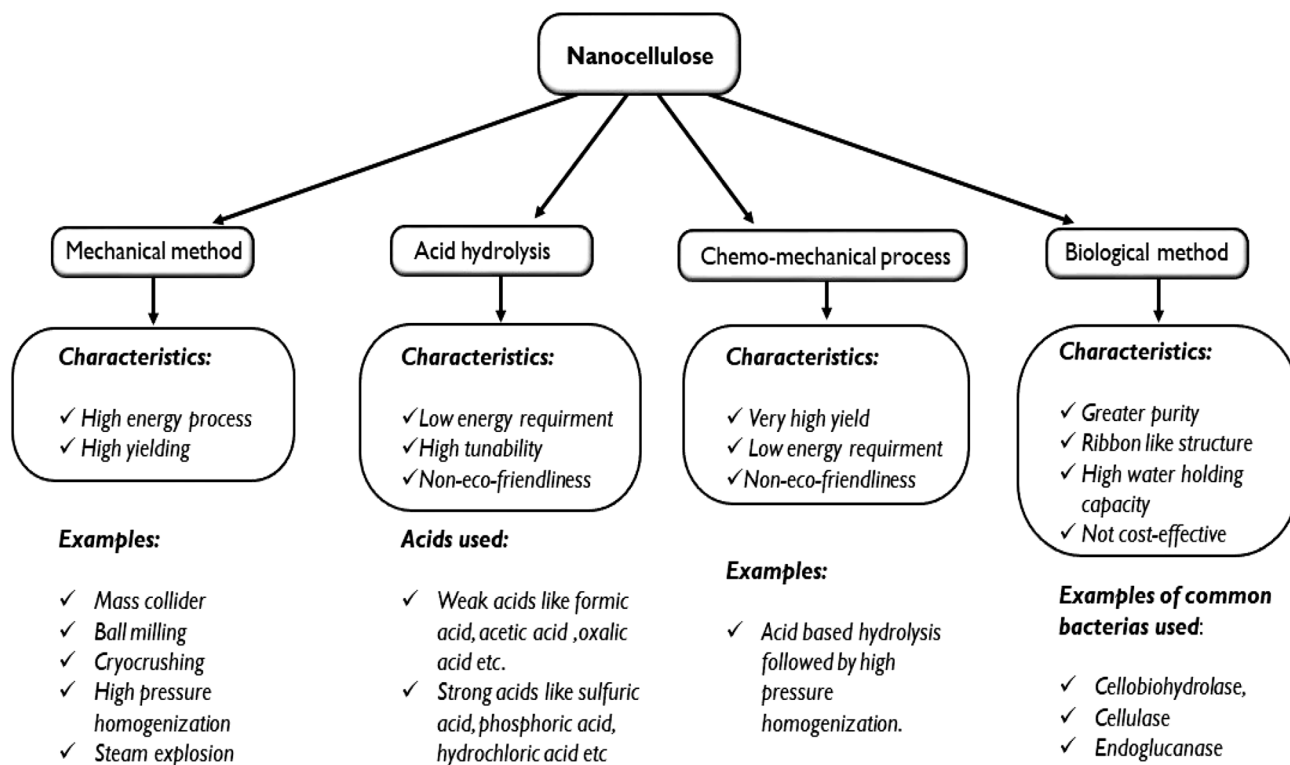


Figure 4 Generalized schematic diagram of different nanocellulose extraction methods.

properties of the obtained CNCs [48]. The acid hydrolyzes the amorphous regions of the cellulose fibrils with ease depending upon the strength of the acid used. This leads to the formation of a stable colloidal dispersion of nanocellulose materials with a very high concentration of crystalline region in the remaining substrate. Later deionised water is used for the neutralisation because without the neutralisation of the nanofibers, the acidity can cause the degradation of nanocellulose. Other than deionised water, low concentrated alkalis such as 0.5 N of sodium hydroxide can be employed for neutralization however it needs to be followed by further washing with deionised water. Other than acids, oxygen and peroxide compounds can also be employed for the extraction of nanocellulose fibre. This also ensures the minimum degradation of cellulose fibre with the elimination of lignin and non-cellulosic components. It is also reported that the chemical treatment with acid hydrolysis influences the surface charge of nanocellulose obtained [49]. Even studies based on the characterisation of cellulosic plant fibre is also been reported. The chemical process often includes methods like wet chemistry

where the extraction of nanocellulose is a by-product of sugar beet chip production.

Combining the chemical and mechanical process is found to be more convenient as it reduces total energy required, reduces operating costs and increases the yield. The technique has the added advantage of the production of cellulosic fibre with very little degradation. The general procedure for combining both chemical and mechanical processes is using chemical treatment in the pretreatment of lignocellulosic pulp and bleaching step and subsequently treating these pulps by mechanical means like cryo crushing and homogenization. Combining sulphuric acid-based chemical treatment with high-pressure homogenisation such as mass colliders has attracted a lot of attention in the isolation of nanocellulose fibres material [50]. This method is employed in nanocellulose isolations from materials such as kenaf bast, agricultural waste, natural fibres and oil palm, fruit bunch etc.

The biological method for nanocellulose extraction by digestion of cellulose is termed enzymatic digestion. The nanocellulose extracted by biological methods are in the form of ribbon-shaped fibril and the length is less than 100 nm and width up to 2–4 nm. The common enzymes employed includes cellobiohydrolase, cellulase and endoglucanase etc. These enzymes function as breaking/catalysis of linking H-bond between the cellulose microfibrils. Hemicellulose hydrolysis is an essential step since hemicellulose shields the cellulose from hydrolysis and also helps in generating monosaccharides [51]. The biological enzymatic methods have the advantage of producing high purity nanocellulose which is used mainly in bio-based applications. Moreover, bacterial cellulose has a higher water holding capacity, hydrophilicity and tensile strength due to the ultra-fine network architecture. Although bacterial cellulose exhibit certain advantages over conventional isolation processes, due to the unproductive production procedures the present cost of bacterial cellulose production is very high.

Generally, CNFs present in biomass could be extracted via mechanical treatments such as high-pressure homogenization, grinding, cryo-crushing and high-intensity ultrasonic treatments. The product, CNFs, exhibits gel-like characteristics. The second type of nanocellulose, CNCs could be extracted via strong acid hydrolysis where strong acid would attack the amorphous portions which led to the formation of CNCs. Since bacterial cellulose has no hemicellulose and lignin, it is more chemically pure than plant cellulose. However, the conventional production process cannot produce bacterial cellulose commercially, further developments using reactor-based production should be accomplished to successfully market bacterial cellulose-based products. In the current scenario, the main challenges are related to developing a green isolation process of nanocellulose from the natural cellulosic biomass. Many green nano cellulose extraction processes are being investigated widely in recent times. The most common ones are using Ionic liquids extraction, deep eutectic solvents and subcritical water [53]. Among

these methods, the most significant emerging green approach for nanocellulose extraction is the extraction and dissolution of cellulose and nanocellulose using ionic liquids. It is also important to note that the Deep eutectic solvents are a derivative of ionic liquid-based extraction techniques. The basic principle of ionic liquid-based and deep eutectic solvents based extraction are the dissolutions of nanocellulose with ionic liquids that allow the comprehensive utilization of nanocellulose. This approach also combines two major green chemistry principles: using environmentally preferable solvents and bio-renewable feedstock. The ionic liquid-based approach has the advantage of higher purity, this has enabled it to use even in biomedical applications. Also, the increased number of research work after 2014 demonstrates the futuristic potential especially since deep eutectic solvents based extraction have become an independent method owing to the large scale of methods available [54]. The subcritical water-based approach uses subcritical water (at temperature conditions between boiling and supercritical temperatures) for the production of CNC via partial hydrolysis [55]. While the above-mentioned methods have futuristic potential, they use mainly cellulose or cotton as raw materials. Thus the use of conventional non-ecofriendly strong chemicals is still unavoidable. Hence an updated mechanical method could be the greener approach for mass-scale production for energy and environmental applications. A generic summary of the advantages and disadvantages of all the extraction techniques is provided in below-mentioned Table 2. This table aims to provide a quick summary of the various extraction techniques.

As discussed above, the characteristics of nanocellulose vastly depend upon the source, extraction method and isolated form. Even though it is not possible to summarize all the characteristics of cellulose in a single division, the major phenomenon behind most of the common and predominant characteristics are similar. Since nanocellulose is being exploited in a wider application spectrum in recent times, it is obvious that the specific characteristics will be looked at with much more precision. This has resulted in separating some of the main characteristics into specialized individual characteristics which

leads to a bigger confusion among relatively newer aspirants. To avoid any such confusion, we are illustrating some of the important characteristics exhibited by the nano cellulosic materials such as crystallinity, thermal degradation, mechanical characteristics, hydrophilicity and surface charge as it is represented in Fig. 5. The objective of the illustration is to provide a quick summary of nanocelluloses major characteristics while the detailed section provided later will aid the reader to correlate characteristics of cellulose with other influencing parameters. Since the review is mostly concentrated on the application of nanocellulose, we are intended to correlate the properties with applications rather than mentioning all the individual properties available in the domain.

Crystallinity

The inherent properties of the nanocellulose can be influenced the crystallinity values. There are multiple approaches for crystallinity analysis namely the Segal peak height method, Peak deconvolution and Rietveld method. Each method has its characteristic significance with questionable accuracies. For instance, the Segal peak height method was questioned when Paul Scherrer demonstrated that the sharp (from large crystals) and broadened (from smaller crystals) peaks were overlapping each other when trying to mimic the peaks arising from model crystal size that obtained from cellulosic samples (a few nanometers) [56]. The same peaks were considered as background

or amorphous regions in the Segal peak height method which cast doubt on the accuracy of crystallinity determination. Whereas the deconvolution and Rietveld methods heavily depend upon visible peaks or mathematical complex equations. However owing to a large number of parameters and software support, these method based analyses could provide better reproducibility and can be recorded for further future references [57]. Regardless, the crystallinity of cellulose nanofibre mostly depends upon three major factors: source, isolation method and type of nanocellulose. The nanocellulose can be identified by the two characteristic peaks at $2\theta = 16.3^\circ$ and $2\theta = 22.6^\circ$ from the XRD patterns, which shows the cellulose type I structure with a crystallinity index value differing from 73 to 90% by the source used. The change in crystallinity index values arises due to the presence of different components within the materials depending upon the sources [58]. Similarly, different steps of isolation play a significant role in the crystallinity index value. The removal of amorphous regions of cellulose by the hydrolysis process prompts hydrolytic cleavage of glycosidic bonds and leads to the rearrangement of cellulose molecules [59]. Alkali treatment leads to the removal of cementing materials like lignin, hemicellulose and pectin and would enhance the percentage crystallinity of the fibre. However, Abraham et al. reported that the amount of crystalline cellulose present in the extracted nanocellulose cannot be exactly defined because both crystalline portions and the noncrystalline portion are not completely perfect.

Table 2 Advantages and disadvantages of various nanocellulose extraction technologies

Nanoparticle preparation method	Pros and cons
High-pressure homogenization (HPH)	Produce nanoparticles with diameters between 20 and 100 nm. Use high energy, clogging of the homogenizer, and damage of the crystalline structure
Microfluidization	Create nanoparticles less than 100 nm in diameter
Grinding	Particle size in the micrometre instead of in the nanometer range. Damages the fibre structure
Cryocrushing	Produce particles with diameters ranging from 30 to 80 nm
High-intensity ultrasonication	Do not use any chemical treatment
Steam explosion	Lower environmental impact
Acid hydrolysis	Low aspect ratio
Electrospinning	Simple and cost
Enzymatic hydrolysis	High cost due to the isolation process of the enzymes and the auspicious hydrolysis required long enzymatic treatment time

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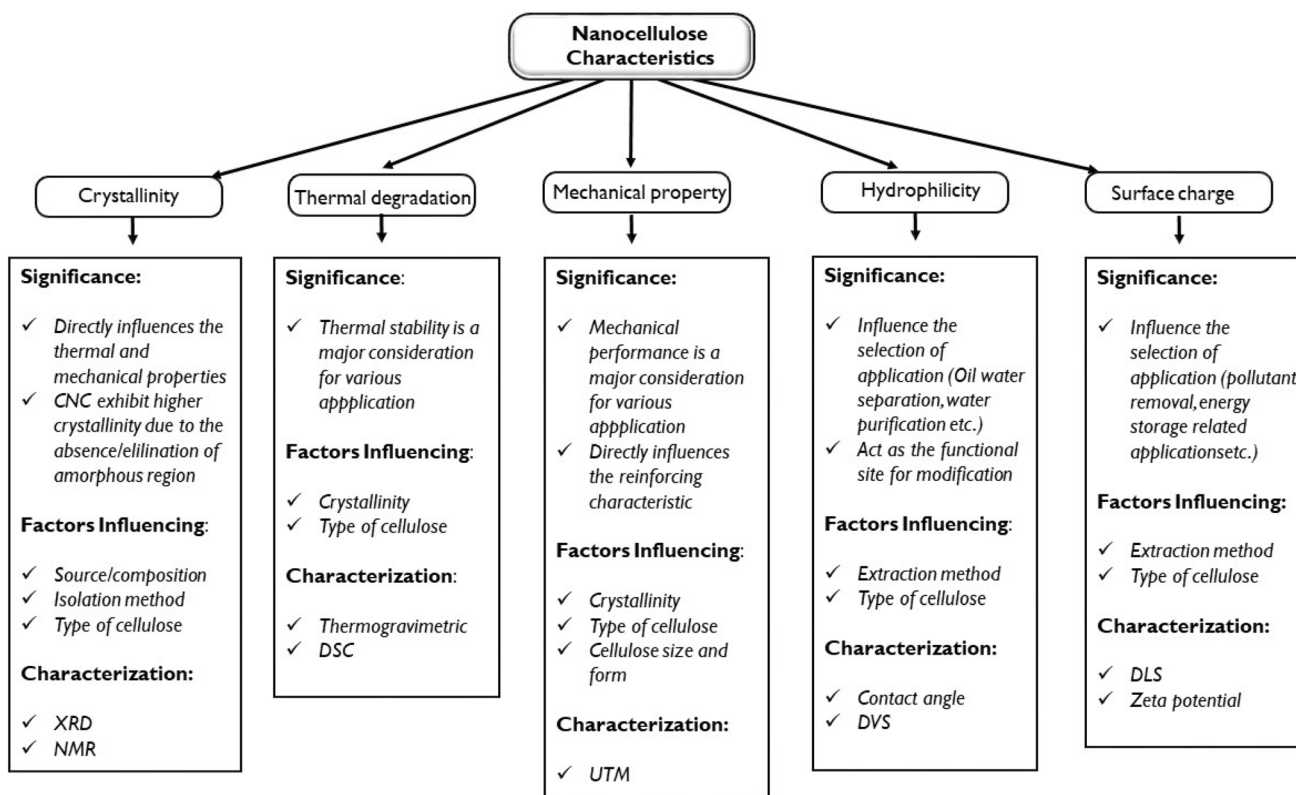


Figure 5 Generalized schematic diagram of different characteristics of nanocellulose.

These semi-crystalline regions of intermediate order are liable to change by the chemical treatment which is the main reason for the change in crystallinity with the process. They have observed that the percentage of crystallinity in the order of PALF > jute > banana which agrees with the values of cellulose content determined in these samples where the cellulose content of the PALF, banana and jute are 89.3, 88.6 and 83.6 respectively. The authors also observed that the crystallinity of the fibre increases during each of these processing steps as illustrated in Fig. 6 and the values are provided in Table 3 [19].

Thermal degradation

The thermal degradation of cellulose mainly depends on the crystallinity and composition of components. The thermogravimetric analysis (TGA) is the commonly used characterization technique for investigating the thermal degradation properties of nanocellulose. Juan et al. extracted nano cellulose by different methods and studied their thermal degradation properties. They reported that cellulose undergoes a two-stage degradation where the

primary degradation occurs from 25° to 140 °C and this is due to the liberation of the water molecule. The second degradation occurs from 255 °C onwards for the nanocellulose isolated from sisal fibre, while the commercial cellulose started decomposition only after 305 °C. In both cases, the solid residues at 700 °C also differ as the nanocellulose isolated from sisal fibre had a residual mass of 15wt% while commercial cellulose had only 1.6 wt% residual mass. The higher residual mass formation of isolated nanocellulose could be explained by the presence of small amounts of hemicellulose or lignin which have not been removed by the extracting procedure. The higher starting temperature for the decomposition of commercial cellulose was attributed to the higher degree of order of the commercial cellulose [60]. However, there are other observations regarding cellulose decomposition. Attia et al. observed a three-stage decomposition of cellulose instead of a two-stage decomposition. They have correlated the first set of decomposition as dehydration which occurs below 200 °C. This was followed by the main mass loss between 200 to 380 °C due to the cellulose chain scission attributed to the breaking of C–C and C–O

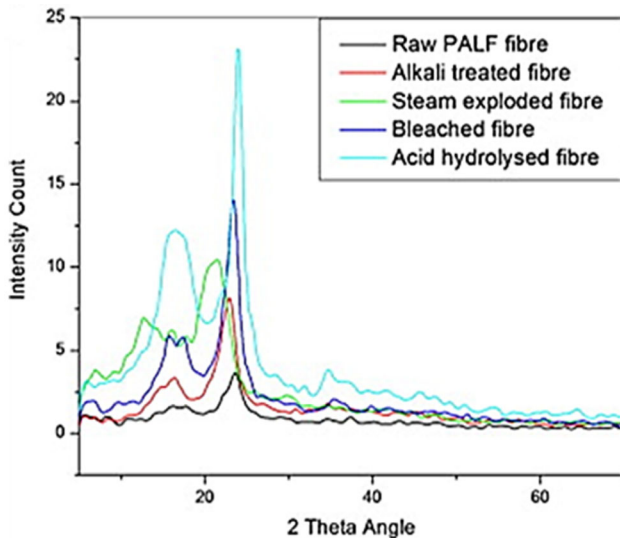


Figure 6 XRD analysis of CNFs from PALF at different stages of extraction. Adapted with permission from [19]. Copyright Elsevier, 2011.

Table 3 Crystallinity index of nanocellulose in various fibres at different stages of extraction

Material	Crystallinity index (I_c)
Raw banana fibre	10.5
Raw PALF	11.3
Raw jute fibre	9.1
Steam exploded banana fibre	54.1
Steam exploded PALF	63.7
Steam exploded jute fibre	52.9
Bleached banana fibre	83.8
Bleached PALF	89.3
Bleached jute fibre	88.6

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bonds. Finally, the third step of decomposition was observed which is attributed to aromatization which occurs beyond 380 °C due to the formation of residual char [61]. Figure 7 represents the mass loss and heat flow graph of commercial cellulose fibre. The mass loss curve follows a similar pattern to what Juhan et al. observed, However, the temperature at which different stages of thermal decomposition occurs is observed to be different. This can be mainly attributed to the higher moisture content bound to the nanocellulose fibres [62]. The 2nd stage of decomposition occurs delayed in comparison with the 200 °C starting point reported by Trilokesh et al., however, the 3rd stage of decomposition occurs

somewhat similar temperature range due to the strength of C–C and C–O bonds. This explains the difference in nano-cellulosic decomposition temperatures in various articles. The difference between the thermal degradation temperatures of the biomass source and the nanocellulose is shown in Table 4. Here from Table 4, it can be seen that coconut fibre has the highest thermal stability due to the higher amount of lignin content (41.2–45.3%) which resulted in the superior thermal stability of nanocellulose from coconut fibres. It is well known that lignin decomposes slower over a broader temperature range of 200–500 °C than cellulose and hemicellulose components of biomass. Moreover, the higher the lignin content in biomass, the lower the crystallinity and the better thermal stability. Differential scanning calorimetry analysis carried out on the commercial nanocellulose sample can be observed in the same Fig. 7. The DSC is distinguished by two exothermic peaks at the exact temperature range of the significant mass loss observed in the TGA. This further confirms the breaking of C–C and C–O bonds of nanocellulose fibre. The second significant narrow peak in the DSC curve signifies the combination of depolymerization with aromatization which reflected significant quantities of heat flow [63].

Mechanical properties

Nanocellulose has been known to be an engineering material for many years due to its excellent mechanical and reinforcing properties. The cellulose nanofibrils exhibit superior properties compared to the less dispersed lignocellulosic fibrillar sources due

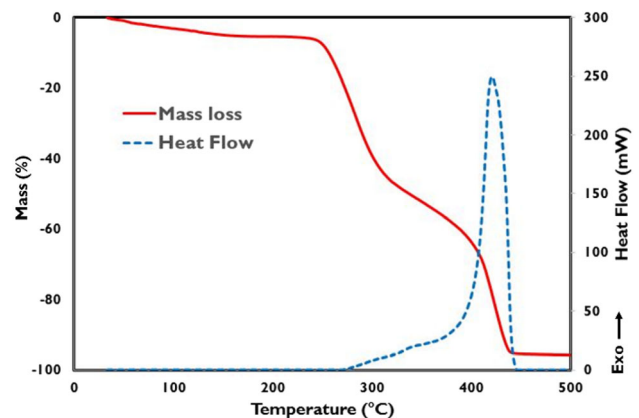


Figure 7 TGA and Heat flow analysis of commercial cellulose nanofiber.

to the better homogeneity. These impressive characteristics of cellulose depend upon many parameters such as isolation method, source, chemical composition, microscopic and molecular defects [66]. Different strategies, both theoretical and experimental, have been employed to determine the longitudinal modulus of CNFs and a broad range of values are reported. However, the average longitudinal modulus value for CNFs is around 100 GPa and 130 GPa for CNCs. While the CNFs exhibited tensile modulus values under 1 GPa the CNCs exhibited significantly higher tensile strengths up to 15 GPa for higher aspect ratios [67]. The relative lower modulus of CNFs is the result of the mixing rule between the modulus of the crystalline domains and the amorphous fraction while CNCs have only crystalline domains. Fernandes et al. demonstrated the reinforcing properties of CNFs by preparing nanocomposite films with chitosan and CNFs at various concentrations. The mechanical property improvement was observed to be in proportion to the CNF concentration. The tensile strength improved 220% and 150% when used with low molecular weight chitosan and high molecular weight chitosan respectively. Similarly, the Young's modulus showed an improvement of 300% and 177% when used with low molecular weight chitosan and high molecular weight chitosan respectively. The influence of CNFs on the mechanical properties of chitosan films is shown in Fig. 8 [36]. Slavutsky et al. studied the reinforcing properties by incorporating the CNCs into starch films at various concentrations by a simple casting technique. They have observed that the composite with the composition of starch: CNC as 4:3 have 6 times higher tensile strength and 5 times higher Young's modulus due to the improved interaction between matrix/filler and filler/filler interactions [68]. Balakrishnan et al. reported CNF as an effective reinforcing filler in thermoplastic potato

starch (TPS) films. The fabricated nanocomposite TPS/CNF films showed improved mechanical properties compared to pristine thermoplastic potato starch (TPS) film. It was found that TPS reinforced with 3 wt% CNF films had a tensile strength of 4.682 MPa whereas neat TPS films showed only 1.58 MPa which means around 196% over the pristine polymer. Moreover, the incorporation of CNF enhanced the barrier properties of films which were due to the formation of a tortuous path that inhibits the penetration of molecules. Additionally, they concluded that the fabricated TPS/CNF films can be used for sustainable packaging applications [69]

Hydrophilicity

Nanocellulose is an attractive renewable material with a large number of surface hydroxyl functional groups. These hydroxyl functional groups are attributed to their hydrophilic nature which makes them sensitive to water and moisture absorption. The reactivity of the hydroxyl groups towards solvents and absorption of water at the surface correlates with the degree of organisation and conformation of the macromolecular cellulose chains [70]. The hydrophilicity can be demonstrated by two different characterization techniques such as XRD and contact angle studies. In XRD analysis, the hydrophilic (110) and (1 $\bar{1}$ 0) faces represent the interaction sites having constrained orientation for the absorbed molecules of cellulose type II. Another characterization technique employed is contact angle studies which give more morphological reasons as the apparent contact angle of hydrophilic surfaces is less than 90° and hydrophobic surfaces have a contact angle higher than 90°. The Shuttleworth–Bailey model demonstrated that the contact angle was lower for nanocellulose papers with the finest pattern while hydrophobicity improved for papers with the most

Table 4 Thermal degradation of various materials and nanocellulose extracted experimented by different authors

Source	Peak degradation (°C)		
	Raw material	Nano-cellulose	Author(s)
Industrial bio residues	270	314	Oksman et al. [33]
Banana	317	346	Abraham et al. [19]
Pineapple leaf	313	338	Abraham et al. [19]
Jute	294	326	Abraham et al. [19]
Phormium tenax	344	355	Fortunati et al. [64]
Coconut fibre	350	365	Rosa et al. [65]

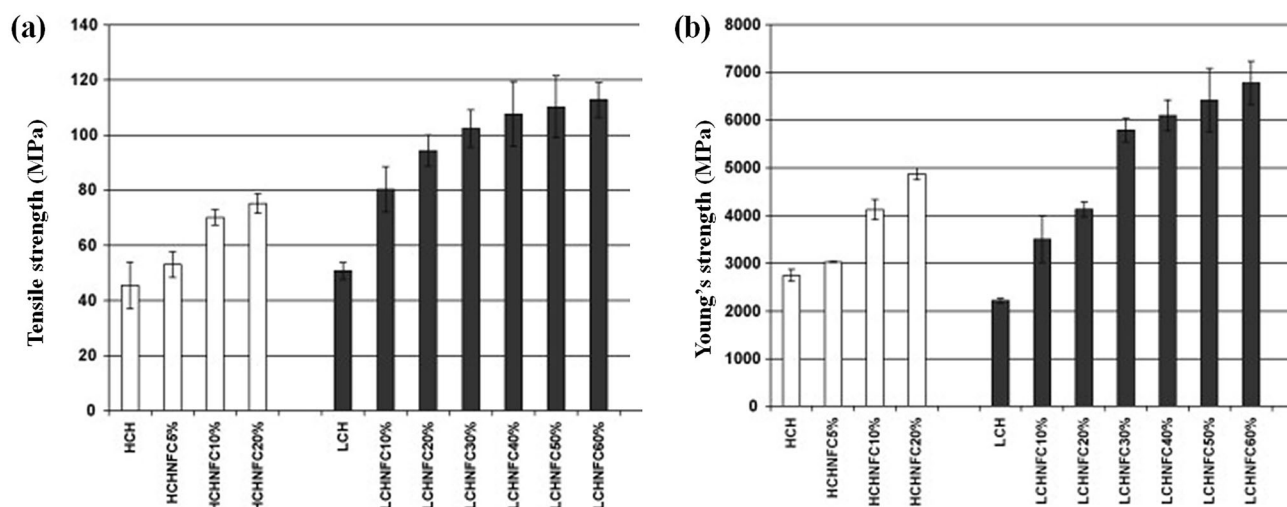


Figure 8 Tensile strength and Young's modulus of different chitosan-based films with different NFC content. Adapted with permission from [36] Copyright Elsevier, 2010.

uneven pattern [71]. Dankovich et al. studied the hydrophilicity of CNC by preparing thin films of both commercial and regenerated CNCs using different processing techniques such as spin coating, casting and simple standing of film. They calculated the different contact angle values of films and the change in values concerning the change in time. They have found out that the regenerated CNCs have higher hydrophobicity due to decreased hydroxyl groups compared to the original cellulose. The contact angle values of CNCs at various processing techniques are shown in Table 5 and Fig. 9 respectively [72].

Surface charge

The surface charge is a characteristic property attributed by the surface hydroxyl groups which contributed to overall negative surface charges to the cellulose fibres which can be characterised by zeta potential (ζ) measurements. This experimentation technique measures the repulsion between similarly charged particles in a dispersion. The higher dispersion in a smaller particulate system with a higher zeta potential value contributed to a stable suspension while the lower zeta potential value indicated the agglomeration or unstable suspension system [73]. Elanthikkal et al. observed that the CNCs prepared using the highly concentrated sulphuric acid, exhibited a greater value of zeta potential compared to CNFs since the higher concentration of sulfate group

on the surface introduces a higher mean surface charge, which causes lower particle-particle interaction. nanocellulose extracted using 76 wt% sulphuric acid solution exhibited the highest negative zeta potential value of -41.32 mV because the hydroxyl surface group was replaced with highly electronegative sulfate groups on the surface of the CNC [74]. Similarly, Han et al. prepared cellulose nanoparticles with 48 wt % of sulphuric acid which exhibited a zeta potential value of -57.07 mV for CNCs and -32.61 mV for CNFs respectively. The CNC showed a higher zeta potential value than CNFs due to the higher $-O-SO_3$ -group concentration on the CNC surfaces compared to CNF [75]. Tibolla et al. found that the enzymatic treatment led to the formation of CNFs with -25.7 mV zeta potential compared to the CNFs obtained by the chemical treatment which only

Table 5 Advancing (θ_a), receding (θ_r) contact angles and hysteresis ($\theta_a - \theta_r$) ($^\circ$) prepared by cellulose nanocrystals

Surface	θ_a	θ_r	$(\theta_a - \theta_r)$
Nanocrystalline cellulose (I)			
Spin-coated film	13.1 ± 0.6	8.0 ± 0.5	5.2 ± 0.9
Cast film	17.8 ± 1.1	10.9 ± 2.6	6.9 ± 3.2
Free-standing film	29.2 ± 2.7	15.5 ± 2.4	13.7 ± 1.7
Regenerated cellulose (II)			
Spin-coated film	48.5 ± 3.8	31.0 ± 6.9	17.5 ± 5.3
Free-standing film	37.6 ± 5.2	18.9 ± 4.3	18.6 ± 4.0

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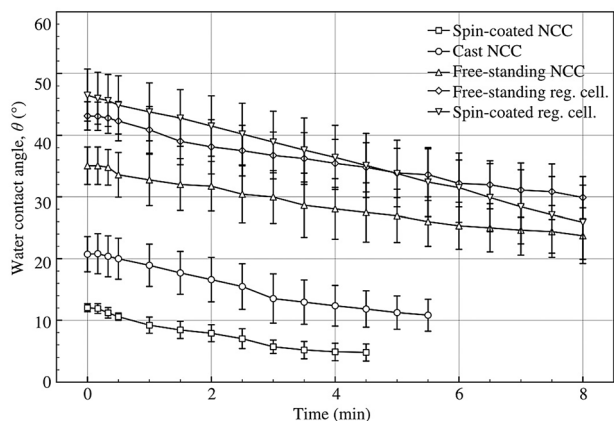


Figure 9 Time dependence of the contact angles on cellulose surfaces with standard deviations for water on cellulose film surfaces. Adapted with permission from [72]. Taylor & Francis Online, 2011.

exhibited -16.1 mV of zeta potential [76]. Tian et al. demonstrated the influence of concentration of acid, type of acids employed and time required to finish the process on the zeta potential value of the CNFs. The different zeta potential values and the various preparation parameters used are demonstrated in Fig. 10 and Table 6 respectively [77]. They observed that the concentration of sulfuric acid and the duration of the reaction directly influences the zeta potential values of the CNFs.

Summary

Extracted CNFs have noteworthy large surface areas and aspect ratios and therefore characteristics are often different from those of bulk materials. Nanocellulose exhibited inherent nature like excellent tensile strength, high crystallinity, longitudinal modulus (100 GPa for CNFs (CNFs) and 130 GPa for CNCs), dimensional stability, thermal stability, chemical functionality making it a very good reinforcement material for polymer composites over the last decade. Moreover, the high surface charge of nanocellulose (-57.07 mV) and high hydrophilicity resulted in the very good stable dispersion of nanocellulose in most of the hydrophilic polymer matrices. The extraction techniques and overall composition were found to have a significant role in the characteristics of the nanocellulose. For instance, the increment in the crystallinity value with each step of isolation and variation of peak mass loss

temperature with different acids used reflects the influence of different materials over the property. Whereas the high crystallinity value exhibited by the nanocellulose extracted from coconut fibre concerning other sources when treated by the same method also reflects the influence of the source (Coconut fibre exhibits higher lignin content). The overall above-mentioned excellent properties of nanocellulose suggest it has huge potential as a promising material for a wide range of energy and environmental applications.

Nanocellulose surface modifications

The surface of nanocellulose consists of three alcoholic hydroxyl groups which include one primary alcoholic and two secondary alcoholic hydroxyl groups. These readily available functional hydroxyl groups could facilitate various surface chemistries which would be tailor-made for specific applications. Several functionalization techniques are being carried and some of the most important ones which we have mentioned in this review are carboxymethylation, phosphating, acylation, amination and sulfonation along with the modified cellulose structure is demonstrated in Fig. 11. The below-mentioned figure is aimed to provide a general summary of the nanocellulose based surface modification. While reviewing the many articles regarding nanocellulose modification, it was evident that nanocellulose

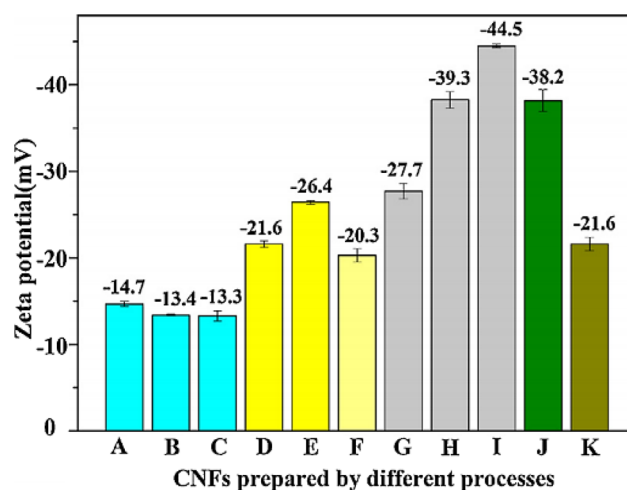


Figure 10 Zeta potential values of CNFs prepared in different conditions where samples (A–J) represented by samples CNFs-1 to CNFs-10, respectively, (K) was the sample of CNFs-H. Adapted with permission from [77]. Copyright Elsevier, 2016.

Table 6 Sample preparation condition for samples (A–J) represented by samples CNFs-1 to CNFs-10, respectively, (K) was the sample of CNFs-H

Sample	Acid type and concentration	Reaction time (min)	Temperature (°C)
CNFs-1	45 wt% H ₂ SO ₄	10	45
CNFs-2	45 wt% H ₂ SO ₄	20	45
CNFs-3	45 wt% H ₂ SO ₄	30	45
CNFs-4	50 wt% H ₂ SO ₄	10	45
CNFs-5	50 wt% H ₂ SO ₄	20	45
CNFs-6	50 wt% H ₂ SO ₄	30	45
CNFs-7	55 wt% H ₂ SO ₄	10	45
CNFs-8	55 wt% H ₂ SO ₄	20	45
CNFs-9	55 wt% H ₂ SO ₄	30	45
CNFs-10	64 wt% H ₂ SO ₄	30	45
CNFs-H	37 wt% HCl	30	45

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surface modification is an area of nano-cellulosic material development which is being widely exploited. Owing to the same reason, a very wide range of modifications is available in the research sphere, below mentioned are the generic description of this area.

TEMPO oxidation

The TEMPO modification is arguably the most common and important functionalization. This provides multi-dimensional advantages like improved stability of the nanocellulose suspension due to the increment in the surface charge. This modification also functions as an intermediate between other modifications while providing an increment in crystallinity values. A typical TEMPO modification process was carried out using 2,2,6,6-tetramethyl piperidine-1-oxyl (TEMPO) in the presence of NaBr and NaOCl. In this procedure, carboxylic acid groups at the surface of nano cellulose and catalytic amounts of TEMPO & NaBr were dissolved in polysaccharide solution at pH 10–11 and then the oxidation process would start by primary oxidant like NaClO solution. Typically, TEMPO mediated oxidation could selectively convert the C6 primary hydroxyls of cellulose into C6 sodium carboxylate groups. The first report of extraction of CNCs via TEMPO-mediated oxidation was reported by Araki et al. They used the TEMPO oxidation procedure for grafting of polyethene Glycol (PEG) and thereby prepared a sterically stabilized cellulose microcrystal suspension[78]. TEMPO oxidation in nanocellulose could result in electrostatic stabilization which would be due to the newly installed carbonyl

groups that imparted negative charges at the surface of the nanocellulose. Similarly, Saito et al. employed TEMPO mediated oxidation for the preparation of homogeneous suspensions of individualized cellulose microfibrils and they found that, after TEMPO mediated oxidation treatment the pristine cellulose were completely disintegrated into long individual microfibrils using a wearing blender which yielded in the transparent and highly viscous suspensions of nanocellulose. Moreover, they concluded that even after TEMPO mediated oxidation, the CNFs could maintain their structural morphological integrity and be capable of forming homogeneous suspension when dispersed in water[79]. In general, the TEMPO modification is a widely applied practice in cellulose surface modification that improves the surface hydrophilicity, introduce water solubility, acts as an intermediate step however this reduces the crystallinity of the cellulose fibre. Due to the higher crystalline nature of nanocellulose, only half of the hydroxymethyl groups are accessible for modification while owing to the application of chemicals, the modification is often considered to be expensive and non-ecofriendly.

Carboxymethylation

Carboxymethylation is the most common functionalization technique which is carried out in two phases: alkalization and etherization. In the alkalization phase, the sodium hydroxide solution and ethanol would disperse the cellulose. In the etherization phase, chloroacetic sodium was added to the solution at 45 to 70 °C. Carboxymethylation could

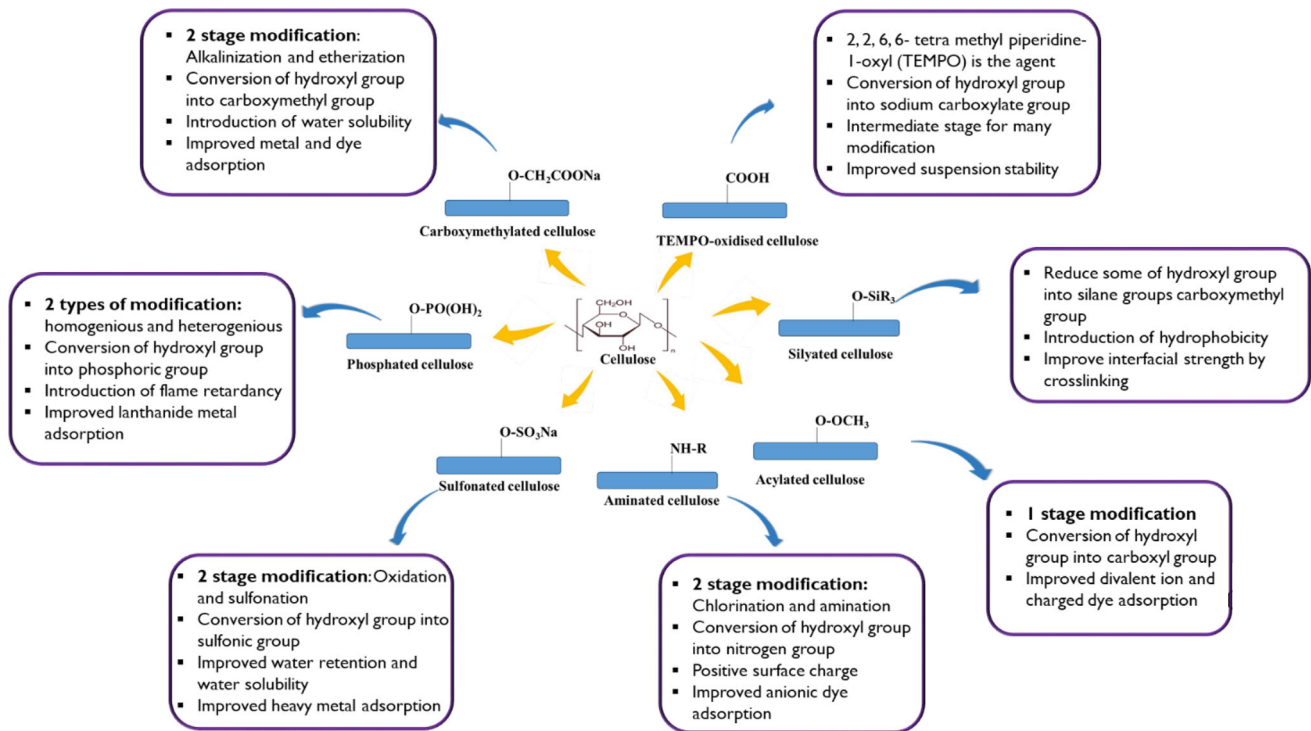


Figure 11 General chemical surface modification of nanocellulose.

change the surface charge of cellulose molecule into an ion exchanger hence it would promote the zeta potential value compared to the unmodified cellulose. This functionalization technique has substantial importance in the area of contaminants removal from the aqueous medium. The reason behind the influence of pH in the adsorption was due to the interaction between adsorbate and adsorbent [5]. The widely available carboxymethyl cellulose is the sodium salt form of CMC. This can be made to the water-insoluble free carboxylic acid by treating it with mineral acid. The CMC had shown impressive metal adsorption which includes 0.32 mmol/g for Ni²⁺ ions. The rate of adsorption was very high, which was about 90% of the total binding capacity that would be accomplished within 1 h [80]. The nanocellulose modification with carboxymethyl groups is often considered as both an intermediate step as well as a final modification which greatly improve certain characteristics such as surface charge, water solubility as well as significant improvement in the heavy metal adsorption which make it an attractive option for water purification.

Phosphating

Another important functionalization technique is phosphating, which is commonly employed for inducing flame retardancy and enhancing drug removal capability from aqueous resources. This could be achieved by the substitution of free hydroxyl groups in positions C2, C3, or C6 in cellulose structure. Another method is the shift of ester or ether group present in the cellulose structure after functionalization. This could be accomplished by a homogeneous reaction of organic solvents which promote partial or total break of cellulose fibres. Commonly used organic solvents are dimethylsulfoxide, methylamine, trifluoroacetic acid, N, N-dimethylformamide, paraformaldehyde, molten or aqueous urea, dimethylformamide and Sodium hydroxide etc. Phosphoric acid (H₃PO₄) has been commonly used for phosphate for phosphating functionalization[81]. Phosphate functionalization can be carried out in both heterogeneous and homogeneous manners. Homogeneous functionalization would be carried out by phosphoric acid in molten urea at elevated temperature followed by the addition of cellulose suspension for 30 min. In a heterogeneous mechanism, H₃PO₄ (85%) was added

into a system that contains only cellulose. The hydroxyl group of cellulose forms an ester linkage with the phosphorous acid group which resulted in the ion exchange capacity of the native cellulose. This improved ion exchange capacity resulted in the adsorption of new metals such as lanthanides metals [82] compared with the unfunctionalized cellulose. Phosphating on the surface of nanocellulose is among the most important modification especially its ability to adsorb lanthanides makes it unique however the non-ecofriendliness and the associated increased price certainly limited the application.

Acylation

Acylation is a functionalization technique employed for the preparation of cellulose derivatives with carboxyl groups. The process is carried out by reacting cellulose with succinic, maleic, or phthalic anhydrides in the absence of solvent. A typical process consists of anhydride melt fusion carried out at cellulose in an anhydride proportion of 1:10 with the mixture stirring for 20 min while, the *N,N*-dimethylacetamide (DMA) could be added in between. The reaction resulted in the formation of carboxyl groups with the covalent incorporation. The solid was separated by filtration with a sintered filter, washed in sequence with acetone and distilled water to remove the unreacted anhydride, DMA and by-products and dried [83]. The functionalization using maleic anhydride, phthalic anhydride and succinic anhydride provides the advantage of high levels of incorporation. This might be due to the progress of reactions at high temperatures in the absence of solvents which would enhance the availability of reagents. The acylated cellulose can be used as an effective material for the adsorption of green malachite dye, divalent metals (Co^{2+} and Ni^{2+}), blue methylene cationic dye [84] etc. The general interactions between the materials and the adsorbates were found to be electrostatic with improved adsorptions occurring at higher pH values. This could be due to the chemical protonation of the functional group in the acidic conditions whereas in an alkaline medium, the carboxyl group losses proton and favours the chelating capacity which increases the divalent metal adsorption [85]. Acylation is an emerging surface modification technique that can improve the zeta potential

values as well as crystallinity values. It can be carried out via both one-step and two-step procedures. However, the relative slower and more complex modification mechanisms are the limiting factors.

Amination

Nitration is a functionalization technique carried out for inducing a positive surface charge to cellulose and it is achieved in two steps. In the first step, cellulose halogenation was being carried out. In halogenation, chlorine addition would more preferable, since it had the most effective allogeneic, whose preferential sequence is: chlorine > bromine > iodine > fluorine [86]. The second step of the reaction consisted of chlorinated cellulose was being replaced with nitrogen derivative. In the halogenation step, thionyl chloride was used as the medium for nucleophilic attack on the cellulose surface where the secondary hydroxyl group was replaced with a chlorine group. In the next step, the chlorinated cellulose is replaced by reacting with ethylene-1,2-diamine or 2-amino methylpyridine under the reflux for 3 h or 4 h respectively in the absence of solvent [87]. Amination is particularly useful for the removal of pollutants from an aqueous medium. The amino-modified cellulose was found to be a better adsorbent due to the complexation process. The cations would be adsorbed into the basic centres of the functionalized cellulose, which resulted in the complexation process. The modified cellulose with ethylene-1,2-diamine also proved to be efficient in divalent cations removal which was quoted above. In this case, the adsorption order was in the order $\text{Co}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+}$ [88]. For mono element adsorption studies, arsenic had shown an adsorption capacity of 5.71 mg/g for As (III) and 75.13 mg/g for As(V), respectively [89]. It has also been found that amino modification provides very high adsorption capability for anionic dyes, particularly in acidic conditions. Amination is an important surface modification technique that can induce a cationic surface charge on the cellulose fibre. The technique can be carried out in both single steps and two steps and is widely used for heavy metal, dye adsorption along providing antibacterial activity. The higher purification requirements along with the deterioration of the mechanical characteristics are some of the limiting factors.

Sulfonation

Sulfonation is another commonly applied functionalization technique for the removal of divalent cation ions from an aqueous medium. This can be done via a two-step procedure. In the first step, cellulose is oxidated by reaction with sodium periodate and in the second step, the oxidised cellulose is sulfonated to form sodium bisulfite [90]. During the process, the ring structure of the cellulosic material could be altered. The sulfonation had improved the water retention capacity as well as introduced water solubility [91]. Also, the sulfonic group in the structure would enhance its affinity towards metal ions via enhanced electronegativity. At higher pH values, due to the deprotonation of sulfonic groups, the sulfonated cellulose showed improved adsorption of divalent cations compared to the unmodified cellulose material. The sulfonation in cellulose would have resulted in the ability to adsorb various heavy metals and the adsorption affinity was mainly dependent upon the electronegativity of heavy metals. Since electronegativity was in the order of $Pb^{2+} > Cd^{2+} > Ni^{2+} > Co^{2+} > Cu^{2+} > Zn^{2+}$, the adsorption affinity of sulfonated cellulose also follows the order of $Pb^{2+} > Cd^{2+} > Ni^{2+} > Co^{2+} > Cu^{2+} > Zn^{2+}$. In this case, Pb^{2+} had the highest electronegativity which resulted in the highest adsorption of Pb^{2+} by sulfonated cellulose whereas, Zn^{2+} having the lowest electronegativity resulted in the lowest adsorption of Zn^{2+} by sulfonated cellulose. In the case of mono element adsorption studies using lead, it was found that sulfonated cellulosic fibre has an absorbance of 1.2 mmol/g at pH 5 [92]. The presence of lignin was also found to be increasing the adsorption capacities significantly. Sulfonation is one of the easiest modifications applied since it can be carried out in the extraction procedure by employing the higher concentrated sulphuric acid. This however has environmental implications which lead to the more environmental friendly periodate based green approaches which have lower charge contents.

Silylation

Silanes have been extensively used as coupling agents with the chemical formula SiH_4 . In cellulose-based composites, usually in the fibre-matrix interface, the silane coupling agents could reduce the

number of cellulose hydroxyl groups and convert the hydrophilic nature of cellulose into a slightly hydrophobic nature which would enhance the compatibility towards most of the hydrophobic polymer matrices. In the presence of moisture, the hydrolysable alkoxy group leads to the formation of silanols. Then the silanols could react with the hydroxyl group of the fibre, resulting in stable covalent bonds to the cell wall that is chemisorbed onto the fibre surface [93]. Therefore, the hydrocarbon chains provided by the application of silane restrain the swelling of the fibre by creating a cross-linked network due to the covalent bonding between the matrix and the fibre. Silane coupling agents are effective to enhance the interfacial strength of the natural fibre-polymer matrix via modifying the natural fibre-polymer matrix interface. Abdelmouleh et al. used organofunctional silane coupling agents in an ethanol/water medium for the surface modification of cellulosic fibres. They found that, after silane modification, cellulose fibres become hydrophobic due to the presence of Si-O-cellulose and Si-O-Si bonds on the surface of the cellulose which was confirmed via water contact angle studies [94]. Silane modification can improve the stability of the nanocellulose network along with the introduction of hydrophobicity which can improve the overall compatibility with similar materials. Often the silane coupling agents are used in combination with amino groups which can further increase the adsorption and anti-bacterial capability.

Esterification

Esterification could be the most common and widely employed nanocellulose modification technique. Certain other modifications were carried out via esterification such as sulfonation, carboxymethylation, amination etc. The esterification can be carried out via both homogeneous and heterogeneous means where the homogeneous means are both surficial and polymer level however the heterogeneous is exclusively surficial modification level. During the esterification, the reaction either occurs on the whole cellulose polymer chains to form conventional cellulose esters or occurs at the outer of cellulose fibres leaving the cellulose crystalline structure in the interior intact. An example of in situ esterification is the production of surface-modified CNCs via one-pot reaction methodology, which combines organic acid-

catalyzed Fischer esterification and concurrent cellulose acid hydrolysis of amorphous cellulose chains which allows the isolation of acetylated CNCs in a single step process [95]. Moreover, this procedure can be applicable to access various esters of nanocellulose. However, it is very difficult to control the esterification degree. In a similar approach, Herrick et al. have proposed in the early development of nanocellulose, the simultaneous acetylation of NFCs during the mechanical shearing using as processing media a mixture of acetic acid and acetic anhydride with sulphuric acid as catalyst instead of water [96]. The esterification could be the most wider modification technique and also the intermediary for most of the nanocellulose derivatives. Owing to the simplicity and efficacy, these techniques have paved the way for many of the modification techniques.

Nanocellulose hybrid materials

Even though the nano cellulose hybrid materials are not considered surface modification techniques, the objectives are similar to the major objective of nanocellulose modification however hybrid materials exhibits added advantages such as lower cost, faster process, improved mechanical, thermal and surficial properties. While these materials possess great advantages, the main advantage is often the overall eco-friendliness of the procedure. There are many examples of nanocellulose hybrid materials that address all the application areas such as carbonaceous materials, calcium phosphates, biochars, metal-organic frameworks (MOFs), biomass, polymers etc. Often the addition of these materials results in synergetic effects that lead to improved properties and added properties [97]. Such as nanocellulose along with excellent adsorbent could be used in the fabrication of composite materials which exhibit multiple application potential. *Guo* et al. fabricated a nanofibrillated cellulose and calcium hydroxyapatite composite which is an excellent fire-resistant material [98]. *Zhang* et al. employed the same material and similar approach for fabricating a composite which was primarily applied for water purification applications. They demonstrated the excellent dye adsorption capacity along with the possibility of size exclusion to further remove many other pollutants making this an excellent water purification composite [99]. The same material is also used in many other applications, especially in the biomedical sector. This

demonstrates the potential application space of nanocellulose hybrid material in the cellulose-derived material application spectrum.

Summary

Being a material that has three surface hydroxyl groups makes cellulose a hydrophilic material, which has poor compatibility with most of the hydrophobic polymer matrices. In this context, to enhance the compatibility and improve the dispersion towards hydrophobic polymer matrices, nanocellulose has been subjected to a wide range of chemical modifications towards increasing its potential in certain fields of interest. These modifications either modulated the chemistry of the nanocellulose itself or introduced certain functional groups onto its surface, which varied from simple molecules to polymers. The surface modifications like carboxymethylation, phosphating, acylation, amination, sulphonation etc. have been well discussed in this section. Among the above-mentioned surface modifications, carboxymethylation modification has been widely employed in the current scenario due to the enormous potential of carboxymethyl cellulose (CMC) in biomedical applications such as oral, ophthalmic, injectable and topical pharmaceutical formulations. The main limitations of the surface modification can be effectively addressed by the incorporation of materials that expand the application horizon of these materials.

Application of nanocellulose-based composites in environmental fields

The inherent properties of cellulose like high mechanical strength, low density, ease of functionalisability, large surface area, film-forming capability etc. make it a potential candidate for various applications such as air filtration, water purification, EMI shielding, antimicrobial applications etc. Because nanocellulose possess a porous structure with large specific surface areas, this was employed to produce various materials like adsorbents, catalyst supports, thermal insulators etc. It was reported that cellulose-based aerogels could act as high-efficiency particulate air (HEPA) and ultralow penetration air (ULPA) filters with high filtering efficiencies of at least

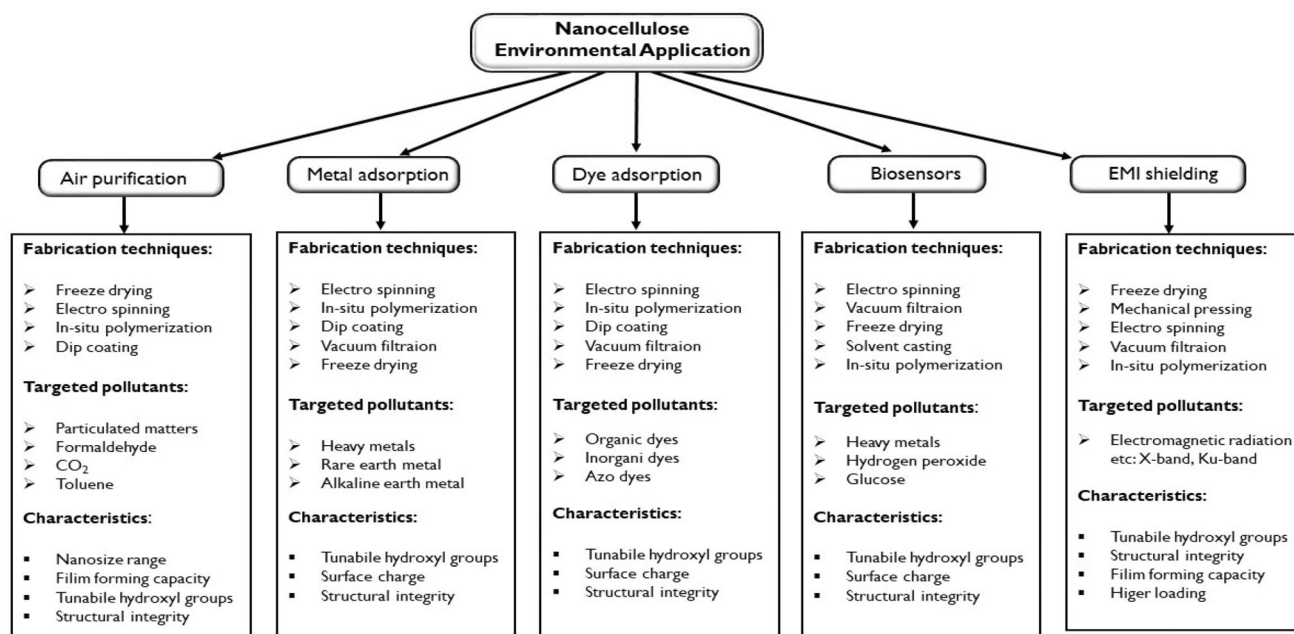


Figure 12 General applications of nanocellulose based material in the environmental area.

99.97%[85]. Without being exhaustive, this paper addresses some of the current and promising applications. While reviewing many articles, we observe that the nano-cellulosic materials are wide-spreading at a greater pace into many areas and replacing the conventional non-sustainable materials. While many applications are being investigated extensively, some applications require further investigation. We are summarizing the most important applications that are being exploited and below mentioned Fig. 12 will provide a generic view of this area.

Air purification

Air pollution is one of the major concerns in the modern industrialised world. This has been addressed by developing certain novel multifunctional materials. The inherent excellent properties of cellulose make it a potential material for developing such sustainable composite filters for air purification. CNFs are promising candidates for air filter applications due to their fibrous nature which can reduce the resistance in filters and thereby enhance the collision frequency between particles and fibres. Figure 13a illustrate an example of a similar air filter fabricated via cellulose fibre/gelatin mixture [100]. Zhao et al. developed a window screen-based porous CNF (CNF) polyhedron membrane on stainless steel for air purification. The demonstrated composite (Fig. 13b)

had excellent adsorption capacity towards formaldehyde which was about 47.71 mg g^{-1} . Moreover, the demonstrated composite could reduce the formaldehyde concentration to less than 0.1 mg m^{-3} which was within the international safety standard [101]. Another work was done by Zhiping et al. where they developed a CFs@ZIF-8 air filter by incorporating Zeolitic imidazolate frameworks (ZIF-8) nanocrystals onto the surfaces of cellulose fibres (CFs) using a simple and effective in-situ growth process. The fabricated composite had an impressive air filtration efficiency of 99.9% and 200 times higher efficiency than neat CFs-filter[102]. Nemoto et al. developed high performance homogeneously dispersed TEMPO-oxidized cellulose aerogel for air filtration application using the freeze-drying technique. This technique has the advantage of having nanoscale, spider-web-like networks of the tempo oxidized CNFs (TOCNs) with large specific surface areas which could pave the way to fabricate high-performance air filters [103].

Metals sorption

Many nano-celluloses based composites have been prepared using techniques such as ion exchange and reverse osmosis, adsorption, membrane filtration etc. The use of cellulose-based adsorbents for the removal of different metal ions such as heavy metals, rare

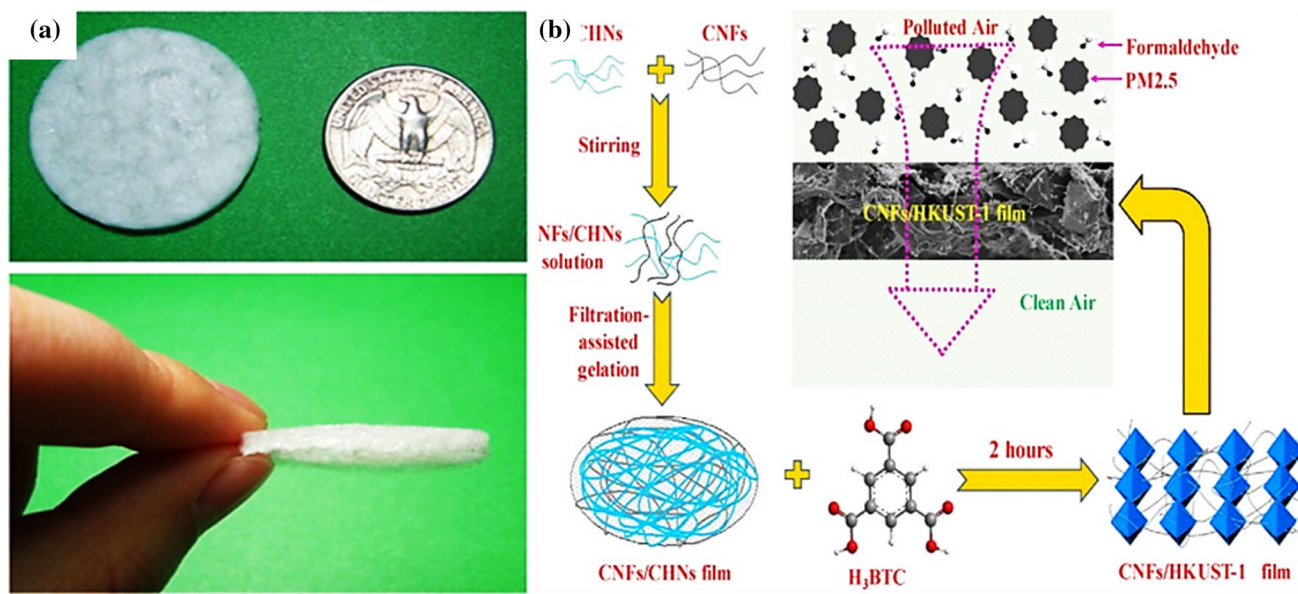


Figure 13 a Macroscale view of dry cellulose fibre/gelatin composite (containing 75 wt% fibres) with different shapes. Adapted with permission from [100]. Copyright Elsevier, 2010.

b Fabrication of porous CNFs/HKUST-1/stainless steel screen. Adapted with permission from [101]. Copyright Elsevier, 2019.

earth metals and alkaline earth metals has received considerable attention due to the inherent excellent properties of cellulose [104]. Maatar et al. developed a poly (methacrylic acid-co-maleic acid) grafted nano-fibrillated cellulose prepared via radical polymerization in an aqueous solution using Fenton's reagent. The aerogel showed excellent adsorption efficiency towards various randomly selected heavy metals like Pb^{2+} , Cd^{2+} , Zn^{2+} and Ni^{2+} . The adsorption value varied from 60 to 90% when the heavy metal concentration was lower than 10 ppm and over 98% of the adsorbed metal ion when the metal concentration of the initial solution was higher than 10 ppm. The fabricated composite had the added advantage of reusability with subsequent washing without noticeable loss of adsorption capacity. The maximum adsorption capacities of Pb^{2+} , Cd^{2+} , Zn^{2+} and Ni^{2+} were 165, 135, 138 and 117 $mg\ g^{-1}$, respectively [105]. Similar to the work, Alatalo et al. were developed a nitrogen-doped carbon aerogel using hydrothermal carbonization of cellulose in the presence of the globular protein ovalbumin. The presence of protein could help to form nitrogen functionalities and act as a structural directing agent with a specific surface area of $38\ m^2/g$. This material had shown an enhanced ability to remove both Cr(VI) ($\sim 68\ mg/g$) and Pb(II) ($\sim 240\ mg/g$)

respectively [106]. Rahman et al. fabricated poly(-methyl acrylate) grafted cellulose via a two-stage chemical modification reaction similar to the approach of Maatar et al. while targeting the adsorption of rare earth metals. In their approach, they created a free radical on the primary hydroxyl group on the nanocellulose molecule. This free radical generated later undergone a copolymerization reaction with methyl acrylate monomers. Due to the excellent chelating capacity of the developed ligands based on nanocellulose, they have managed to attain very impressive adsorption capacity towards the elements in the order of La^{3+} , Ce^{3+} , Pr^{3+} , Gd^{3+} , Nd^{3+} , Eu^{3+} and Sm^{3+} with values of 260, 245, 235, 220, 210, 195, and 192 $mg\ g^{-1}$, respectively [107]. Zhang et. al prepared an environmentally friendly filter using ultralong hydroxyapatite nanowires on the cellulose fibre's matrix using a vacuum filtration mechanism. Polyamidoamine-epichlorohydrin (PAE) resin is incorporated to improve the wet mechanical properties. The high-performance filter paper had a porous structure with superhydrophobic nature, due to this it exhibited a pure water flux of $287.28\ L\ m^{-2}\ h^{-1}\ bar^{-1}$ under cross-flow conditions. It exhibited excellent adsorption capabilities like 100% removal of bacteria, > 98.61% removal of TiO_2 nanoparticles, 273.97 $mg\ g^{-1}$ and 508.16 $mg\ g^{-1}$ adsorption of

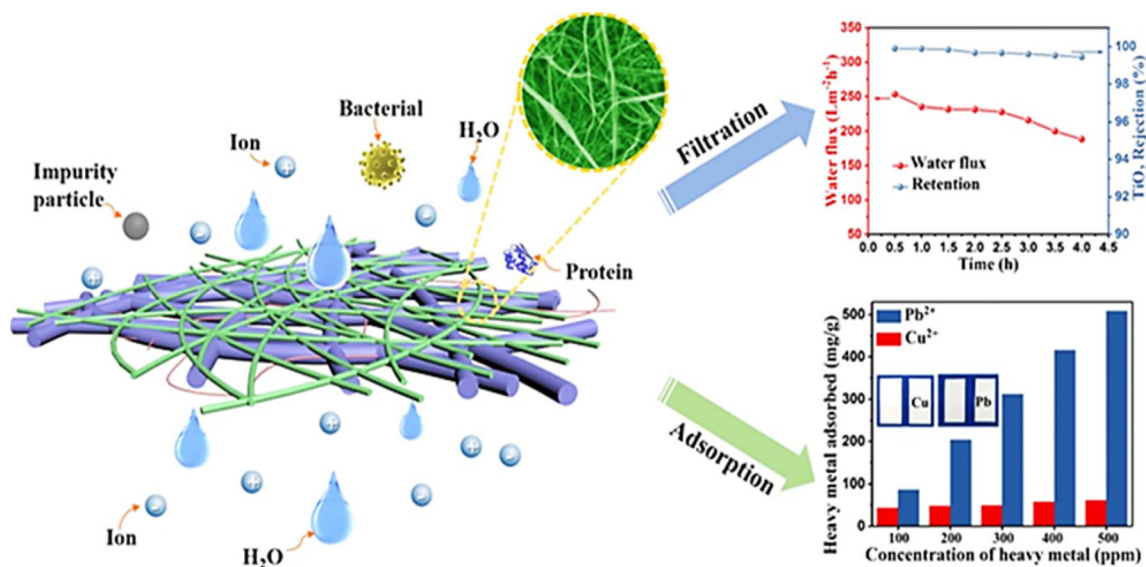


Figure 14 Ultralong hydroxyapatite nanowire/cellulose/poly amidoamine-epichlorohydrin based filter paper for high-performance water purification. Adapted with permission from [108]. Copyright ACS publications, 2019.

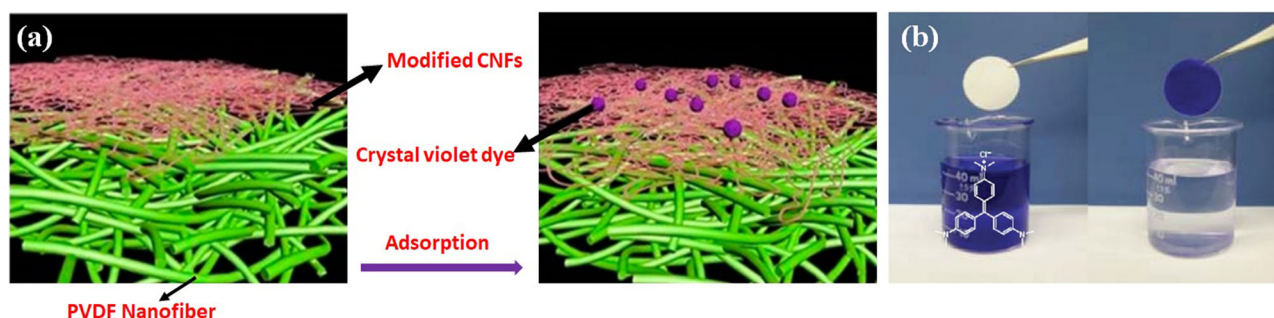


Figure 15 a Schematic representation of crystal violet removal by Meldrum’s acid-modified CNF-based PVDF nanofibrous MF membrane. Adapted with permission from [2]. Copyright ACS

Publications, 2017. **b** Adsorption efficiency of positively charged crystal violet dye concentration. Adapted with permission from [111]. Copyright ACS Publications, 2011.

methyl blue and Pb^{2+} ions respectively which is demonstrated in Fig. 14 [108]. This demonstrates the vast flexibility in the fabrication of nanocellulose for given applications.

Dye adsorption

Toxic and harmful synthetic dyes are widely used in textile, paper, plastic industries and other industries etc. The excellent readily functionalizable hydroxyl groups of cellulose could help to convert into a versatile material for the removal of a wide range of organic dyes and bacteria via an adsorption mechanism. Many works have been carried out recently for water purification [109]. Gopakumar et al.

removed the toxic crystal violet dyes from water by using a CNF-based PVDF membrane via Meldrum’s acid modification (Fig. 15a). The composite membrane was prepared by a nonsolvent assisted procedure using Meldrum’s acid as an esterification agent to enhance the adsorption towards positively charged crystal violet dyes. They have achieved crystal violet (CV) adsorption of 3.984 mg/g for the Meldrum’s acid CNF-based PVDF membrane compared to the unmodified CNF-based PVDF membrane which had an adsorption value of only 1.368 mg/g. This enhancement in the adsorption capacity was due to the electrostatic interaction between the protonated crystal violet dyes and Meldrum’s acid-modified CNF [2]. Beyki et al. removed congo red dye by using

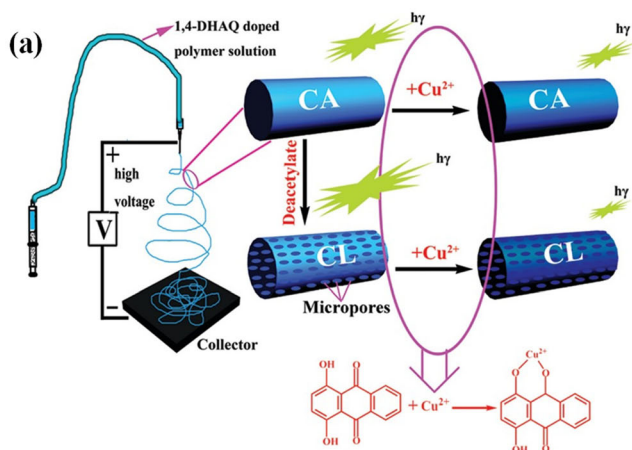
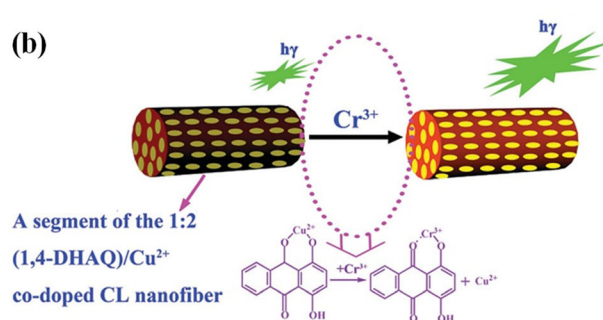


Figure 16 a Schematic showing the electrospinning setup (left) and sensing mechanism of the 1,4-DHAQ@CL microporous nanofiber film for Cu^{2+} (right), and **b** sensing mechanism of the



(1,4-DHAQ)- Cu^{2+} @CL microporous nanofiber film for Cr^{3+} . Adapted with permission from [114]. Copyright ACS Publications, 2012.

an efficient magnetic Fe_3O_4 cellulose core. They synthesised magnetic Fe_3O_4 cellulose core by a one-step method where magnetic Fe_3O_4 cellulose has been further reacted with epichlorohydrin and 1-methylimidazole to generate magnetic polymeric ionic liquid. Their results have revealed that different factors like contact time, adsorbent dyes and ionic strength have a significant effect on congo red dye adsorption[110]. Ma et al. fabricated a multilayered nanofibrous microfiltration (MF) membrane which exhibited 16 times higher adsorption capacity against a positively charged dye over a commercial nitrocellulose-based MF membrane which is demonstrated in (Fig. 15b). This experimental membrane showed full retention capability against bacteria, for example, *E. coli* and *B. diminuta* have decent retention against bacteriophage MS2 [111]. Wang et al. developed a novel class of microfiltration membrane by infusing modified CNF into an electrospun polyacrylonitrile (PAN) and polyethylene terephthalate (PET) scaffold. It had an effective porosity of 80% with a maximum pore size of $0.78 \pm 0.03 \mu\text{m}$ and a mean flow pore size of $0.66 \pm 0.01 \mu\text{m}$. The scaffold was capable of the complete removal of *E. coli* by size extrusion with Cr (VI) ion adsorption of 100 mg/g and Pb (II) ion adsorption of 260 mg/g respectively. This work is particularly interesting as it can remove toxic contaminants like viruses, bacteria, heavy

metals etc. and thereby makes an ideal material for drinking water purification [112].

Biosensors

Research and development of biosensors have gained considerable interest among the scientific community due to the huge potential of the biosensors to contribute substantially in next-generation medicines and as ultrasensitive point-of-care detection of markers for diseases[113]. Wang et. al developed a reusable nanocellulose membrane via electrospinning and subsequent deacetylating after doping with 1,4-dihydroxyanthraquinone (1,4-DHAQ). The fabricated membrane was highly sensitive and very useful for selective fluorescence detection of Cu^{2+} in an aqueous solution. The prepared 1,4-DHAQ doped CNF film showed recovered fluorescence by extra addition of Cr^{3+} nitrate solution. The sensing mechanism for Cu^{2+} was ascribed to the formation of phenolate between 1,4-DHAQ and Cu^{2+} , while that for Cr^{3+} was attributed to the reversing reaction from Cu^{2+} based phenolate to Cu^{2+} and Cr^{3+} based excited complex with recovered fluorescence. This indicates their potential applications in the environmental monitoring of Cu^{2+} and Cr^{3+} in polluted water. The design concept in this work might also open a door to the design of effective fluorescence probes for other

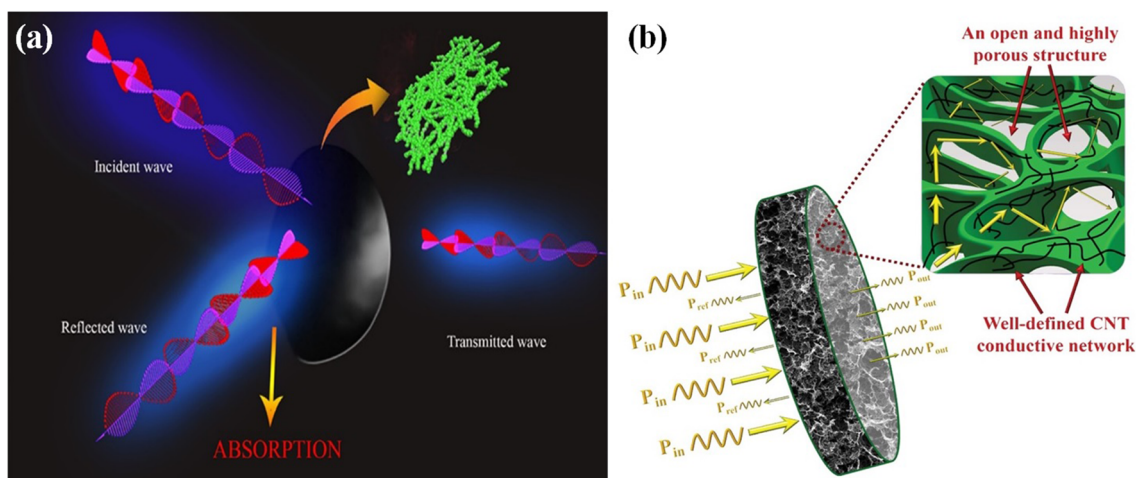


Figure 17 Schematic description of **a** EMI shielding interference of the demonstrated PANI/CNF flexible paper. Adapted with permission from [3]. Copyright ACS Publications, 2018.

b Electromagnetic microwave dissipation in the CNT/cellulose composite. Adapted with permission from [117]. Copyright RSC Publications, 2015.

heavy metal ions and this is demonstrated in Fig. 16 [114]. In another work, Kumari et al. developed cellulose from pine needles using cellulose etherified, oxidized and modified with Schiff base by reacting with L-lysine. They used this characterized cellulose as sensor adsorbent for Hg (II) from an aqueous solution. The decyl chain was observed to be an efficient adsorbent of Hg(II) with a very high maximum adsorption capacity of 258.75 mg g^{-1} [115].

Electromagnetic interference shielding

Cellulose aerogels are highly porous materials consisting of ultra-high-volume gas-phase fractions and three-dimensional networks of solid substrates with large open pores, ultra-high specific surface area, ultra-low density etc. Infusing electrically conductive nanofillers into the aerogel shows potential as one of the most promising strategies to significantly reduce the density of electromagnetic Interference (EMI) shielding materials. Hence, many studies have been carried out on this aspect [116]. Gopakumar et al. fabricated flexible, lightweight, and highly conductive cellulose nano papers were fabricated through in situ polymerization of aniline monomer onto CNFs. The authors claimed to achieve average shielding effectiveness of ca. -23 dB ($>99\%$ attenuation) at 8.2 GHz even with 1 mm thick paper. The claimed attenuation is 360% higher than the shielding effectiveness value reported by the previous studies. This green conductive aerogel showed an impressive electromagnetic shielding for high engineering

application which is schematically demonstrated in Fig. 17(a)[3]. Huang et. al developed an ultra-light and highly conductive aerogel by a simple, efficient and environmentally benign strategy. The carbon nanotube (CNT)/nanocellulose (NC) suspension was homogenised under high pressure in the presence of surfactant. This is later rapidly frozen in liquid nitrogen and then lyophilized in a freeze drier resulting in the formation of CNT/NC aerogel composite. The composite material had excellent electromagnetic interference (EMI) shielding effectiveness of $\sim 20.8 \text{ dB}$ with shielding effectiveness as high as $\sim 219 \text{ dB cm}^3 \text{ g}^{-1}$ with microwave absorption as the dominant EMI shielding mechanism in the microwave frequency range of $8.2\text{--}12.4 \text{ GHz}$ at a density of as low as 0.095 g cm^{-3} . The porous structure and conductive nature of the typical nanocellulose based aerogel is demonstrated in Fig. 17b [117]. Similarly, Jung et al. developed silver nanowire coated cellulose papers with an efficient and facile dip-coating process. This was supported by the anisotropic apparent electrical conductivity of the fabricated AgNW/cellulose papers depending on in-plane or thickness direction. This modification showed an improved electrical conductivity of 0.34 S/cm which was many times higher as compared to neat cellulose which had an electrical conductivity of $\sim 10\text{--}11 \text{ S/cm}$. The electrical conductivity of the papers was in a plane that could increase significantly from 0.34 for the neat cellulose to 67.51 S/cm after the multiple dip-coating cycles. The composite

material also exhibited a high EMI shielding performance of ~ 48.6 dB at 1 GHz [118].

The emerging global trend towards green and sustainable alternatives replacing conventional synthetic products is a good sign for cellulose and other biomass material. At the same time, questions about the cost of this nanofiller should also be considered. With the ever-increasing environmental concerns and movement toward green materials, researchers should think about outside-the-box applications to move cellulose nanomaterials forward considering alternative sustainable raw materials like agricultural and industrial wastes. There is a significant amount of cellulose-based research is being carried out with the above-mentioned applications such as EMI shielding, biosensors, dye adsorption, heavy metal adsorption etc. The new government policies and regulations have prompted initiatives for the commercial exploitation of nanocellulose have arisen, such as cellulose, American Process, Alberta Innovates – Technology Futures, US Forest Service’s Forest Products Laboratory, Blue Goose Biorefineries, FPInnovations, Melodea, Paperlogic, Borregaard, Innventia, Cellutech AG, Stora Enso, SAPPI, and Oji Holdings Corporation. This could further improve the application of cellulose in the environmental sector. Some of the recent works based on cellulose are listed in Table 7 below.

Application of cellulose-based composites in energy application

Nanocellulose based composite in various forms such as flexible thin films, fibres, networks, aerogels having mesoporous structures, other networks is extensively developed for photovoltaic devices, energy storage systems, mechanical energy harvesters, and catalysts components etc. showing tremendous materials science value and the application potential in many energy-related fields. Some of the most common application includes fuel cells, supercapacitors, lithium-ion battery, biofuels and solar cell substrates; While reviewing many articles, we observe that the nano-cellulosic materials are widespreading at a greater pace into many areas and replacing the conventional non-sustainable materials. While many applications are being investigated extensively, some applications need to be further investigated. We are summarizing the most

important applications that are being exploited and below mentioned Fig. 18 aimed to provide a generic view.

Fuel cells

Fuel cells are electrochemical devices that convert the chemical energy of a fuel, preferably hydrogen into electrical energy. The conversion process is continuous if the fuel is supplied into the device and the byproducts are removed for the effective functioning of the cell. Due to the higher fabrication costs, polymer electrolyte membrane-based fuel cells are not yet commercialized even if it was a source of efficient and clean energy. In a typical fuel cell, a proton-conducting electrolyte membrane is usually sandwiched between an anode and cathode electrocatalyst layers. The ability to form clean and flexible fuel cells have recent time attracted many researchers in this area[138]. Bayer et al. developed a fuel cell with nanocellulose membranes with a much lower operating temperature of 80 °C while being biodegradable and environmentally friendly. These CNC paper membranes had maximum conductivity of 4.6 mS cm^{-1} at 120 °C. Interestingly, CNC paper membranes showed 92 times higher maximum conductivity than the corresponding CNF paper membranes. The higher value could be attributed to the increased number of charge carriers, better hydrophilicity and the presence of sulfuric acid groups which was introduced at acid hydrolysis during the isolation process. The reason behind the higher efficiency was explained by the Grotthuss-like water-mediated proton conduction mechanism in combination with the low activation energy of 0.22 eV. This is evident since, at low humidity levels, nanocellulose membranes exhibited only very low proton conductivities but the proton conductivities drastically increase beyond 70% relative humidity which is shown in Fig. 19 [139]. Lu et al. developed a CNC based robust composite film with a range of CNC contents from 20 to 60% with silica gel hybrid and poly (vinyl alcohol) in solid electrolyte form for alkaline fuel cells. Their study demonstrated the significance of optimisation of the concentration of the components. The ratio of 60% CNC and 40% binder (PVA: silica gel) exhibited a low water swelling of about 5% and maximum water uptake up to 80% with higher dimensional stability and showed a maximum conductivity of 0.065 S cm^{-1} at 60. The decreased CNC contents

Table 7 Cellulose-based composite and modification in environmental application

Composite	Applications	Fabrication technique	Inferences	Author(s)
Poly(vinyl alcohol)/CNCs (CNCs)	Removal of particulate matter (PM) from air	Electrospinning	PM _{2.5} removal efficiency: The quality factor (Qf) PM _{2.5} PVA/CNC-15-6 = 96.0:0.054 PVA/CNC-20-6 = 95.1:0.054 PVA/CNC-20-8 = 99.1:0.052	Zhang et al. [119]
CNFs (CNFs) with Methyltrimethoxysilane (MTMS)	REMOVAL OF PARTICULATE MATTER PM _{1.0} , PM _{2.5} AND HUMIDITY FROM AIR	Freeze-drying with post silanization	Filtration efficiency of PM _{1.0} and PM _{2.5} was 99.31 and 99.75% respectively Low-filtration resistance of 42 Pa A quality factor of up to 0.122 Pa ⁻¹	Liu et al. [120]
CNFs (CNFs) with Chitosan	Removal of particulate matter and CO ₂	Freeze-drying	Maximum filtration efficiency (PM _{2.5}) of 99.56% and 4.8 mmol/g of CO ₂ adsorption obtained by 2% modified CNF	Sepahvand et al. [121]
Metal – organic Frameworks: MIL-101 and UiO-67 with Cotton	Removal of particulate matter	Surface coating via dipping	A quality factor of up to 0.085 Pa ⁻¹ Removal efficiency above 90%	Yoo et al. [122]
CNC (CNCs) and polyamide 6 (PA-6)	Toluene adsorption from indoor air	Electrospinning	Composite with 17 wt% PA-6 and 1.5 wt% CNC exhibit 50% toluene adsorption efficiency	Buyuhada et al. [123]
Zeolitic imidazolate framework-L and cellulose fibres (nano and micro)	Adsorption of tellurium with antibacterial effects	dip-coating and in-situ growth process	Maximum adsorption capacity of 0.3415 mg/cm ² Good antibacterial effects against <i>S. aureus</i> and <i>E. coli</i>	Li et al. [4]
Palladium nanoparticles and bacterial cellulose	Organic dye adsorption and oil–water separation	Vacuum filtration followed by dip coating	Oil–water separation efficiency = 97% Water flux = 3832.7 L m ⁻² ·h ⁻¹ ~ 99% reduction of Methylene blue(MB) within 170 s	Yu et al. [124]
Cu-MOF and Cellulose acetate (CA)	Removal of dimethoate pesticide from water	Solution casting and Dip coating	The maximum adsorption capacity was 321.9 for 40% Cu-BTC@CA membrane (207.8 mg/g for neat CA membrane)	Abdelhameed et al. [125]
Chitosan and cellulose	Removal of Co(II)	Wet-spinning process	The maximum adsorption capacity of 23.6 ± 2.5 mg g ⁻¹	Zhuang et al. [126]
TiO ₂ and cellulose	Removal of Phosphate Anti-microbial property	Hydrolysis-precipitation	Maximum removal of 96% in the solution after 2 h	Zong et al. [127]
Carboxymethyl cellulose and Chlorapatite nanoparticles	Removal of zinc and cadmium	Co-precipitation	Maximum Langmuir sorption capacity of 141.1 mg g ⁻¹ for Zn ²⁺ and 150.2 mg g ⁻¹ for Cd ²⁺	Li et al. [128]
CNC and activated carbon nanofibers	Adsorption of Volatile organic compound (VOC)	Electrospinning	CNC reinforced samples exhibited 3 times more adsorption capacity than neat PAN membrane	Awad et al. [129]
Cellulose and Graphene nanoplates	Removal of Congo red	Colloidal suspending	The maximum adsorption capacity of 139.6 mg/g	Lopez et al. [130]
Cornstalk cellulose	Adsorption of Cd (II)	TEMPO-modification	The maximum adsorption capacities of 5.83 and 5.12 mg/g at pH 7 and pH 5	Yu et al. [131]
CNCs (CNCs) and poly(<i>N,N</i> -dimethylacrylamide-co-	Removal of methylene blue	Gelation by stirring	The maximum adsorption capacity of 131.58 mg/g	Hossain et al. [132]

Table 7 continued

Composite	Applications	Fabrication technique	Inferences	Author(s)
3-methacryloxypropyl trimethoxysilane)				
Cellulose and salicylaldehyde thiosemicarbazone	Cu ²⁺ sensing	In situ polymerization and vacuum filtration	The detection limit of 0.086 μM with a Linear correlation coefficient of 0.9914	Yue et al. [133]
Cellulose nanofibrils and carbon dots	Hydrogen peroxide and glucose detection	Microwave irradiation and TEMPO modification followed by Vacuum filtration	The detection limit of 1.73 μM with a Linear correlation coefficient of 0.993 and 0.99 for Hydrogen peroxide and glucose respectively	Bandi et al. [134]
Nickel Nanoparticle with Nanowire-Coated Cellulose	Electromagnetic Interference Shielding	Intermitted dipping with sputter coating	EMI SE of up to 88.4 dB at 10.3 GHz	Zhan et al. [135]
Liquid metal and CNF	Electromagnetic Interference Shielding	Freeze drying	EMI shielding effectiveness of 65 dB in the wide frequency of 4–18 GHz covering C-band, X-band and Ku-band	Liao et al. [136]
Ti ₃ C ₂ T _x MXene and cellulose paper	Electromagnetic interference shielding	pressured-extrusion followed by mechanical pressing	59.76 ± 0.50 dB on X band with electrical conductivity of 1672.0 ± 7.1 S cm ⁻¹	Qian et al. [137]

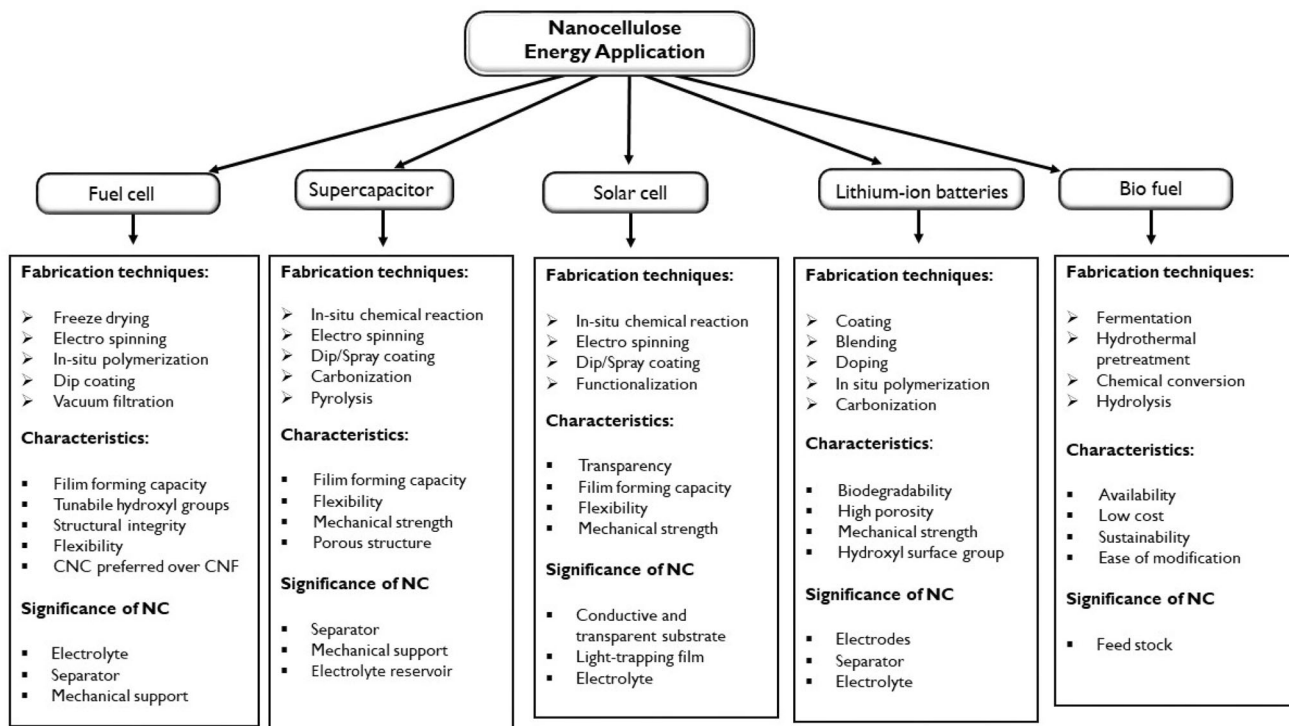


Figure 18 General applications of nanocellulose based material in the energy-related areas.

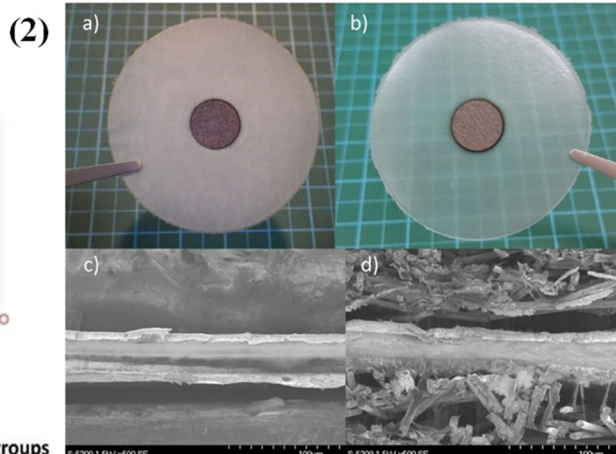
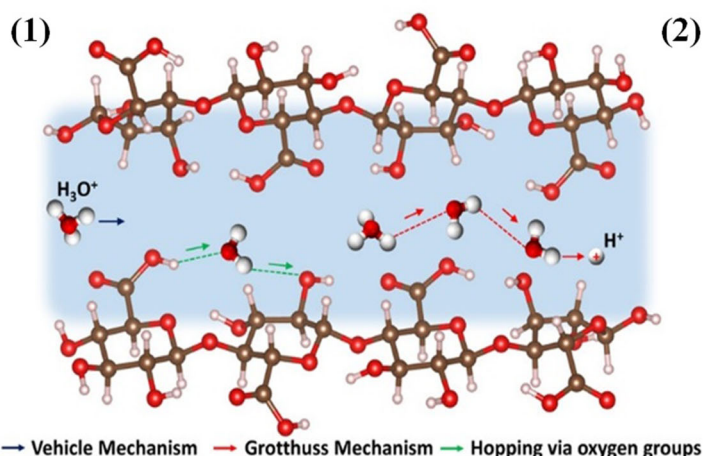


Figure 19 (1) Schematic of possible proton conduction mechanisms and pathways in nanocellulose paper fuel cells (2) nanocellulose fuel cells. Photographs of MEAs were prepared from **a** CNF (CNF) membrane and **b** a CNC (CNC) membrane.

exhibited improved hydroxide conductivity with higher water swelling of about 16% with weak mechanical properties. These results demonstrated the use of CNC as a component for a solid electrolyte for the fuel cell. The optimisation of the components suggests greater potential for improvement while maintaining the conductivity of existing anion exchange membranes in the solid-state alkaline fuel cell [140].

Supercapacitor

The supercapacitor is a device that can bridge the power/energy gap between traditional dielectric capacitors and batteries/fuel cells with a combination of high power and reasonably high energy density. The electroactive conductive polymers (ECPs) such as polyaniline, polythiophene, polypyrrole etc. are typically used to coat on cellulose substrates for the preparation of supercapacitors [141]. Wang et. al prepared a flexible supercapacitor based on polypyrrole (PPy) coated on bacterial cellulose composite networks by oxidative polymerization of pyrrole with iron (III) chloride on the ultrathin bacterial CNFs (TOBC) in an aqueous medium. The fabricated Py-TOBC supercapacitor cell had a homogenous coating of polypyrrole nanoparticles on the CNF network, the electrode with very high porosity of $101 \text{ m}^2/\text{g}$ resulted in high conductivity around 6.63 S cm^{-1} . The Py-TOBC supercapacitor cell when fabricated with PVDF-EMIMBF₄ (1-Ethyl-3-methylimidazolium tetrafluoroborate) polymer electrolyte to form a

Post-operation cross-sectional SEM images of **c** CNF and **d** CNC nanocellulose fuel cells. Adapted with permission from [139]. Copyright ACS Publications, 2016.

polymer cell it exhibited an impressive specific capacitance value of 153 F/g with a high energy density of 21.22 Wh/kg and current density of 0.2 A/g . The nanofiber-network structure-based substrate of the supercapacitor could provide good bending stability, this contributed to the higher cyclic stability of around 93% even after 100 cycles. This is shown in Fig. 20a [142]. Wu et al. synthesised a high cyclable supercapacitor with a stability of 91% and 87% even after 1000 and 2000 cycles, respectively with an excellent specific capacitance of 322.6 F/g via polymerizing polypyrrole with PVP/CNC in different mass ratios, which was later freeze-dried, powdered and made into pellet under pressure. The demonstrated composite exhibited a maximum conductivity of 36.9 S/cm at 10% PVP/CNC mass ratio and a maximum capacitance of 338.6 F g^{-1} at 2 A g^{-1} . This value was 35% higher than the similar study carried out with the TEMPO modified-CNC system of materials with the same composition while having a fast scan rate of 0.1 V/s [143]. The schematic illustration of CNFs and PVP/CNCs having different morphologies of the product is demonstrated in Fig. 20b.

Solar cell

The main requirements for a typical solar cell substrate include good mechanical strength, optical transparency, maximum processing etc. The inherent excellent properties of cellulose nano paper make it a potential substrate for the solar cell which was

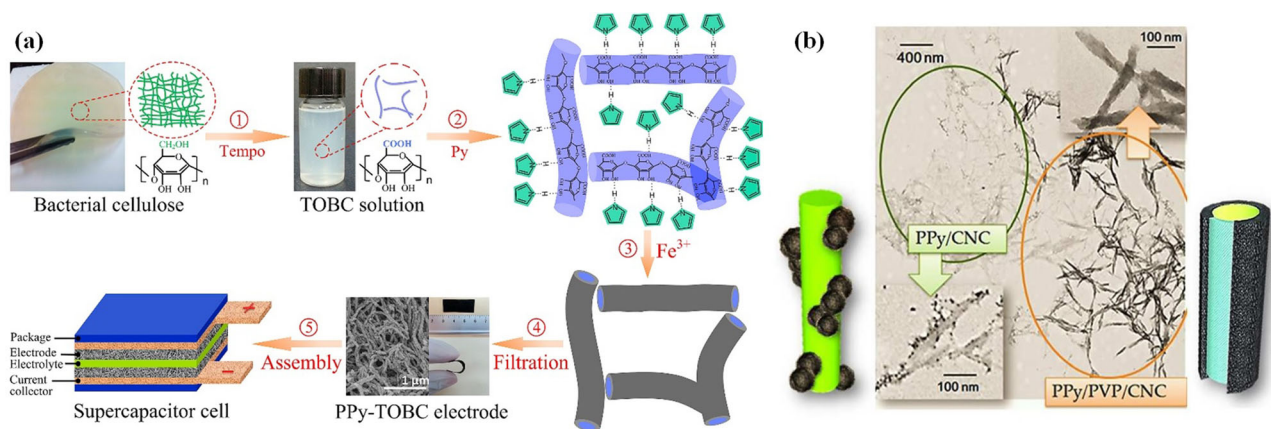


Figure 20 a Schematic illustration of preparation bendable and flexible supercapacitor and layered structure of supercapacitor cell. Adapted with permission from [142]. Copyright Elsevier, 2016. **b** PPy polymerization in the presence of equal amounts of pristine

CNCs and PVP/CNCs with cartoon illustrating the two drastically different morphologies of the end products. Adapted with permission from [143]. Copyright RSC Publishing, 2014.

extensively reported in recent literature. These reports are particularly significant on the modern concept of more sustainable and renewable materials for energy production, conservation and storage[144]. Zhou et al. developed a recyclable organic solar cell based on CNC substrates by using Ag/polymer surface modification as one electrode and $\text{M}_2\text{O}_3/\text{Ag}$ as another electrode without any aqueous medium usage. This approach resulted in the maximum power conversion efficiency of 2.7% with an average fill factor of 0.54. This solar cell composite could be separated into major components by simple low-energy processes, which opens up for a fully recyclable solar cell technology for sustainable and environmentally friendly energy production (Fig. 21) [145]. Fang et al. developed a highly transparent and highly hazing solar cell using TEMPO/NaBr/NaClO oxidation which weakens the hydrogen bonds of original nanocellulose by the introduction of carboxyl groups which resulted in swelling up and thereby resulted in the formation of a highly dense film with excellent optical properties. The fabricated film had very high properties such as optical transmittance and haze with a low fabrication cost. In their study, they demonstrated that the fabricated composites could improve power conversion efficiency from 5.34 to 5.88% by simple lamination of TEMPO/NaBr/NaClO oxidation into the transparent paper [146].

Lithium-ion batteries

Lithium-ion batteries (LIBs) are broadly used as energy storage devices in automobiles and portable electronic devices. Due to the recent advancement in portable devices, the requirement for safer, high energy and power-dense battery with lower manufacturing cost have attracted sustainable biopolymer-based battery research. The high-level application potential of LIBs has been restricted due to their lack of flexibility. To counter this problem, cellulose-based LIBs are being studied. Its excellent chemical and physical properties along with the functionalizable surface makes it a suitable candidate for battery [147]. Hu et al. fabricated a cellulose-based LIB by coating carbon nanotubes (CNTs) and silver nanowires into a commercial Xerox paper. This composite paper exhibited a sheet resistance of around 1Ω per square and good film adhesion. They concluded that the large porous surface of cellulose facilitated accommodating more nanotubes and achieving a better coating of conductive materials[148]. Zhang et al. fabricated a superior thermal-resistant cellulose-based lithium-ion battery separator composite by electrospinning of cellulose acetate followed by dipping in polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HPF). The fabricated membrane had excellent heat tolerance, high ionic conductivity and good electrolyte wettability. The battery using thermal-resistant cellulose as separator exhibited a superior capability and enhanced capacity retention

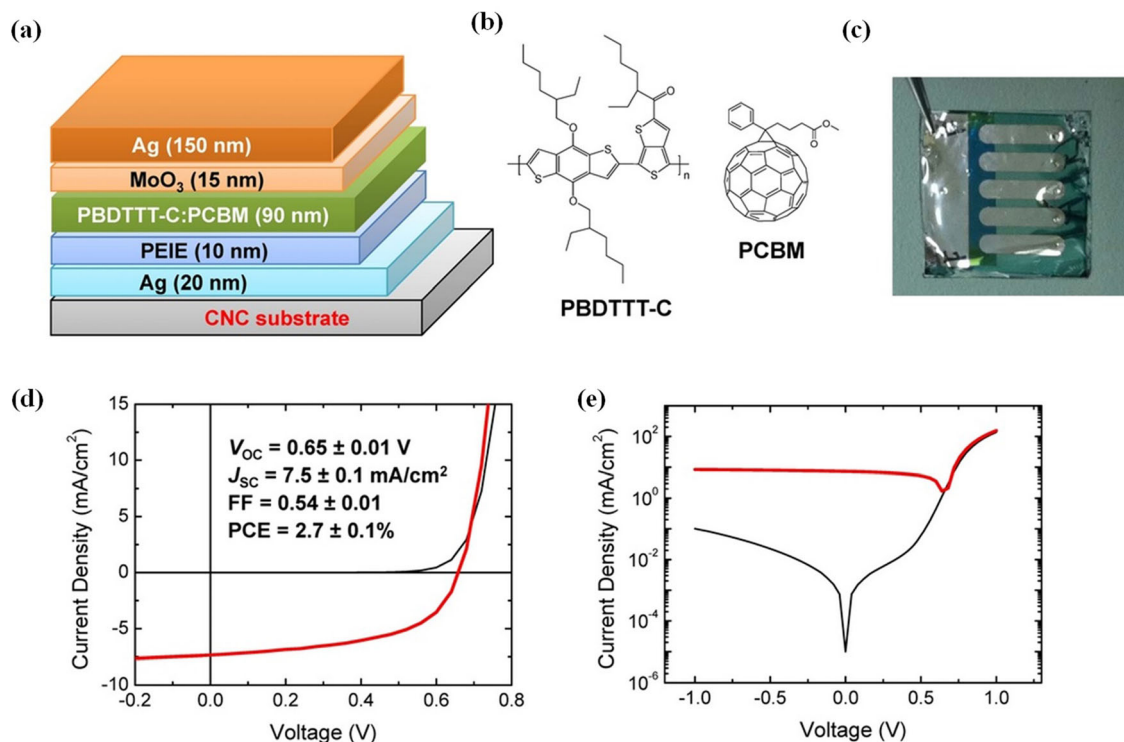


Figure 21 **a** Device structure of solar cells on CNC substrates: CNC/Ag/PEIE/PBDTTT-C: PCBM/MoO₃/Ag. **b** Chemical structure of PBDTTT-C and PCBM. **c** a picture of a fabricated solar cell. **d** J–V characteristics of the solar cell on CNC substrate in the dark (thin black line) and under 95 mW/cm² of AM1.5

illumination (thick red line). **e** the J–V characteristics on a semi-logarithmic scale in the dark (thin black line) and under illumination (thick red line). Adapted with permission from [145]. Copyright Nature, 2013.

compared to those of battery using commercialized polypropylene separator. They showed that the renewable composite is a suitable alternative to the conventional separator for high-power lithium-ion batteries [149]. This composite preparation is demonstrated in Fig. 22.

Biofuel

Recent advances in the thermochemical processing of cellulosic material for the production of biofuel indicates their long term feasibility. The renewable fuel standards and emission policies from various governments are a positive sign for the commercialization and further studies of cellulosic material for biofuel production. These changing policies have been boosted the number of researches carried out in this specific area. Demirbaş et al. synthesised ethanol by hydrolyzing the cellulose portion of the biomass via enzymatic hydrolysis. The process converted cellulose to glucosic sugar which was later fermented to bioethanol using enzymes. The produced

bioethanol could be used as fuel either in neat form or mixed with gasoline [150]. Dutta et al. successfully converted cellulose and lignocellulosic biomass into liquid biofuels such as 5-hydroxymethylfurfural (HMF) and 5-ethoxy methyl-2-furfural (EMF) using metal chloride catalysts. They had obtained this conversion in a special microwave reactor with programmable pressure and temperature controller. Among different metal chloride catalysts employed, Zr(O)Cl₂/CrCl₃ catalyst was claimed to be most effective for producing HMF from both cellulose and sugarcane bagasse in N, N-Dimethylacetamide-Lithium Chloride (DMA–LiCl) solvent with and without 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) additive. The conversion efficiency for HMF was 57% and 42% from cellulose and sugarcane bagasse respectively. Furthermore, Zr(O)Cl₂/CrCl₃ catalyst had 90% selectivity in EMF for converting sugarcane bagasse and HMF substrates into a mixture of EMF and ethyl levulinate (EL) [151]. The chemical reaction involved is illustrated in Fig. 23.

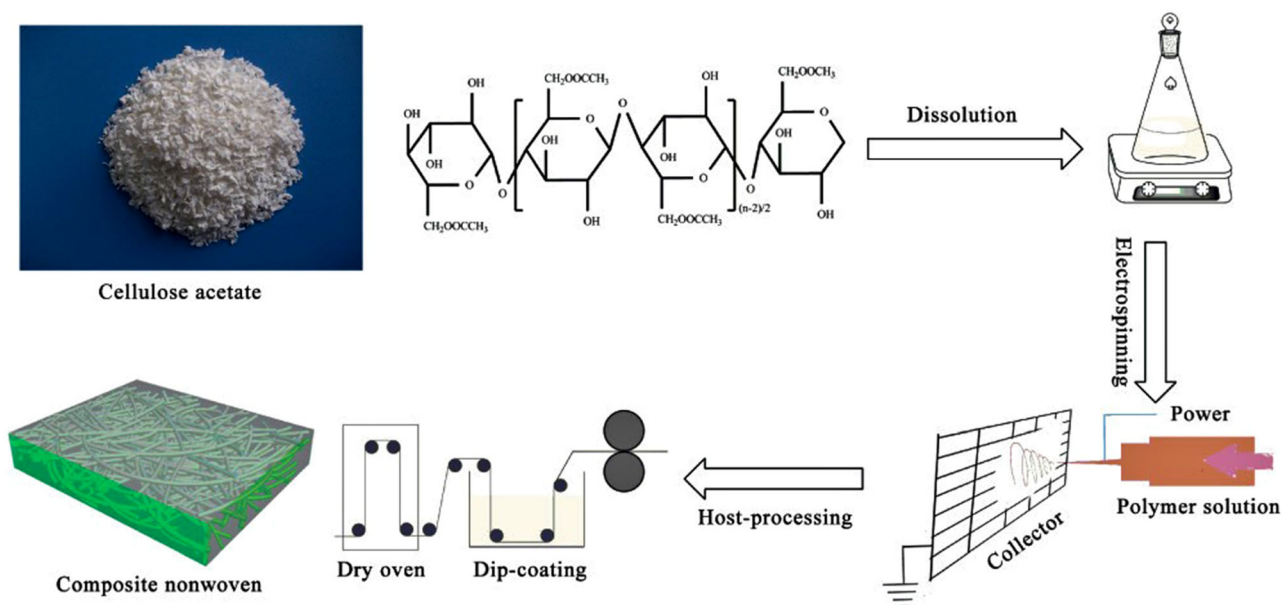


Figure 22 Schematic illustration for the renewable cellulose-based composite separator preparation. Adapted with permission from [149]. Copyright ACS Publications, 2013.

Nanocellulose possesses many unique features and advantages as a biomass-derived biopolymer and exhibits a unique combination of chemical, structural, dielectric, and optical properties that can be rarely found in other polymer systems. This helped in using cellulosic materials for many energy-related applications such as fuel cells, supercapacitors, solar cells, biofuel and lithium-ion batteries. The use of cellulose nanomaterial as a functional component in modern energy could lead to a new paradigm of materials innovation. Therefore, we have highlighted the relevant studies in this paper that have gained a lot of attention that could accelerate the functional cellulose

nanomaterials development. Although most of the above-mentioned applications have just emerged in recent years, these unprecedented application potentials have been seen in various directions. Some of the recent works based on cellulose in energy applications are listed in Table 8 above. It is foreseeable that functional cellulose nanomaterials are going to take on a more and more important role in the family of energy materials. Compared to the conventional application of cellulose in bio-fuel generation, cellulose-based cells could be the next breakthrough since they could be the cheap and flexible eco-friendly power source for the future.

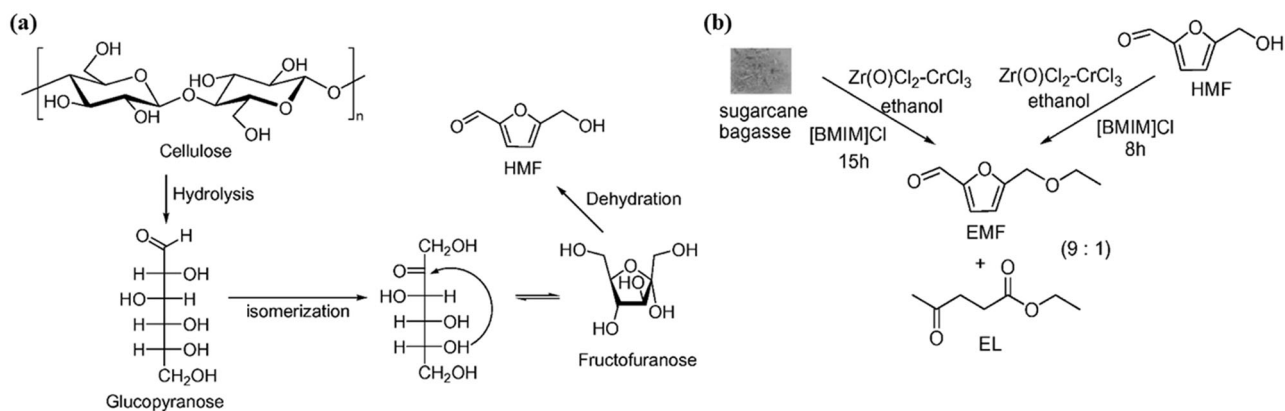


Figure 23 a Chemical pathways for cellulose transformation to HMF b Synthesis of EMF from sugarcane bagasse and HMF with $Zr(O)Cl_2/CrCl_3$ catalyst in ethanol in the presence of [BMIM]Cl. Adapted with permission from [151]. Copyright Elsevier, 2012.

Table 8 Cellulose-based composite and modification in energy application

Composite	Applications	Fabrication technique	Inferences	References
Platinum, graphene with bacterial nanocellulose	Thin-film fuel cell catalyst	Freeze drying, carbonization and layer layer assembly	2000 cycles of minimal decay. The surface area of 174 m ² /g	Kim et al. [152]
Polyaniline, titanium dioxide with bacterial cellulose	Bioanode for microbial fuel cell	In situ by oxidative polymerization	15-fold higher Maximum power density in comparison to neat BC (P_{max} of 38.89 W/m ³)	Truong et al. [153]
Multi-walled carbon nanotubes (CNT), nano-zycosil (NZ) with bacterial cellulose	Membrane electrode assembly in fuel cell	Vacuum filtration and brushing	The maximum power density of 1790 W/m ³	Mashkour et al. [154]
Sulfonated cellulose	Electrolyte membranes for fuel cells	Spray deposition	The maximum power density of 156 W/m ³ . Proton conductivity of 2.1 mS cm ⁻¹	Bayer et al. [155]
Phosphotungstic acid (PTA) with nanocellulose	Electrolyte membranes for methanol fuel cells	Phase inversion method	Proton conductivity at 13.17 mS cm ⁻¹ . Methanol permeability of 6.29 × 10 ⁻⁷ cm ² s ⁻¹	Priyanga et al. [156]
Activated carbon from corncob cellulose	Supercapacitors	Mechanical fragmentation with carbonization	The specific capacitance of 208.5 F g ⁻¹ at 1 A g ⁻¹ . Cycling stability with 97.2% capacitance retention after 20000 cycles under 10 A g ⁻¹	Ai et al. [6]
Zeolite imidazole framework (HZ) with CNF (CNF)	Electrochemical supercapacitors	In situ chemical reaction with pyrolysis	The specific capacitance of 146 F/g at 1 A/g. Cycling stability of 90% after 2000 cycles	Yadav et al. [157]
Ni, Au ions and cellulose	Flexible supercapacitor	Electroless plating	The specific capacitance of 49.1 F/g at 1 A/g. Cycling stability of 91.4% after 2000 cycles	Zhang et al. [158]
Nanocellulose fibre and epoxy substrate	Flexible solar cells	Hybridization	The conductivity of 835 S/cm	Wang et al. [159]
Chlorodeoxyhydroxyethylcellulose (CDHC), hydroxyethylcellulose (HEC) and Methylammonium lead iodide (CH ₃ NH ₃ PbI ₃)	Perovskite solar cells	Chemical deposition and spin casting	The current density of 17.73 mA cm ⁻² . The open-circuit voltage of 0.96 V. Power conversion efficiency of 10.38%	Chu et al. [160]
Commercial cellulose separator (NKK paper), CNF	Lithium-ion battery separator	Vacuum filtration	Ionic conductivity 0.71 (mS cm ⁻¹)	Lv et al. [161]
Tin sulfide (SnS) and bacterial cellulose (CBC)	Anode in lithium-ion battery	Freeze drying and carbonization	The maximum reversible capacity of 872 mA h g ⁻¹ . Retention of 527 mA h g ⁻¹ after 1000 cycles	Yuan et al. [162]
CNF and chitosan	Anode battery material in lithium-ion battery	Electro-spinning	Maximum specific capacity of 399 mAh g ⁻¹ . Retention of 210 mA h g ⁻¹ after 300 cycles	Wang et al. [163]

Table 8 continued

Composite	Applications	Fabrication technique	Inferences	References
Cellulose from Sugarcane	Biofuels production	Hydrothermal pretreatment	The highest hydrogen production (33.77 mmol/L). Methane production (5.53 mol/L). Ethanol production (61.6 mol/L)	Soares et al. [1]
Cellulose from lignocellulose biomass and potato straw	Bioethanol production	Fermentation	Maximum bioethanol yield of 24%	Madadi et al. [164]

Summary

Charge (electron) mass transport capacity is the most important parameter in the case of energy storage. Owing to the excellent modification and composite forming capabilities, nanocellulose can be used as a flexible substrate to form a conductive polymer layer or as a versatile binder [165]. Moreover, the excellent modification and composite forming capabilities enable the energy device to be tuned to have optimal properties. It is also important to note that an unmodified nanocellulose is an excellent insulator. Given the wide range of devices that are currently in practice, pinpointing a particular type of cellulose and modification is rather difficult. In general, CNF is an excellent option for devices that are needed to endure various mechanical deformations. However, CNF has a significantly more amorphous region compared with CNC reflected as reduced crystallinity of CNF. As crystallinity is inversely proportional to the water permeability, the high water permeability of CNF limits its application in devices containing nonaqueous electrolytes [166]. CNC on the other hand does not form for good films but the water penetration is lower. This favours CNC in battery devices and supercapacitors which have nonaqueous electrolytes. In the case of modification, the specific type of modification is rather much more difficult to generalize. When it comes to energy devices, the use of nanocellulose as the matrix of a composite is preferred over a modification. Since nanocellulose based composite is cheaper, efficient and overall better control over the output (the addition of material have a more linear correlation to the output in comparison with modification) [167, 168]. However, methyl modification is seen to be used in

devices to use nanocellulose to use as a binder material. This modification also enables the polymer matrix to combine with the other cross-linking agents. Several studies have identified that strong interactions through the chemical bonding of the binder to the active material would influence the stability of electrodes. Also, methyl modification is a well-established modification technique that is also relatively cheaper and easier in comparison [169, 170].

The selection of nanocellulose is much simpler for environmental applications compared with energy applications. The main objective of nanocellulose in the environmental application is to form the matrix where the active materials are deposited. As cellulose nanofibrils have excellent film-forming capacity owing to the long fibrillar nature, it is preferred over CNC and BC. While BC can perform the same function as CNF, the current state limit the application of BC owing to its higher cost. It is important to keep the price of nanocellulose as low as possible in the case of environmental applications [171, 172]. In general, the film-forming capacity of CNF is much more suited to form a composite via techniques like freeze-drying, vacuum filtration etc. whereas the CNC is more suited for electrospinning techniques owing to the shorter length. In terms of modification of nanocellulose, carboxymethylation is the most explored option since it enhances the electronegativity of nanocellulose. As most of the heavy metals, dyes, organic materials are either positively charged or have a positively charged part, this enhanced electronegativity increases the ability to remove the adsorb these pollutants more efficiently [173].

Conclusion and future developments

In this review, we discuss the most recent scientific developments along with the contemporary application of nanocellulose in energy and environmental areas. As addressed in the introduction part, nanocellulose possesses certain advantages such as abundant availability, sustainability, renewability, functional ability, biodegradability and eco-friendliness altogether have attracted many researchers towards nanocellulose. Moreover, the tunability of nanocellulose has been a significant driving factor for the exponential growth of research on nanocellulose among polysaccharide families. With the advancement in nanomaterials, nanocellulose can be tailor-made for various specific applications in the energy and environmental sectors. This mainly includes certain specific areas such as air purification, heavy metal and dye adsorption, biosensor, electromagnetic shielding, fuel cells, supercapacitors, lithium-ion battery, biofuels and solar cell substrates. Most of the energy and environmental applications of nanocellulose-based composites have been discussed in this review. The above-mentioned applications are scalable at the industrial level which gives a promising green and sustainable future. These emerging applications is a standing testimony to the multifaceted roles played by nanocellulose composites in various applications. Although multiple areas offer promising achievements at a laboratory or pilot scale, it is necessary to point out that there are several challenges still to be addressed to successfully fabricate any potential and useful nanocellulose-based composites viable for commercial application. A major obstacle in this regard that needs to be considered for the successful commercialization of nanocellulose-based products is its extraction cost in comparison with the conventional synthetic counterparts. Against all the current challenges, due to the abundant availability of nanocellulose across the globe, bio-renewability and the fast-growing technologies on its production, nanocellulose has the potential to become the main alternative to the current synthetic alternative solutions. The aforementioned proposal can be validated by the numerous researches published on nanocellulose in the last years. In this context, it is foreseeable that in nearby future, nanocellulose will be extensively found in the food, biotechnology, medical and electronic industries.

While reviewing all the articles based on nanocellulose, it was evident that even though nanocellulose is an attractive material, the inherent characteristics are insufficient for the intended applications. Also, the nano-cellulosic material characteristics are non-uniform since influenced by different factors such as source, methods of isolation, type of nanocellulose etc. This non-uniformity could cause a greater hindrance in the future as the dependency on this nanocellulosic material is expanding rapidly. The non-uniformity in combination with the limited inherent characteristics could create friction between expectations and reality. Moreover, one of the main approaches exploited to address the aforementioned problems are chemical modifications such as carboxymethylation, amidation, esterification, silylation, sulfonation etc. Even though at first glance, one might believe that these modifications have addressed the disparity in the requirements from nanocellulose, the greater compromise of nanocellulose is often left unaddressed, which is the price. While cellulose is an abundant natural polysaccharide in the sphere of potential sustainable materials, when considering the price, it's one among the expensive materials. To bring into perspective, most chemical prices are calculated in Tons, yet unmodified nanocellulose price starts from a dollar per gram. The chemically modified nanocellulose is much more expensive depending upon the functional group and characteristics. In some areas such as energy storage where the dissolved nanocellulose is employed as an electrolyte, modification is inevitable. However, opting for modification of almost all the requirements could bring financial constraints which limit the main intention behind the selection of nanocellulose. As the human race moves towards a greener, sustainable, carbon-neutral future, nanocellulose and its derivatives have a great role in it.

The literature shows that nanocellulose based heterogeneous composites could be the direction that needs to be further exploited. This approach has certain advantages like reducing the overall cost, the introduction of multi-dimensional properties, simple and faster fabrication process, a green approach, scalability etc. There as many examples of these materials and most of them are mentioned passively in this review. However, some of the most common material which can be employed includes carbon derived materials, TiO_2 , monoliths, phosphates, bio-char etc. While there are many such materials

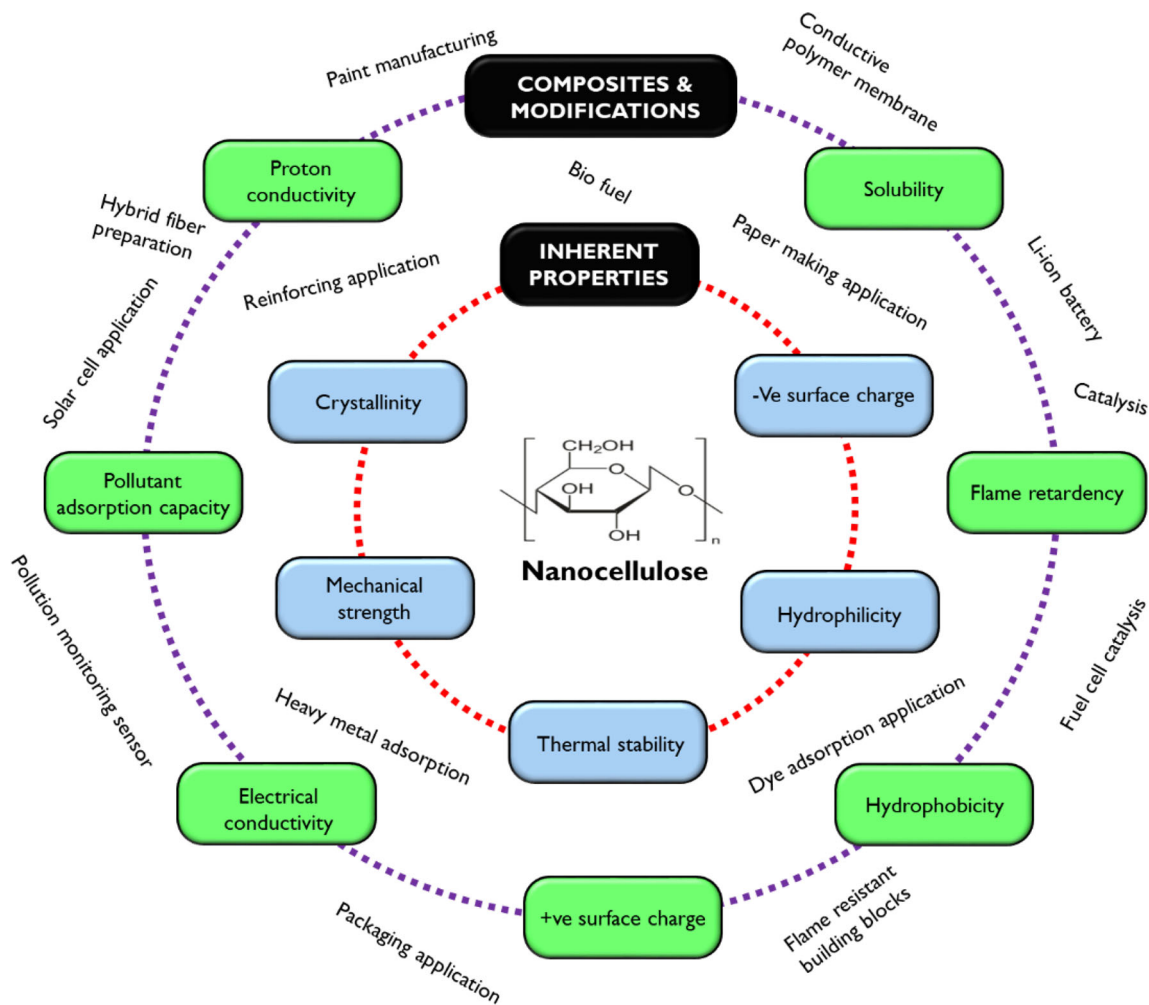


Figure 24 Schematic Illustration for the comparison of nanocellulose application with inherent properties and with modifications.

available, calcium phosphate and nanocellulose composite could be an interesting futuristic materials. These two materials are available, calcium phosphate is cheap and exhibits multidimensional properties such as flame retardancy, heavy metal adsorption, dye removal, pollutant gas adsorption, reduction of cost, thermal stability, biomimicry etc. Moreover, such composite fabricated for a specific application can be employed for a wider range of applications. This is one of the major advantages that we obtain while fabricating a heterogeneous nanocellulose composite in comparison with nanocellulose chemical modification. To further elaborate our view necessity for nanocellulose modification we have illustrated it in Fig. 24. The figure demonstrates the expansion of the application potential of nanocellulose with the modification and incorporation of heterogeneous materials. In the inner circle (Red dotted lines) the inherent characteristics and adjacent

to which, direct application exploiting the inherent characteristics are provided. In the exterior circle (Violet dotted line) the different characteristics introduced by certain modifications/incorporation of heterogeneous materials are provided. The exponential expansion in nanocellulose based material is evident after the modifications. The proper usage of inherent properties in combination with acquired properties by modification/incorporation of heterogeneous materials has greatly enhanced the application potential of nanocellulose and nanocellulose-based composites.

To conclude, nanocellulose is an interesting material that would certainly pave the way for a green sustainable future. While the exploitation of this material was carried out with great success so far, certain grey areas in the nanocellulose overall perspectives require to be addressed. For instance, as many of the nanocellulose extraction techniques have

been widely exploited for mass production, most of them are not a green approach. An energy conservative nanocellulose extraction that is green, sustainable and scalable is yet to be fulfilled. In our view, the bacterial nanocellulose based approach can address all these issues with the added advantage of producing a very high purity of nanocellulose. Another grey area is in the commercial application, while the nanocellulose is considered and dealt with as a non-toxic material, the “cheaper” nanocellulose available in the commercial market is unusable for biomedical applications. This is another reason that supports bacteria-based nanocellulose production to be a likely future route. Another main area that needed to be addressed in this regard is an application that is not yet exploited enough with nanocellulose. To name of few, nanocellulose based composites are yet to be exploited deeply for heat storage applications, rare earth metal adsorption, high impact adsorption materials, engineering material development, piezoelectric material related application, efficient fuel generation etc. Despite the above-mentioned challenges, we expect that nanocellulose-based materials will certainly improve people’s quality of life in the future through the development of the next generation of materials.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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