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Nanocellulose a Versatile Green Platform: From Biosources to Materials and their Applications

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Abstract

With increasing environmental and ecological concerns due to the use of petroleum based chemicals and products, the synthesis of fine chemicals and functional materials from natural resources is of great public value. Nanocellulose may prove to be one of the most promising green materials of modern times due to its intrinsic properties, renewability and abundance. In this review, we present nanocellulose-based materials from sourcing, synthesis, and surface modification of nanocellulose, to materials formation and applications. Nanocellulose can be sourced from biomass, plants or bacteria, relying on fairly simple, scalable and efficient isolation techniques. Mechanical, chemical, enzymatic treatments, or a combination of these, can be used to extract nanocellulose from natural sources. The properties of nanocellulose are dependent on the source, the isolation technique and potential subsequent surface transformations. Nanocellulose surface modification techniques are typically used to introduce either charged or hydrophobic moieties, and include: amidation, esterification, etherification, silylation, polymerization, urethanization, sulfonation and phosphorylation. Nanocellulose has excellent strength, Young's modulus, biocompatibility, and tunable self-assembly, thixotropic and photonic properties, which are essential for the applications of this material. Nanocellulose participates in the fabrication of a large range of nanomaterials and nanocomposites, including those based on polymers, metals, metal oxides and carbon. In particular, nanocellulose complements organic-based materials, where it imparts its mechanical properties to the composite. Nanocellulose is a promising material whenever material strength, flexibility and/or specific nanostructuring are required. Applications include functional paper, optoelectronics and antibacterial coatings, packaging, mechanically reinforced polymer composites, tissue scaffolds, drug delivery, biosensors, energy storage, catalysis, environmental remediation and

electrochemical controlled separation. Phosphorylated nanocellulose is a particularly interesting material, spanning a surprising set of applications in various dimensions including bone scaffolds, adsorbents, flame retardants and as a support for the heterogenization of homogeneous catalysts.

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1. Introduction

Cellulose represents the most ubiquitous structural amphiphilic renewable polymer resource in the biosphere, with an estimated annual production of 7.5×10^{10} tons^{1,2}. This nearly unlimited supply of sustainable polysaccharide possesses remarkable physical and chemical properties allowing its use in a wide range of materials and products including fine chemicals³. The extensive use of cellulosic fibers as lumber, textile or cordage dates back to many thousands of years. Industrially, cellulose has been used as a raw material in products including paper,

cellophane films, explosives, textiles, and dietary fibers⁴. Lignocellulosic matter is the basic building block of plant matter and trees, which has been traditionally used as combustible and load-bearing materials in construction. In addition to these humble yet indispensable applications, cellulose is being used for much more sophisticated applications in modern times (see Table 1). These applications are based on the fact that when cellulose fibers are subjected to mechanical shear or controlled acid hydrolysis, elongated fibrillar rodlike crystalline particles are produced, featuring nanosized width and lengths ranging from 50 nm to μm ⁵. Nanocellulose, which is either isolated from plant matter or biochemically produced in a lab, holds many of the desirable properties for which cellulose is known, including low density, non-toxicity and high biodegradability. But it also holds unique properties, such as high mechanical strength, reinforcing capabilities, and tunable self assembly in aqueous media, arising from its unique shape, size, surface chemistry and high crystallinity⁵. Nanotechnology involving these cellulosic substrates has generated tremendous attention during the last few decades. Chemical, biochemical and mechanical methods allow to access and modify nanocellulose with enhanced properties such as flame retardancy, transparency and high flexibility, thus greatly expanding traditional applications of wood.

The 21st century marks an explosion in the demand for materials, energy, food and water, driven by a growing world population and rapidly developing technologies. Society could aim to rely more heavily on renewable resources, such as biomass, to produce the desired materials. Sustainable development requires products to be made from renewable sources that are environmentally friendly, non-petroleum based, present low health and safety risks and that are economically affordable. Nanocellulose has a Young's modulus in the range 20–50 GPa and a surface area of several hundreds of m^2/g ⁶, which means, many new promising properties and

applications can result. Scientists have responded with a concerted international effort to produce innovative materials for novel and emerging applications from nanocellulose, which originates from renewable and abundant biomass. Biomass can be considered as a valuable commodity, a source for biofuels and chemicals, providing an excellent alternative to petroleum. Nanocellulose is used to produce a variety of high-value products with low environmental and societal impact. Nanocellulose can now be produced industrially at the ton/day scale⁷.

Table 1: Identified and well-established applications of nanocellulose, categorized into high volume, low volume and novel and other emerging applications.

High volume applications	Low volume applications	Novel and emerging applications
Cement ^{1a}	Wallboard facing ^{1b}	Sensors-medical, environmental, industrial
Paper applications ^{1c}	Insulation ⁸	Diagnostics ^{1d}
Automotive body ^{1e}	Aerospace structure ^{1f}	Reinforcement fibre-construction ^{1g}
Automotive interior ^{1h}	Aerospace interiors ¹ⁱ	Water filtration
Packaging coatings ^{1j}	Aerogels for the oil and gas industry	Air filtration ^{1k}
Paper coatings	Paint-architecture ¹ⁿ	Viscosity modifiers ^{1l}
Low calorie food ^{1m}	Paint-special purpose	Purification ^{1o}
Paper filler ^{1p}	Paint-OEM application	Cosmetics ^{1q}
Packaging filler ^{1r}	Cellulosic ethanol-	Excipients

	transportation fuel	
Replacement - plastic packaging ^{1s}	Membranes ^{1v}	Organic LED ^{1t}
Plastic film replacements ^{1u}	Filtering	Flexible electronics
Hygiene and absorbent products		Photonics ^{1x}
Textiles for clothing ^{1w}		Recyclable electronics
		3D printing
		Novel materials as catalysts ^{1y}
		Photocatalytically active materials ^{1z}
		Self-cleaning materials ^{1aa}
		Porous materials ^{1ab}
		Antibacterial materials ^{1ac}

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This comprehensive review presents nanocellulose-based research over the last 100 years, with an emphasis on recent research as another comprehensive review was previously published in 2011⁹. Many other specialized reviews and highlights have been published on this topic, showcasing the breadth of the field⁵. The scope of this current contribution covers nanocellulose sourcing and isolation methods, surface modification, incorporation into composites and hybrid

materials and the applications of nanocellulosic materials. The term nanocellulose encompasses a number of cellulose-based materials, where chemical and physical properties vary typically as a function of their source and extraction method: cellulose nanocrystals (CNCs), nanofibrillated cellulose (NFC), and rigid bacterial nanocellulose (BNC). The surface chemistry is important to the processability and the functionality of the material to be produced, and thus we focus herein on the large variety of current surface modification techniques. We find phosphorylation to be a particularly exciting domain of surface modification, which is poorly explored to date. Thus, we give special attention to the state of the art of nanocellulose phosphorylation techniques, current applications and future prospects. Nanocellulosic materials find application in many interdisciplinary areas, as listed in Table 1. When interwoven, they can form highly porous and mechanically strong materials such as nanopapers, nanocellulose films, aerogels and hydrogels, extending their application to the paper industry, biomedicine, environmental remediation, optoelectronics and engineering applications. Nanocellulosic materials form strong networks with high tensile stiffness and strength, and thus are used to reinforce bio/nanocomposites¹⁰⁻¹². The development and application of polymer composite materials reinforced by rigid nanocellulosic particles from renewable sources have attracted both scientific and industrial attention. With growing public consciousness towards environmentally friendly and naturally sourced products, nanocellulose is destined for an important role in commercial society.

2. Cellulose structuration and subunit composition

One thousand to one: that is the mass ratio of plants to animals, with cellulose being one of the major constituents of plant mass. Cellulose is one of the basic structural units of algae, tunicates, and certain bacteria¹³. Cellulose is renewable, biodegradable, non-toxic, and is the

most prominent nanostructured component occurring in wood, cotton, hemp, flax and other plant-based materials.

The hierarchical structure of a tree may be described as follows, from the macro- to the nanoscale (Fig. 1): a whole tree can be up to 100 meters, the cross-section contains structures on the centimeter scale, growth rings measure in millimeters, the cellular anatomy is tens of micrometers, the configuration of hemicelluloses and lignin in the cellulose microfibrils measure tens of nanometers, and the molecular structure of cellulose is nanometric¹⁴.

Cellulose fibrils are structural entities formed through a cellular manufacturing process, cellulose biogenesis, stabilized by hydrogen bonds and van der Waal forces¹⁵. The fibrils contain crystalline and amorphous regions, the latter being preferably degraded to release nanoscaled components from the cellulose source by mechanical, chemical or a combination of mechanical, chemical and enzymatic processes. The repeat unit, cellobiose, is a dimer of D-glucose. Linear β -D-glucopyranose units are linked together by β -1,4-linkages. Individual polymer chains assemble into fibers through intermolecular hydrogen bonds and hydrophobic interactions. The terminal groups of each cellulose chain provide directional asymmetry. The reducing end of the cellulose chain contains a hemiacetal group. The non-reducing end bares a pendant hydroxyl group⁴. Fig. 1 shows the structure and molecular asymmetry of cellulose.

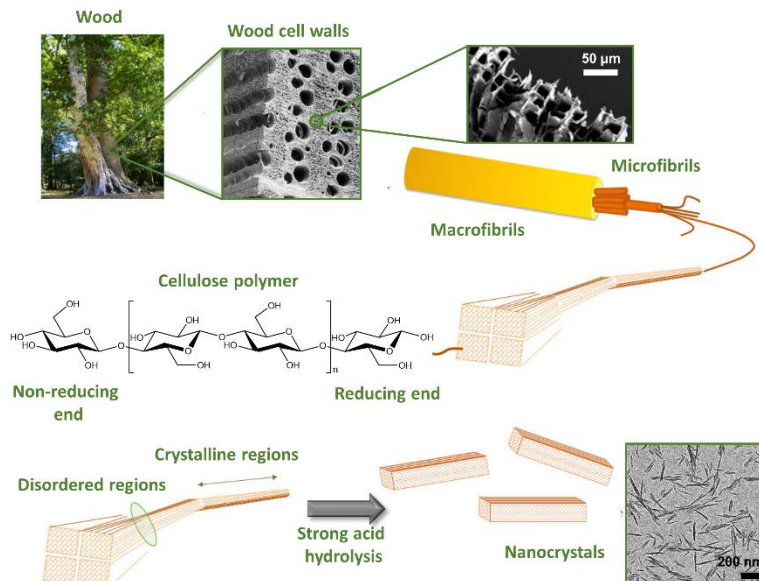


Figure 1: (Top) Cellulose within a living plant or tree is hierarchically structured from the meter to the nanometer scale. Polymeric structure of one strand of cellulose showing the reducing and non-reducing ends. (Bottom) Schematic of the reaction of cellulose with strong acid to afford nanocellulose. Reproduced with permission from ref. 16, copyright Creative Commons (<https://creativecommons.org/licenses/by/3.0/>). (Top right) SEM image of cellulose microfibrils reproduced with permission from ref. 17 (Copyright 2007, Elsevier).

One of the most distinguishing and useful characteristics of cellulose is the high degree of hydroxylation along the polymer chain; each non-terminal monomer contains three hydroxyl groups. Hydrogen bonding arises between OH groups conveniently positioned within the same cellulose molecule (intramolecular) and between neighboring cellulose chains (intermolecular). Intermolecular hydrogen bonding creates fibrillar structures and semicrystalline packing, which governs the physical properties of cellulose: namely its high strength and flexibility. Moreover, primary hydroxyl groups ($-\text{CH}_2\text{OH}$) are readily chemically modified, for example through phosphorylation, providing large scope for these materials.

There are three main classes of nanocellulose, cellulose nanocrystals (CNCs), nanofibrillated cellulose (NFC) and bacterial nanocellulose (BNC), classified according to their morphology (Fig. 2) and source. CNCs and NFCs are obtained via a top-down approach consisting of the disintegration of plant matter via chemical or mechanical treatment¹⁸. Cellulose is biosynthesized in plants and forms partially crystalline fibers. Mechanical shearing or acid hydrolysis will first weaken and destroy the least crystalline regions to yield the expected nanocellulose. The amorphous sections have different physical properties to crystalline cellulose, forming cellulose nanoparticles by breaking the fibrils at amorphous points. The cellulose fibers can be deconstructed using either mechanical shearing or controlled acid hydrolysis, yielding different structures according to the approach used⁴. Acid hydrolysis results in nanometer-long and highly crystalline rod-like fragments, referred to as CNCs. Mechanical shearing techniques disintegrate cellulose fibers into their sub-structural nanoscale units, resulting in NFCs, which are typically longer, being micrometric in length⁵. BNC is produced via a bottom-up approach using cultures of bacteria to synthesize the material.

Other denominations of nanocellulosic materials can be found in the literature including: cellulose nanofibrils, nanofibrillated cellulose, microfibrillated cellulose, cellulose nanofibers, cellulose whiskers, cellulose nanowhiskers, cellulose nanocrystals, and nanocrystalline cellulose. Fibrils typically describe higher aspect ratio materials than whiskers or crystals, although there is no strict definition for each of these. No single term is unanimously applied to describe ‘nanoscale cellulose’. We will now explain how the three classes of nanocellulose are produced and the unique properties of each.

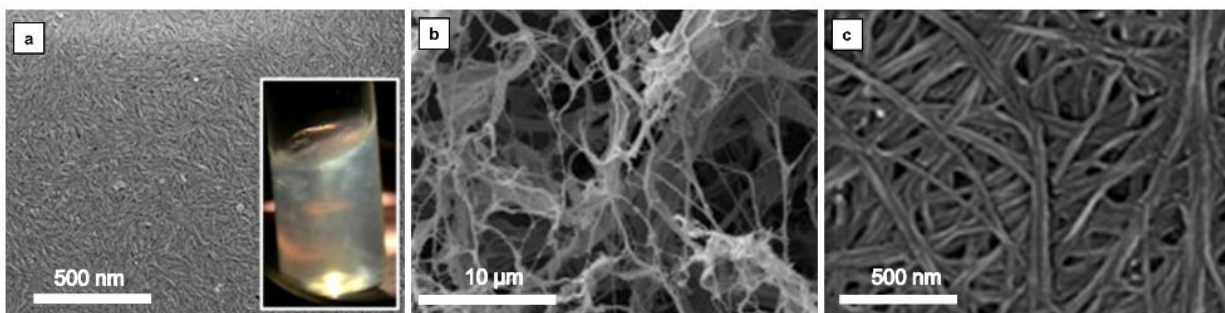


Figure 2: Images of (a) CNC; (b) CNF; and (c) BNC, adapted with permission from refs. 19 (Copyright 2016, Elsevier), 20 (Copyright 2016, Elsevier) and 21 (Copyright 2012, American Chemical Society).

2.1 Cellulose Nanocrystals (CNCs)

CNCs, also known as nanowhiskers, exhibit elongated crystalline rod-like shapes, and have high rigidity compared to NFC because a higher proportion of the amorphous regions are removed²². The degree of crystallinity in CNCs ranges from 54 to 88%²³. Although processes involving enzymatic hydrolysis exist to produce CNCs²³, strong acid hydrolysis, particularly sulfuric acid hydrolysis is the most common preparation technique⁴. A typical procedure for the production of CNC begins with alkali and bleaching pretreatments followed by acid hydrolysis, washing, centrifugation, dialysis and ultrasonication to form a suspension which may be further subjected to lyophilization (freeze drying or spray drying) as required²⁴. Both the reaction conditions and the cellulose source impact several of the obtained properties of CNCs, for instance the degree of crystallinity, the aspect ratio and dimensional dispersity, and the morphology²⁴. CNCs are rods or whiskers, typically ranging from 3-50 nm in width and 50–500 nm in length. CNCs combine high axial stiffness (105-168 GPa)²⁵, high Young's Modulus (20-50 GPa)⁶, high tensile strength (~9 GPa)²⁶, low coefficient of thermal expansion (~0.1 ppm/K)²⁷, high thermal stability (~260 °C)²⁸, high aspect ratio (~10-70)²⁹, low density (1.5–1.6 g/cm³)³⁰, lyotropic liquid crystalline behavior and shear thinning rheology^{31,32}. Fig. 3 shows a diagram of the remarkable properties exhibited by CNC. Recently, Malucelli and co-workers presented a comprehensive review on the sourcing, preparation, properties and future perspectives of cellulose nanocrystals from agro-industrial residues³³.

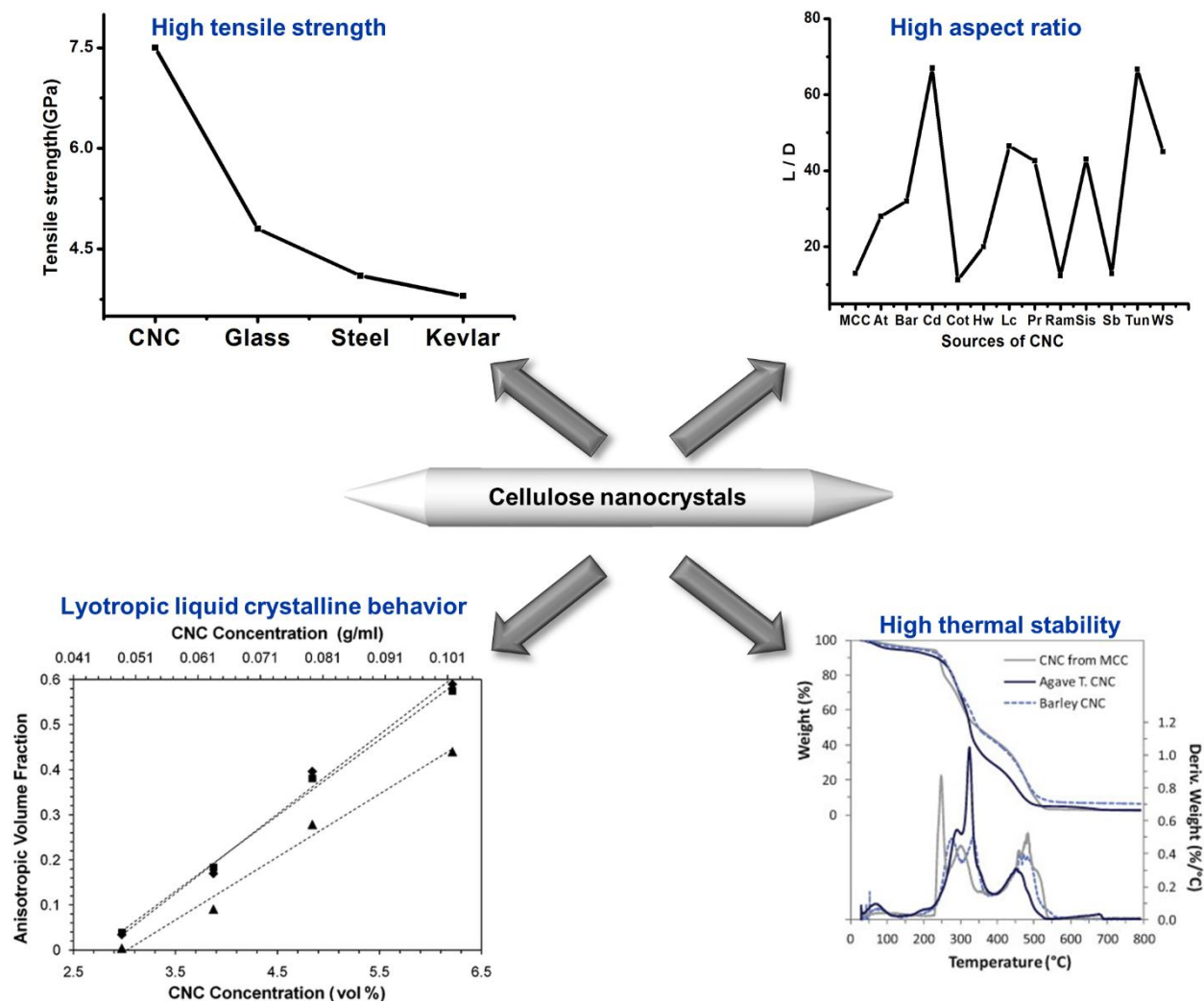


Figure 3: CNCs combine high tensile strength, high aspect ratio, lyotropic liquid crystalline (LCP) behavior (Adapted with permission from ref. 32, Copyright 2011 American Chemical Society) and high thermal stability (Adapted with permission from ref. 34, Copyright 2014, SpringerLink and 35, Copyright 2014, Elsevier).

Marchessault and coworkers discovered in the 1950s that CNC aqueous solutions possess liquid crystal properties³⁶, with impressive photonics properties³⁷. Above a critical concentration (~4.5 wt%), they will form chiral nematic structures^{24,38}, which can be revealed by polarized optical microscopy³⁸. Ureña-Benavides, *et al.* investigated the phase behavior of lyotropic CNC

suspensions of sulfonated CNCs produced from cotton³². Between 3.07 and 10.4 vol%, a phase separation occurred in the suspension, yielding liquid crystalline and isotropic domains. By 12.1 vol%, the isotropic phase disappeared, giving a fingerprint texture which is characteristic of a cholesteric liquid crystal. Upon moving to even higher concentrations, the fingerprint texture of the liquid crystal phase disappeared as well, and the suspension behaved as a rheological gel. Fig. 4 depicts the phase separation behavior using cross-polarized images of the CNC suspensions at different concentrations.

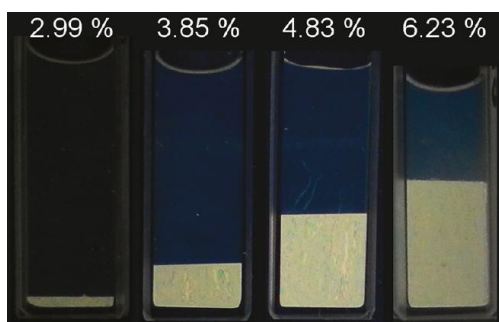


Figure 4: Cross-polarized images of CNC suspensions show the phase separation present between 2.99 and 6.23 vol%. The lower LC phase is birefringent while the dark upper region is the isotropic phase. (Adapted with permission from ref. 32, Copyright 2011, American Chemical Society)

Interfacing CNCs with other natural or synthetic polymers yields functional composites. A detailed discussion of various methods to prepare CNC composites is found in reviews by R. J. Moon and A. Dufresne³⁹. In addition, surface modification techniques are found to alter the self-assembly behavior of CNCs in suspensions and control the interfacial properties within composites. CNCs bestow composite materials with enhanced mechanical properties, low

density and high surface area. The main differences between CNF, CNC and BNC are listed in Table 2.

Table 2: Essential differences between nanocellulose fibers, cellulose nanocrystals and bacterial nanocellulose, including the extraction/production approach, sustainability of the process, morphological and crystalline nature, dimensions and applications.

Properties/ Applications	Type of nanocellulose		
	CNF	CNC	BNC
Nature	Nanofibrillated Cellulose	Elongated rod-like cellulose crystals, cellulose (nano) whiskers or spherical	Microbial cellulose fibers
Source	Sugar beet ^{2a-2c} , potato tuber cell ^{2d,2e} , lemon and maize ^{2f} , banana ^{2g} , bagasse, wheat straw ^{2h} , jute ²ⁱ , hemp ^{2j} , kenaf fibers ^{2k} , aquatic weeds ^{2l} , palm oil ^{2m} , pineapple leaf ²ⁿ , mulberry ^{2o,2p} , cassava ^{2q} , alpha fiber, rice husk ^{2r} , lotus leaf stalk ^{2s} and cotton ^{2t} , coir ^{2u,2v} , soy hull ^{Erreur ! Signet non}	Microcrystalline cellulose, bacterial cellulose, cotton, wood, sisal, pineapple leaves, coconut husk fibres, bananas, wheat straw, pea hull fibre, branch-barks of mulberry, bagasse, bamboo and ramie.	Synthesized in microbial culture using bacteria (such as <i>Acetobacter</i> <i>Xylinum</i> ^{2x,2y,2z,2aa} <i>Agrobacterium</i> , <i>Pseudomonas</i> , <i>Rhizobium</i> , <i>Sarcin</i>)

	defini.,2w		
Mode of preparation	Converting large lignocellulosic units (cm) to smaller units (nm).	Converting large lignocellulosic units (cm) to smaller units (nm).	Construction from tiny units (Å) to small units (nm)
Methodology	Mechanically induced destructuring strategy- High-pressure homogenization and/or grinding before and/or after chemical or enzymatic treatment. Multiple mechanical shearing actions can effectively delaminate individual microfibrils from lignocellulosic fibers.	Chemically induced destructuring strategy, such as acid hydrolysis, most significantly sulfuric acid	The microbial process requires no intensive chemical/physical steps to remove unwanted impurities or contaminants such as lignin, pectin and hemicellulose
Energy and chemical requirements and sustainability	High energy process with corrosive chemical reagents. Overall the method is not	High energy process with corrosive chemical reagents. Overall the method is not	Noncorrosive chemicals and hence a completely green approach

	currently very sustainable	currently very sustainable	
Crystalline nature	CNF consists of both individual and aggregated nanofibrils made of alternating crystalline and amorphous cellulose domains	Through the removal of amorphous regions a highly-crystalline structure is produced	With the combination of glucose chains, microfibrils are formed and aggregated as ribbons
Dimensions and aspect ratio	Fiber width varies from 10 to 100 nm depending on the source of the cellulose, defibrillation process and pre-treatment. It is not so easy to determine the length of CNF (commonly regarded as higher than 1-10 μm). Very high aspect ratio.	Diameter of 5–30 nm, and lengths of 100–500 nm. Low aspect ratio.	Diameter of 20–100 nm with different types of nanofiber networks. Low aspect ratio.
Cost	Low cost due to the use of renewable biomass as the source and inexpensive chemicals.	Low cost due to the use of renewable biomass as the source and inexpensive chemicals.	High cost to support the growth of bacteria in a suitable culture medium.

Yield	Low yield	Low yield	Very low yield
Advantages	Lightweight, biodegradable, and less abrasive to processing equipment, nanoscale dimensions, high surface area, unique morphology, low density and mechanical strength, easy to chemically modify, renewable, and biodegradable. ^{2ab}	Comparative low water holding capacity, crystallinity, and degree of polymerization, high axial stiffness, tensile strength, low coefficient of thermal expansion, lyotropic liquid crystalline behavior at high concentrations, and shear-thinning rheology, renewable, and biodegradable. ^{2ab,2ac}	Excellent biological affinity, biocompatibility and biodegradability, high porosity, high flexibility, high water holding capacity, high purity, high degree of polymerization and crystallinity, renewable, and biodegradable. ^{2aa}
Applications	Photonic crystals, barrier films, shape-memory polymers, light healing materials, composite reinforcing, drug- delivery, mechanically adaptive	Transparent barrier films, photonic, crystals, shape-memory polymers, drug carriers, composite materials, optical and electronic devices, energy	BNC has earned particular interest due to its wide range of applications in biomedical field including antimicrobial products, skin therapy, artificial blood

	<p>nanocomposites, membranes for water-treatment, biomedical devices, and traditional high volume applications including paper, packaging, paints, composites and food, stimuli-responsive nanodevices, odor elimination materials^{2ad}, energy storage, flexible electronics and light-emitting diodes and displays^{2ae}, construction, separations, cosmetics, and food applications^{2af}.</p>	<p>harvesting materials^{2ae} supercapacitor electrodes, actuation and sensing, selective filtration, packaging, and structural composite applications, rheology modifiers, industrial applications, such as paints, coatings, adhesives, lacquers, food, cosmetics, drugs, and cements, stimuli-responsive nanodevices, construction, separation, and food applications^{2af}.</p>	<p>vessels, tablet modification, potential scaffold for tissue engineering, cartilage, bone and menisci materials, support material for cornea wound care products, drug, hormone and protein delivery, contact lenses, vascular grafts, artificial organs (esophagus, urethra)^{2ag}, food industry, paper industry, flexible power source, flexible supercapacitors, photocatalysis, (bio)sensors^{2ah} and optical devices.</p>
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2.2 Nanofibrillated cellulose (NFC)

NFC is a bundle of stretched cellulose nanofibers⁴⁰. The cellulose chains are entangled and flexible with a large surface area. Nanofibrillar cellulose⁴¹, cellulose nanofibers (CNF)⁴², and cellulose nanofibrils⁴³ are some of the synonyms for NFC. Unlike CNCs, NFCs consist of significant amorphous regions, with soft, long chains of widths ranging from ten to a few hundred nanometers and lengths on the micron scale⁴⁴. Mechanical, chemical and biological approaches have been used to isolate NFCs from various sources, where mechanical treatments are most commonly employed. High pressure homogenization, cryocrushing and grinding are some of the mechanical treatments used to extract cellulose nanofibers⁴⁵⁻⁴⁷. Chemical treatment includes alkali treatments while biological approaches make use of enzymatic treatments^{48,49}. A combination of these techniques is adopted by many researchers to get the desired product. Analogous to CNCs, the fundamental properties of NFCs also vary in accordance with the raw material source and the specific extraction process employed. With all of these differing treatment methods the resulting NFC can vary dramatically in shape, degree of fibrillation, morphology and properties. Desmaisons, *et al.* have developed a quality index, based on eight criteria to benchmark the variety of reported NFCs⁵⁰.

2.3 Bacterial nanocellulose (BNC)

Bacterial nanocellulose is synthesized and secreted by the *Gluconoacetobacter xylinus* family⁵. Certain other bacterial species, such as *Agrobacterium*, *Pseudomonas*, *Rhizobium* and *Sarcin* also produce BNC⁵¹. BNC is produced by cultivating bacteria for a few days in an aqueous culture media containing glucose, phosphate, carbon and nitrogen sources. The structures and properties of BNC tubes can be regulated by cultivation conditions including

nutrient source, oxygen ratio, bacterial strain type, incubation time, and cultivation in a bioreactor⁵²⁻⁵⁴. Systematic studies of the effects of cultivation conditions on the properties of BNC tubes have been recently reported⁵⁴. *Gluconacetobacter xylinus* CGMCC No. 1186 has been incubated with either fructose or glucose in silicone tube bioreactors. Using fructose improved the nanocellulose yield. Changing the reactor changed the quantity of dissolved oxygen and therefore the structure of the obtained nanocellulose tubes.

The cell membrane of the bacteria used to produce BNC is composed of a cellulosic network structure of ribbon shaped fibrils that are less than 100 nm wide, assembled from bundles of much finer nanofibrils⁵⁵, 2 to 4 nm in diameter. The fibrils are fairly straight, continuous and have low polydispersity in terms of their dimensions. The bundles exhibit excellent intrinsic properties owing to their high crystallinity (84-89%)⁵⁶. Along with an elastic modulus of 78 GPa, BNC is reported to have high water holding capacity and a molecular weight up to 8,000 Da⁵⁷. BNCs promise to appear in functional materials as scaffolds with attractive magnetic (*e.g. in situ* Fe₃O₄ nanoparticle impregnation to yield a magnetic bacterial nanocellulose or use in the preparation of ferromagnetic cobalt ferrite nanoparticles^{58,59}), optical, and mechanical properties due to their low apparent density and high surface area⁶⁰. Extensive applications for BNC in the biomedical field have been reported⁶¹, BNC combines high physical strength, an extremely hydrophilic surface and an interpenetrating structure, which recommends this material for biomedical applications⁶², such as implants and scaffolds for tissue engineering, wound dressings, artificial skin⁶³, and as drug delivery carriers⁶⁴. They may also be used to protect neurons, and to replace small blood vessels⁶⁵. Furthermore, bacterial cellulose membranes could be used in regenerative medicine, including guiding tissue regeneration, periodontal treatments and as membrane replacements^{66,67}.

3. Biomass sources

Nanoscale cellulosic materials are extracted from various plant fibers (biomass) and bacterial sources. International research aims to extract a valuable resource, nanocellulose, while efficiently managing biowaste. All agricultural, forest crops and residue sources can be referred to as lignocellulosic biomass⁶⁸. Nanocellulose sourcing and isolation methods have recently been reviewed³³.

Lignocellulosic biomass is composed of cellulose, hemicellulose, and lignin of vegetal origin (Fig. 5). Lignocellulosic biomass contains 30–50 wt% cellulose⁶⁹, 19–45 wt% hemicellulose⁷⁰, and 15–35 wt% lignin⁷¹. Together these polysaccharides form a heteromatrix that varies in its composition and structure as a function of the biomass source⁷². Cotton is an almost pure form of cellulose with >90% composition. Complex physicochemical interactions are responsible for forming the hierarchical lignocellulosic biomass structure and for shielding the cellulose, hemicellulose, and lignin from the environment.

Cellulose is the most abundant natural biopolymer, with sources including: (i) agricultural residues (sugarcane bagasse, straw, cornstover, coconut husks, corncobs, wheat and rice husks, palm oil residues, maize straw and fruit skins); (ii) tree trunks and dead forest matter (hardwood and softwood); (iii) energy crops; (iv) food waste; and (v) municipal and industrial biowaste such as used paper, carton and wood from demolition sites^{69,70,73}.

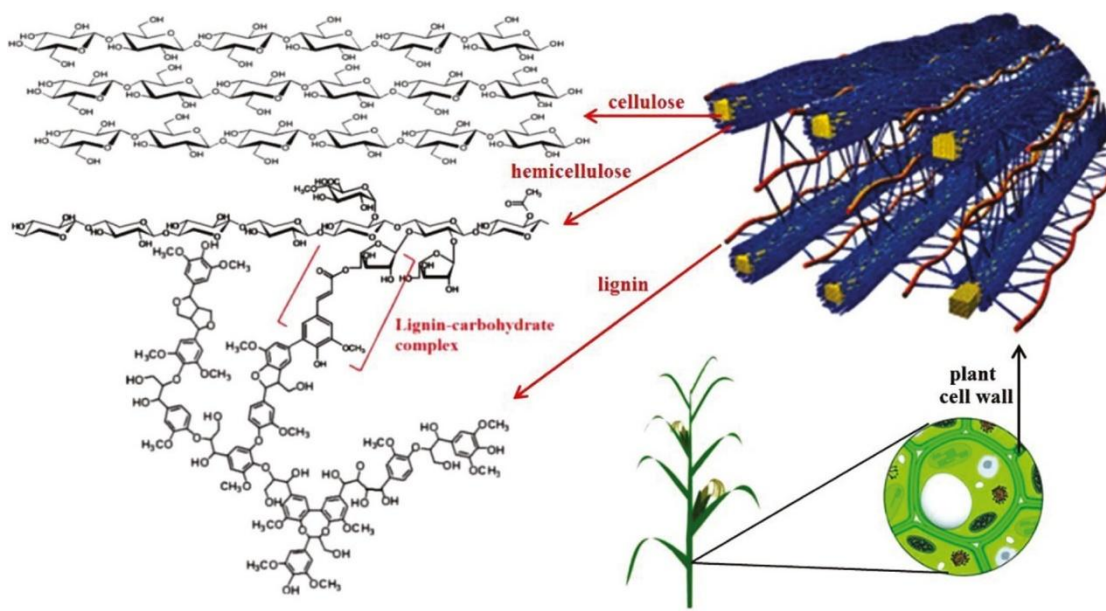


Figure 5: Scheme showing the structure of the three major components of lignocellulosic biomass: cellulose, hemicellulose, and lignin. Reproduced with permission from ref. 74, Copyright 2017, DeGryter.

Acquiring nanocellulose from biomass proceeds in two steps. First, the lignocellulosic material needs to be deconstructed to recover cellulose, alone and as pure as possible. Second, cellulose will be treated to yield nanocellulose. The lignocellulosic structure is such that the strong covalent and H-bonded attractions between layers of lignin, hemicellulose and cellulose prevents an easy access to cellulose itself, thus conferring to wood and plants their ability to resist pest attacks and chemical degradation⁷⁵. A multistep bio-refinery process can be employed to degrade the non-cellulosic content in the lignocellulosic biomass while preserving cellulose. Lignin covalently cross-links cellulose and hemicelluloses via ester and ether linkages. This cross-linking restricts structural disintegration, referred to as *lignocellulosic biomass recalcitrance*⁷⁶. In practice, a combination of certain chemicals and mechanical treatments is commonly applied to rupture the biomass structure and obtain nanocellulose. For large scale

production, this goal is achieved via Kraft pulping, a method combining mechanical and chemical treatments of biomass to achieve almost pure cellulose⁷. Recently a new, environmentally friendly method has been reported where poplar wood flour was mixed with different deep eutectic solvents and then subjected to microwave irradiation for 3 min⁷⁵. Eighty% of the lignin content was extracted, leaving behind a cellulosic residue that was 75% crystalline cellulose. The major benefits of this separation technique are the low energy consumption of the microwave treatment and the use of recyclable, bio-sourced deep eutectic solvents. Once pure cellulose is isolated, a further treatment is needed to recover nanocellulose. This typically involves the use of strong acids, as described in details below.

Table 3 lists the most recent bio-sources, the isolation method, the type of nanocellulose obtained, the dimensions of the isolated nanocellulose and their applications.

Table 3: Most recent bio-sources of nanocellulose, nanocellulose isolation method, type of nanocellulose obtained, isolated nanocellulose dimensions and the applications of nanocellulose extracted from bio-sources.

Source	Type	Method of Isolation	Dimensions of isolated CNC/CNF		Application	Ref.
			(<i>l</i>)	(<i>d</i>)		
Sisal fibres	CNF	Acetic acid hydrolysis	658 ± 290 nm	27 ± 13 nm	Translucent CNF film	77
Amorpha fruticosa	CNF	Acetic acid hydrolysis	~10 µm	~10 nm	Transparent nanopaper	3a
Flax plant	CNC	Sulfuric	20 nm	300 nm	Reinforcing	3b

		acid hydrolysis			agents	
Garlic straw residues	CNC	Sulfuric	~480 nm	~ 6 nm	Reinforcing	3c
		acid hydrolysis			agents	
Rice straw, wheat	CNC	Sulfuric acid	~700 nm	~20 nm	Reinforcing	3d
straw, barley straw		hydrolysis			agents	
Bamboo	CNF	Microwave		2–30 nm	Reinforcing	3e
		liquefaction			agents	
Pinecones	CNF	Mechanical		~15 nm	Reinforcing	3f
		Grinding			agents	
Waste pulp residues	CNF	Mechanical		10-100 nm	Permeable	20
		disintegration			membranes	
<i>Gelidium elegans</i>	CNC	Sulfuric acid	~547 nm	~21.8 nm	Reinforcing	3g
red algae		hydrolysis			agents	
	CNC	Sulfuric acid	~198 nm	~5.5 nm	Further study is	3h
Corncob residue					required to	
	CNF	TEMPO-oxidation;	~438 nm	~2.1 nm	determine end	
		Pulp refining	µms		user applications	
				~43.1 nm		
Sunflower Stalks	CNC	Sulfuric acid	~175 nm	5–10 nm	Reinforcing	19
		hydrolysis			agents	
	CNF	Steam Explosion		5–10 nm		

Cotton Stalks	CNF	1) Sulfuric acid hydrolysis	100-500 nm	10-50 nm	Industrial applications	3i
		2) TEMPO-oxidation	10-100 nm	3-15 nm		
Tomato Peels	CNC	Sulfuric acid hydrolysis	~135 nm	~7.2 nm	Biocomposites	3j
Waste Sack Cloth	CNF	H ₂ O ₂ /HNO ₃ hydrolysis medium	100's of nm	20-50 nm		3k
Jute fibers	CNF	Steam Explosion		~50 nm	Reinforcing agents	3l
<i>Agave tequilana</i>	CNC	Sulfuric acid hydrolysis	~322 nm	~11 nm	Reinforcing agents	35
<i>bagasse</i> , Barley Husks			~329 nm	~10 nm		
Banana Peels	CNF	Sulfuric acid hydrolysis	455 nm	~10.9 nm	Reinforcing agents	78
		Enzymatic treatment-Xylanase	2890 nm	~7.6 nm		
<i>Helicteres isora</i>	CNF	Steam Explosion		~60 nm	Reinforcing agents	3m
Maize Straw	CNW	Sulfuric acid hydrolysis	~388 nm	15 to 25 nm	Nanofillers in polymer matrices	34

Saw dust wastes	CNC	Hydrothermal processing	101-107 nm	18-35 nm	Biomedical applications	3n
Coir fibre	CNF	Steam explosion		~37.8 nm	Industrial, biomedical	2u
Dry Softwood Pulp	CNF	High shear homogenization		16-28 nm	Optical applications	3o
Sugarcane bagasse	CNC	High pressure homogenization		10-20 nm		3p
Eucalyptus kraft pulp	CNF	Sulfuric acid hydrolysis	100-150 nm	10-20 nm	Polymer composite applications	49

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To summarize nanocellulose isolation methods and the obtained products:

- CNCs range in diameter from 5-35 nm and have a length of a few hundred nanometers. CNFs on the other hand have larger diameters of between 3-100 nm and are micrometers in length.
- Sulfuric acid hydrolysis is the most frequently used technique to isolate CNC from cellulose.
- Acid hydrolysis is used in combination with a mechanical treatment to produce CNF.
- Both CNCs and CNFs are extensively used as reinforcements in polymer matrices, highlighting their prominence in composite applications.

4. Nanocellulose isolation

The manner in which the nanocellulose is isolated from the plant matter has a large effect on the morphology and properties of the obtained material. We will now discuss the main isolation methods: mechanical treatment, chemo-mechanical treatment (Kraft pulping), and enzymatic-mechanical treatment.

4.1 Mechanical treatments

The first two methods to produce microfibrillated cellulose were reported by Herrick, *et al.*⁷⁹ and Turbak, *et al.*⁸⁰ in 1983. The procedure for isolating MFC/NFC consists of disintegrating the cellulose fibers along their longitudinal axis. Dilute suspensions of cellulosic wood pulp in water pass through a mechanical homogenizer. Microfibrillation is induced by a large pressure drop¹¹.

Cellulosic fibers disintegrate into their sub-structural fibrils, having a length on the micron scale and a width ranging from 10 to a few hundred nanometers, depending on the type of cell walls typical to the plant source. Since this first attempt, a variety of mechanical treatments have been developed to produce cellulose-based nanomaterials. Stelte and Sanadi fibrillated nanofibers obtained from hardwood and softwood pulps by refining and homogenizing these fibers at 50 MPa⁸¹. High pressure homogenization⁸², high shear homogenization^{83,84}, cryocrushing⁸³, high speed blending⁸⁵, microfluidization⁸⁶, grinding^{84,87}, high intensity ultrasonication⁸⁸, hammer milling⁸⁴, and electrospinning⁸⁹ are alternative mechanical treatments reported in the literature. Cherian, *et al.* employed a steam explosion process to extract cellulose nanofibrils from the fibers in pineapple leaves⁹⁰. These different treatments have been employed independently and in combination to obtain cellulosic nanomaterials. Fig. 6 shows the morphologies of fibrillated cellulose materials obtained from different sources.

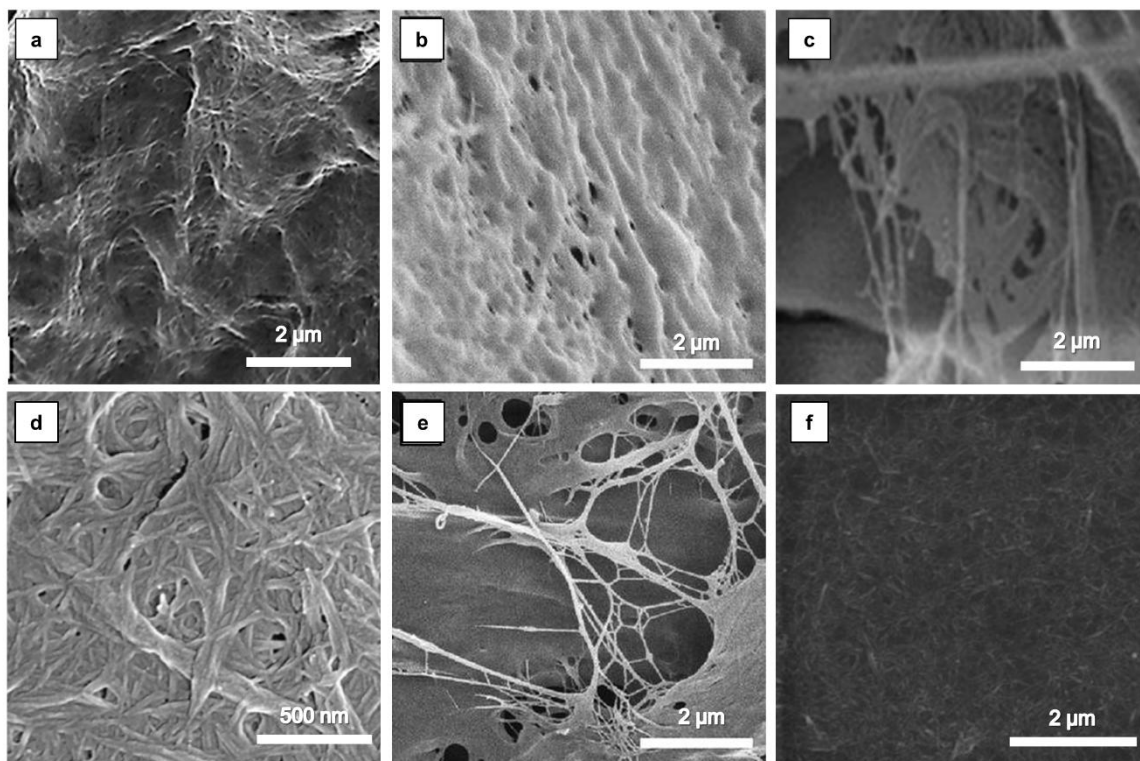


Figure 6: SEM micrographs showing morphological changes as a result of defibrillation: (a) microcrystalline cellulose (adapted from ref. 91, Copyright 2010, American Chemical Society), (b) MFC by homogenization through 20 passes at 80 MPa (adapted from ref. 92, Copyright 2011, SpringerLink) (c) bleached pulp treated using cryocrushing in a PFI mill (adapted from ref. 93, Copyright 2009, NC State University), (d) ultrasonication derived nanocellulose:(adapted from ref. 94, Copyright 2012, Budapesti Muszaki Egyetem), (e) MFC by microfluidization through 5 passes at 1000 MPa (adapted from ref. 92, Copyright 2011, SpringerLink**Erreur ! Signet non défini.**), (f) MCC obtained via high shear homogenization, deposited from a 0.05 wt% aqueous dispersion (adapted from ref. 84, Copyright 2014, Elsevier).

Energy consumption and production costs are high when mechanical treatment alone is used to delaminate the fibers⁹⁵⁻⁹⁷. A significant amount of energy is required to liberate nanosized cellulose from the natural fibers, due to the highly ordered hydrogen bond network of cellulose.

By increasing fibrillation, cellulose films can increase in both transparency and mechanical properties. Sharma, *et al.* hot pressed cellulose films with differing degrees of microfibrillation (Fig. 7)⁹⁸. Films with a higher degree of fibrillation had the same film thickness, but a higher density, and thus their tensile strength changed from no defined tear behaviour before microfibrillation to 134.5 MPa for the most fibrillated film.

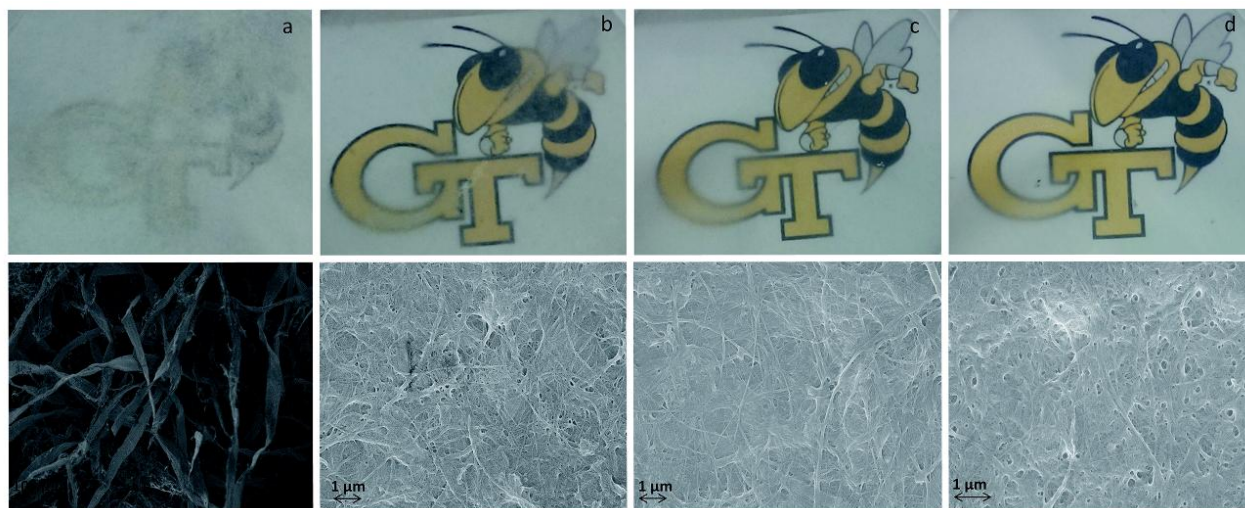


Figure 7: Photos of cellulose films showing their increasing transparency and corresponding SEM images of (a) disintegrated cellulose, (b) PFI cellulose refining, and (c) 20 passes or (d) 60 passes of micro-grinding in the super mass collider. Reproduced with permission from ref. 98, Copyright 2015, Royal Society of Chemistry.

In order to decrease the energy demands of the mechanical isolation process, chemical pre-treatments may be applied, such as acid hydrolysis⁹⁹, enzymatic exposure^{45,100}, ionic liquid treatment¹⁰¹, and carboxymethylation¹⁰², and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation to modify the surface¹⁰³. In each of these cases, charged functionalities are introduced to the cellulose backbone, internal repulsions emerge and defects to the hydrogen

bond network are created. By combining chemical and mechanical treatments (chemo-mechanical treatment), individual fibrils (3-5 nm wide) or fibril aggregates (10-20 nm wide) several micrometers in length can be obtained for a reasonable cost when compared to the use of mechanical treatments alone.

4.2 Chemo-mechanical treatment (Kraft pulping)

First chemical pretreatments aim to remove non-cellulosic materials like waxes, ashes, lignin, pectin and hemicellulose. Hemicellulose is a random, amorphous material that is dissolved from the lignin structure by breaking the linkages between the carbohydrates and lignin using an acid-alkaline pre-treatment¹⁰⁴. A pretreatment can reduce the energy consumed by mechanical processing from between 20,000-30,000 kWh/ton to 1000 kWh/ton¹⁰⁵. Alkaline treatment targets the removal of the lignin content and the degradation of hemicelluloses, though hemicellulose is never completely removed. Reaction conditions should be controlled, so as to prevent cellulose degradation. Alkali treatment usually employs 5 wt% NaOH at 90 °C for almost 1 h. The obtained pulp is then washed with deionized water until neutralized. The cycle may be repeated 2-3 times depending on the lignin content of the source material. The hemicellulosic content that still prevails is usually removed via hydrolysis.

Once cellulose is recovered, acid hydrolysis is undoubtedly the most common chemical treatment employed to obtain nanocellulose crystals. In acid hydrolysis, the hydronium ions penetrate the amorphous regions of cellulose chains and hydrolytically cleave glycosidic bonds, to release individual crystalline cellulose nanoparticles. Acetic acid can also be used to reduce intermolecular hydrogen bonding by acetylating pendant hydroxyl groups⁷⁷. However, acid hydrolysis is usually avoided for the isolation of NFCs as it may result in transverse cleavage of

amorphous regions producing CNCs upon homogenization/ultrasonication. Sulfuric acid is the most common reagent reported for acid hydrolysis to date, and is used highly concentrated (~64%)¹⁰⁶. This method results in the partial functionalization of the surface hydroxyl groups with sulfate half esters, which confer surface charges and thus aqueous suspendability to the resulting CNCs. Like sulfuric acid, phosphoric acid can be used to introduce negative surface charges by modifying the surface of the nanocrystal with phosphate ester groups. These groups stabilize nanoparticle suspensions through electrostatic interactions. However, sulphuric acid yields a much higher density of surface charges on the nanocrystals^{107,108}. Phosphorylation introduces negatively charged groups to the cellulosic surface in different forms such as phosphate, or phosphite esters.

Acid hydrolysis is the method used industrially⁷. Most mineral acids including, hydrochloric acid¹⁰⁹, phosphoric acid¹¹⁰, hydrobromic acid^{111,112} and nitric acid¹¹³ are also capable of yielding crystalline cellulosic nanoparticles, although with lesser properties in terms of CNC suspendability, because they result in fewer or no charge incorporation to the surface. The current limitations with acid hydrolysis include the corrosive nature of the acids and the production of large amounts of chemical waste, although recycling strategies have been devised at the industrial scale.

Alternatively, nanocellulose can be recovered by oxidative processes. Cellulose may be oxidized with TEMPO radicals prior to a mechanical treatment¹⁰³. TEMPO-mediated oxidation facilitated CNC isolation under mild aqueous conditions¹¹⁴, with surface hydroxyl being converted to carboxylic acid. Ammonium persulfate have also being used to afford similar materials^{115,116}. With hydrogen peroxide, in ethanol, a nice one step procedure allowed to go directly from biomass to oxidized CNCs¹¹⁷. With these methods, nanocellulose is recovered in a

form of an aqueous suspension, which is then used as is, or further Soxhlet extracted⁷, air, freeze or spray dried¹¹⁸, the later being the method of choice for large scale, flow production.

4.3 Enzymatic-mechanical treatment

Enzymatic pre-treatment can be used to isolate nanocellulose, and has been discussed in detail in a recent review¹¹⁹. Enzymatic treatment allows milder hydrolysis conditions than acid hydrolysis. Fig. 8 shows TEM images of CNFs obtained by chemical and enzymatic treatments, where slightly different morphologies can be observed. Enzymatic hydrolysis is considered to be environmentally friendly. As an example of enzymatic hydrolysis, xylanases are hydrolytic enzymes that modify the hemicelluloses present in plant fiber. They can also initiate random hydrolysis of the β -1,4 non-reducing terminal regions located between the glycosidic linkages of the glucose units¹²⁰. Enzymes modify or degrade the lignin and hemicellulose, restricting the degree of hydrolysis or selectively hydrolyzing specified components in the cellulosic fibers. Henriksson, *et al.*¹⁰⁰ and Pääkkö, *et al.*⁴⁵ showed that *endoglucanase* can be used to facilitate the disintegration of wood fiber pulp into MFC nanofibers. Tibolla, *et al.*⁷⁸ compared the chemical and enzymatic pre-treatment of cellulose nanofibers. In general, yields of enzymatically produced nanocellulose are typically much lower than those achieved by mineral acid production methods from cellulosic biomass sources. However, the enzymatic route can be tuned to meet societal demands on clean chemical processes for the production of materials and fine chemicals. An elegant example of this approach is the coproduction of nanocellulose and biofuels using multifunctional cellulolytic enzymes using *Caldicellulosiruptor bescii*. This method to produce nanocellulose from lignocellulosic biomass using thermophilic bacteria improved the kinetics, increased the mixing rate, lowered the oxygen solubility, reduced the risk of microbial

contamination, and reduced the costs for cooling and heating during the bioconversion process^{121,122}.

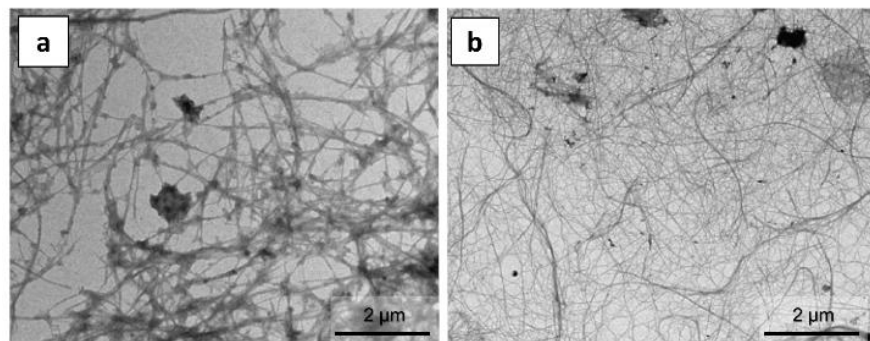


Figure 8: TEM images of the cellulose nanofibers obtained by (a) chemical treatment and (b) enzymatic treatment. Reproduced with permission from ref. 78, Copyright 2014, Springer.

The surface charge of nanocellulose are also affected by the nature of the treatment. Enzymatical treatment, using xylanase in order to remove lignin and hemicellulose residues, afforded nanocellulose fibers with a higher zeta potential compared to a classic sulfuric acid treatment. These thus formed more stable suspensions, although authors did not explain the functionality responsible for this property⁷⁸.

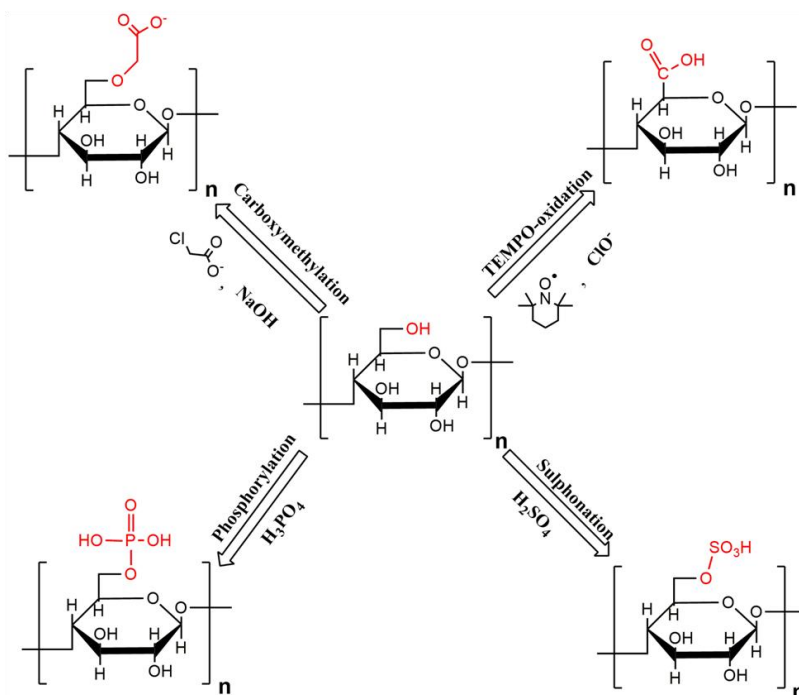
5. Chemical modifications of nanocellulose

The surface chemistry of cellulose can be easily tuned. Surface-modified cellulosic nanomaterials are an excellent platform, designed for targeted applications. The broad applicability of nanocellulose is compromised by its poor dispersibility in non-polar solvents, and its incompatibility and poor interfacial adhesion with hydrophobic matrices. To overcome this issue, researchers have tried a number of modifications—both to the surface and to the

nanocellulosic structure. Chemical modification of the surface of cellulose nanoparticles employs pendant surface hydroxyl groups, essentially the primary alcohol group ($-\text{CH}_2\text{OH}$). Different chemical modification strategies were performed on nanocellulosic materials with the aim to: 1) enhance the efficiency of the isolation process and 2) to change the surface hydrophobicity, which in turn improves the compatibility and the dispersability of nanocelluloses in specific solvents. This topic was reviewed in 2014 by Eyley and Thielemans¹²³.

5.1 Imparting ionic charges to nanocellulosic surfaces

As explained in 4.2, the synthesis of nanocellulose by sulfuric and phosphoric acid hydrolysis does result in partial functionalization of the surface with sulfate or phosphate half esters. This introduces the charges necessary for aqueous suspendability and isolation process. Further introduction of ionic charge to the cellulosic surface *via* phosphorylation, carboxymethylation, oxidation and sulfonation reactions has been studied. Scheme 1 shows the different techniques by which ionic charges can be incorporated onto the nanocellulosic surface.



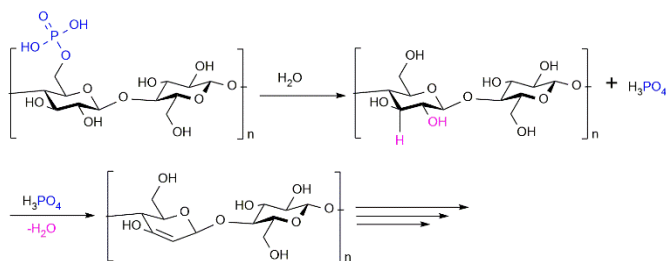
Scheme 1: Different surface modification techniques through which ionic charges are imparted to the nanocellulosic surface, giving it a hydrophilic character.

5.1.1 Phosphorylation of cellulose

The incorporation of phosphate ester groups onto a cellulosic backbone significantly alters the original properties. Phosphorylation of cellulose is a well-known surface modification strategy for producing suitable materials for applications in diverse areas including orthopaedics¹²⁴, biomedical applications¹²⁵, textiles¹²⁶, flame-retardant fillers¹²⁷, soil and dye resistant fabrics¹²⁸, osteogenic activities¹²⁹, fuel cells¹³⁰, bio-chemical separations¹³¹, ion exchange capacity, and protein adsorbents¹³². Phosphate ester functionalized cellulose has been shown to be compatible with calcium phosphate to opening pathways toward hybrid material formation. Therefore this material could be used as an implantable biomaterial in bone and tissue engineering¹²⁵. Phosphorylated cellulose is capable of binding metal ions like Ag^+ , Fe^{3+} , and

Cu^{2+} , and thus these materials can be used as ion adsorbents to filter water and industrial effluents¹³³.

Phosphorylated cellulose (*p-cellulose*) was also reported as a flame retardant in textiles¹³⁴. Cellulose is a material of low thermal stability and high flammability (hence extensively used as firewood). Nanocrystalline cellulose is comparably more thermally stable, because the amorphous sections in cellulose are more reactive to combustion. The inorganic ester functionalization of the CNC surface upon their synthesis brings about flame retardancy properties to CNCs. Both sulfate esters and phosphate esters, introduced during the treatment with their corresponding acid, have the ability to favor dehydration and thus the formation of char (scheme 2), which is responsible for flame retardance^{131,135}. Phosphorylated and sulphated esters are able to free phosphoric and sulphuric acid during heating, which catalyzes dehydration of the cellulose chain to form stable carbon-carbon double bonds during charring. This phenomenon is also accompanied by a drop in the temperature at which thermal decomposition starts and by a smaller weight loss compared to unfunctionalized CNC, obtained by HCl hydrolysis^{131,135}. The obtained flame retardant-phosphocellulosic material could be blended into polymeric materials for use in a large variety of composite applications¹³⁶.



Scheme 2: Proposed mechanism of thermally stable char formation of phosphorylated cellulose.

Many cellulose phosphorylation methods have been reported, which appear in a number of reviews over the last 100 years^{137,138}. The process is conducted by reacting the free hydroxyl groups of the C₂, C₃, and C₆ positions. Over the last decades, reagents like phosphorus oxychloride (POCl₃), phosphorus pentoxide (P₂O₅), phosphoric acid (H₃PO₄)¹³⁹, diammonium hydrogen phosphate (NH₄)₂HPO₄¹⁴⁰, and organophosphates have been used in combination, as phosphorylating agents. Typically either N,N-dimethylformamide, pyridine, or urea are used to swell cellulose fibers to increase the homogeneity of the phosphorylation reaction¹⁴¹. The degree of substitution heavily depends on the molar ratio between the phosphorylating agent and the cellulose monomer units, and the reaction time and temperature¹³⁶.

In 1956, Touey, *et al.* first reported a method using H₃PO₄/P₂O₅/EtO₃PO in hexanol for the synthesis of a water-soluble and nondegradable flame-resistant textile material¹³⁴. This method yielded products with a degree of substitution as high as 1.0, which was comparable to the maximum degree of substitution obtained by the most widely-used methods of the time. Later Granja, *et al.* used the same method but optimized the reaction conditions of the first report, producing an average degree of substitution of approximately 2¹²⁵. A maximum degree of phosphorylation of 2.5 is obtained using the following procedure: To a stirring suspension of cellulose in hexanol, add a portion of phosphorus pentoxide in triethyl phosphate and orthophosphoric acid. Stir the mixture at 30 °C for 72 h and then filter. Wash the filter cake successively with hexanol and ethanol, and then rinse repeatedly with water, to wash away excess H₃PO₄. Fig. 9 shows a synthetic scheme of the reaction and SEM images of unmodified cellulose and the obtained triphosphate gels. The filtrate was then centrifuged prior to purification. Purification was carried out by Soxhlet extraction with deionized water and ethanol,

for at least 24 h, until tests for inorganic phosphate were negative. The obtained gel was then freeze-dried.

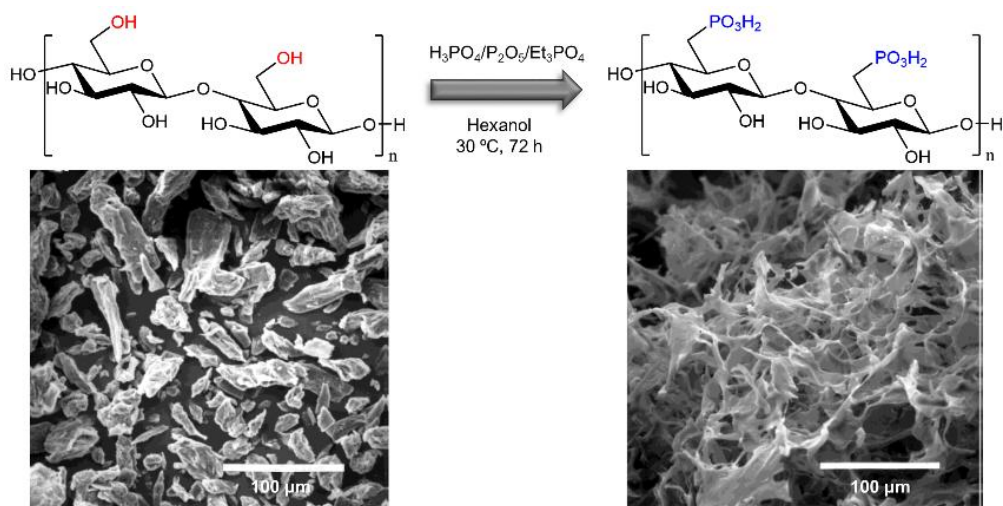


Figure 9: Scheme of the phosphorylation reaction of unmodified cellulose. SEM images correspond to (left) unmodified cellulose and (right) the lyophilized triphosphate gels. Adapted with permission from ref. 125, Copyright 2001, Wiley.

One downside with the $\text{H}_3\text{PO}_4/\text{P}_2\text{O}_5/\text{Et}_3\text{PO}_4$ /hexanol method is that it has been shown to cause side-reactions, such as intermolecular crosslinking¹⁴². To address this point, in 2002, Tzanov, *et al.* developed the phosphorylation of cotton cellulose¹²⁶, using a site-specific hexokinase-mediated reaction employing the phosphoryl donor adenosine-5'-triphosphate. Phosphorylation of 0.03% of the glucopyranose units in the cellulose provided a textile material with improved colorability and flame-resistance.

Later in 2014, Božič, *et al.* used the enzyme hexokinase with adenosine-5'-triphosphate and Mg-ions to phosphorylate CNFs¹⁴³. Phosphate groups were created predominantly at the C₆ position hydroxyl groups of the cellulose monomer rings. By varying the quantity of enzyme,

MgCl₂ and ATP, the degree of CNF phosphorylation produced a degree of substitution between 0.00033 and 0.43. Since a high degree of substitution per enzyme is important from an economical view point, the impact of enzyme activity on the degree of phosphorylation was studied. Enzyme activity of 35 U/mL resulted in the highest degree of functionalization (*i.e.* 0.42). The biomimetic growth of Ca–P crystals was studied for use of p-CNFs in medical applications. The SEM images of CNF before and after phosphorylation and after 10 days of incubation in 1.5 times-simulated body fluid appears in Fig. 10. Quantitatively more and larger Ca–P particles were identified on the phosphorylated-CNF surface, while only small Ca–P crystals were found on the native CNF surface after 10 days of culturing the samples in 1.5 simulated body fluid. The native CNF surfaces lack the necessary functional groups to bond calcium ions and therefore to induce nucleation. Introducing phosphate groups onto the CNF surface, even if only to a small degree, greatly enhanced Ca–P crystal growth.

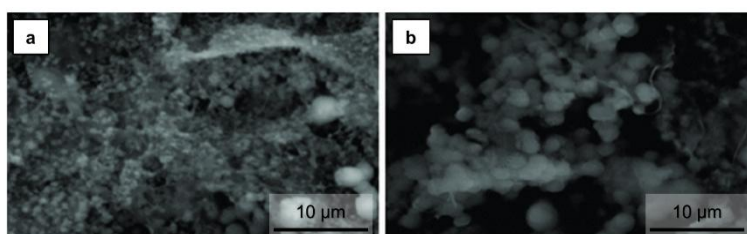


Figure 10: SEM images of hydroxyapatite growth on (a) native CNF and (b) phosphorylated CNF after 10 days of incubation in 1.5 times-simulated body fluid. Reproduced with modifications from ref. 143, Copyright 2014, SpringerLink.

Gospodinova, *et al.* have efficiently phosphorylated microcrystalline cellulose using a solvent-free microwave synthesis¹⁴⁴. These authors compared the degree of substitution obtained

by heating a solution of phosphoric acid, urea and the cellulose, using either classical heat transfer or microwaves. Here urea is used as an additive, able to disrupt the hydrogen bonding in cellulose to improve accessibility of reagents to hydroxyl functionalities. Conventional heating to 100 °C for 6 h produced a maximum degree of cellulose substitution of 1.4. The degree of substitution was dramatically higher when using microwave heating at the same temperature. For instance, mono-substituted phosphoric acid esters with a degree of substitution of 2.8 were obtained after 2 h of microwave irradiation.

Kokol, *et al.* pushed this concept and used molten urea as a solvent¹⁴⁵. Specifically, they studied the properties of nanosized fibrillated and crystalline cellulose, comparing heterogeneous (aqueous phosphoric acid) and homogeneous (phosphoric acid in molten urea) phosphorylation methods¹⁴⁵. During the phosphorylation of cellulose using phosphoric acid, surface phosphate groups and tautomeric phosphite structures were formed, mostly involving the C₃- and C₆-hydroxyl groups, while preserving the crystalline structure. Two different phosphorylation reaction methods afforded nanofibrillated cellulose with different charge densities of 18.55±2.3 mmol kg⁻¹ and 1173.43±26.1 mmol kg⁻¹, and nanocrystalline cellulose with 435.21±7.2 mmol kg⁻¹ and 1038.05±9.9 mmol kg⁻¹, respectively, *i.e.*, a 60-fold increase in the case of NFC and a 2-fold increase in the case of NCC.

5.1.2 Carboxymethylation

Carboxymethyl groups are introduced to cellulosic surfaces via the carboxymethylation process rendering the surface negatively charged. These charges create electrostatic repulsions and facilitate the degradation of lignocellulosic fibers into nanosized particles. Wågberg produced NFCs by passing carboxymethylated cellulosic fibers through a homogenizer, yielding

NFCs with a diameter of 5-15 nm¹⁰². Monochloroacetic acid served the purpose of supplying the carboxymethyl groups. Siro, *et al.* applied homogenization steps to carboxymethylated softwood pulp finding that carboxymethylated NFC gels could potentially form extremely transparent films acting as oxygen barriers¹⁴⁶. In a recent study, Arvidsson, *et al.* conducted a comparative study of enzymatic and carboxymethylation pretreatments for the production of CNF¹⁴⁷. They found that even though CNF produced using the carboxymethylation route clearly had a high environmental impact (as the process employed large volumes of organic solvents like ethanol, isopropanol, and methanol and monochloroacetic acid as the carboxymethylating agent), the pretreatment enabled the production of CNF suspensions with lower turbidity. The higher transparency of these suspensions means they could be used in transparent films and composite applications.

5.1.3 Oxidation

2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO) mediated oxidation can be used both as a pretreatment to facilitate nanofiber isolation, and as a means to render the nanocellulose surface hydrophobic. De Nooy, *et al.*¹⁴⁸ first reported this method and showed that TEMPO can only oxidize the primary hydroxymethyl groups of polysaccharides, leaving the secondary hydroxyl groups unaffected. The method selectively converts the exposed C₆ alcohol functions of the glucose unit to a carboxylic acid^{149,150}.

Mechanistically, stable nitroxyl radicals from TEMPO enable the conversion of hydroxyl groups to aldehydes, which are subsequently oxidized to carboxylic acids (Fig. 11). When TEMPO/NaOCl/NaOCl₂, are used to catalytically oxidize cellulose¹⁵¹, a high degree of charge is obtained due to the oxidation of the C6-position, into anionic carboxylates thus resulting in better

dispersability in water. The negative charges on the CNC surface introduced *via* this oxidation technique increase electrostatic repulsions. Araki, *et al.* reported a TEMPO-mediated oxidation of CNCs after hydrolyzing the cellulose fibers with HCl¹⁵². The oxidized CNCs had identical morphology to the CNC substrate and could be readily suspended in water. The rheological properties of TEMPO-oxidized CNCs have been studied by Lasseguette, Roux, and Nishiyama¹⁵³.

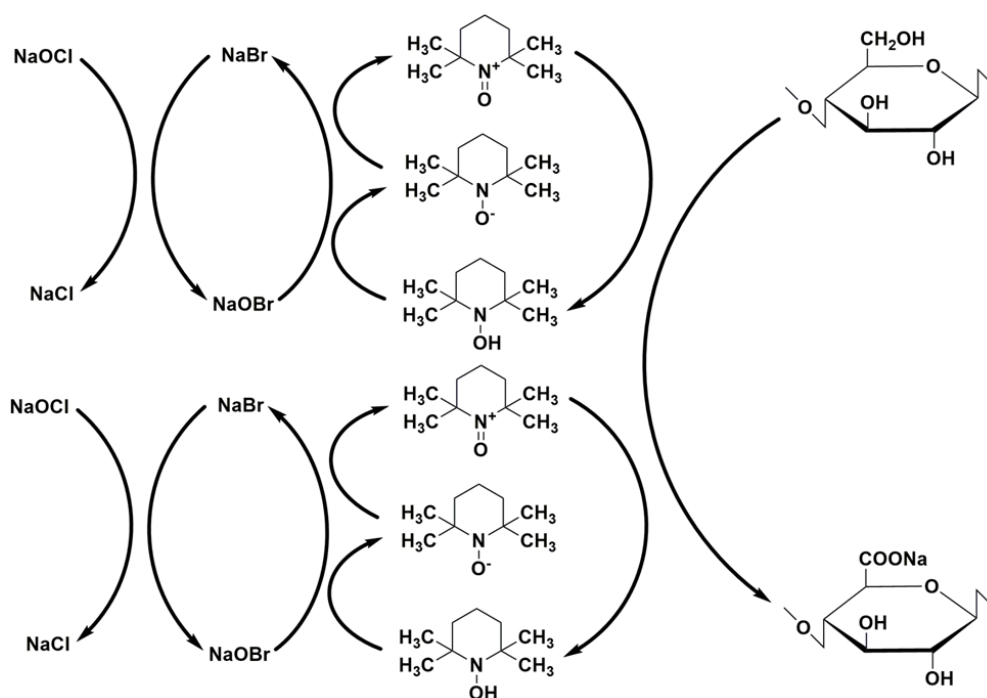


Figure 11: Mechanism of TEMPO-mediated oxidation pathway of nanocellulose. Adapted with permission from ref. 4, Copyright 2014, Royal Society of Chemistry.

5.1.4 Sulfonation

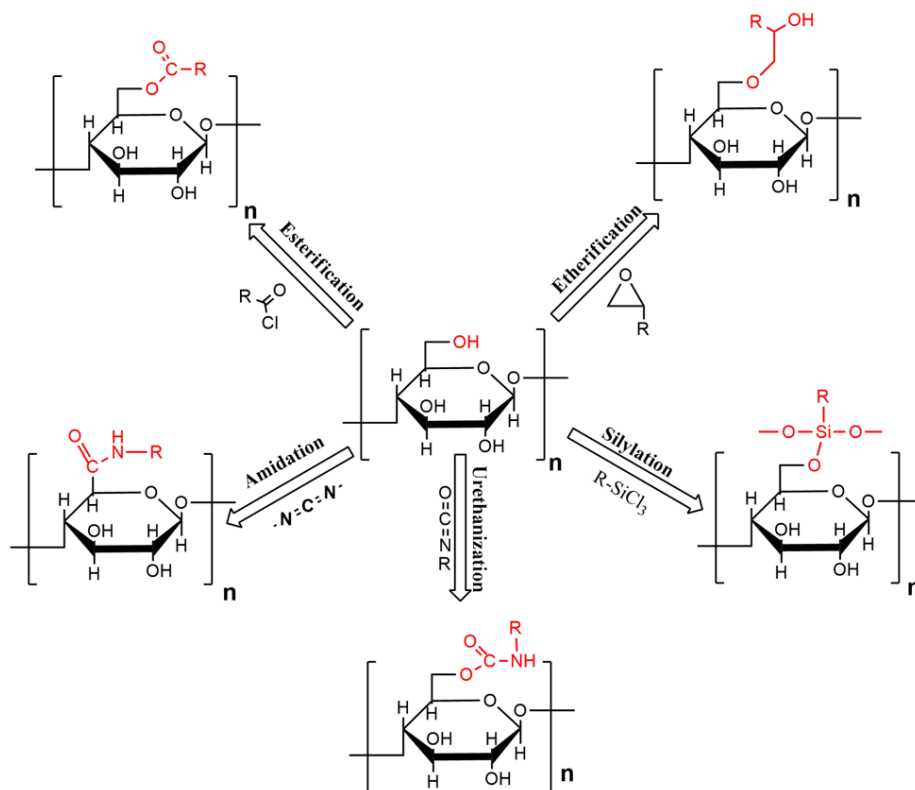
Sulfonation is another technique to impart anionic charges to the surface of nanocellulosic materials. Concentrated sulfuric acid used for CNC synthesis both catalyzes the hydrolysis of the sources, and enables the formation of sulfate half esters from CNCs

hydroxyl groups. Sulfuric acid hydrolysis leads to stable colloidal suspensions of cellulose nanocrystals¹⁰⁶, which display phase separation into equilibrium ordered chiral nematic phase above a critical concentration¹⁵⁴. The presence of these sulfate esters at the surface of the CNCs leads to the formation of highly stable colloidal suspensions, which after controlled drying, produces optically active films¹⁵⁵. The presence of negatively charged sulphate groups on the surface induces the formation of a negative electrostatic layer covering the nanocrystals and improves the dispersion capacity in water. However, it compromises the thermostability of the nanoparticles, especially for a high degree of functionalization with sulfate groups¹³⁵. Perhaps, the thermal stability of H₂SO₄-prepared nanocrystals can be increased by neutralization of the nanoparticles with sodium hydroxide. Hydrolyzing with a combination of sulfuric and hydrochloric acid while sonicating generated spherical CNCs¹⁵⁶. Due to a lower density of surface sulfate groups, these spherical CNCs demonstrated better thermal stability compared to those obtained by hydrolyzing with pure sulfuric acid. Liimatainen and co-workers used periodate and bisulfite to nanofibrillate hardwood pulp, obtaining sulfonated NFCs with widths between 10–60 nm¹⁵⁷. To enable nanofibrillation, a density of 0.18 mmol g⁻¹ of sulfonate groups is required, which also yields a highly transparent and viscous gel. Ruiz-Palomero, *et al.* reported the use of sulfonated nanocellulose for the efficient dispersive micro solid-phase extraction and determination of silver nanoparticles in food products¹⁵⁸. This sulfonation process avoids the use of halogenated wastes, and thus is considered green.

5.2 Generation of nanocellulosic materials with hydrophobic surfaces

As cellulose is hydrophilic, it absorbs water upon exposure. The sensitivity of nanocellulosic materials towards moisture can be tuned by using various chemical modification techniques such

as esterification, silylation, amidation, urethanization and etherification making the cellulosic surface hydrophobic. In accordance with the commonly accepted definition, a surface is defined to be hydrophilic when its contact angle with water is smaller than 90° and hydrophobic otherwise¹⁵⁹. Irrespective of the ultimately desired surface chemistry, modification techniques rely almost exclusively upon the reaction of nanocellulose surface hydroxyl groups. The challenge for these chemical modification techniques is to change only the surface of the nanocellulose, preserving the original morphology and the complex structure of the internal hydroxyl groups. Scheme 3 shows the different surface modification techniques which render the nanocellulose surface hydrophobic.



Scheme 3: Different surface modification techniques reported in the literature to give hydrophobicity to the nanocellulose surface.

5.2.1 Acetylation

Acetylation of cellulosic fibers is commonly performed to increase hydrophobicity. The lignocellulosic fibers are plasticized upon the acetylation of cellulosic alcohols¹⁶⁰. Acetylation of nanocellulose usually involves the gradual addition of acetic anhydride and dry acetic acid with either sulfuric or perchloric acid to catalyze the reaction. Sassi and Chanzy were the first to propose the two main mechanisms of acetylation¹⁶¹. These two mechanisms, respectively named the *fibrous process* and the *homogeneous process*, rely on the presence or absence of a swelling diluent. For instance, in the fibrous process, a diluent such as toluene is added to the reaction medium where acetylated cellulose remains insoluble. A high degree of acetylation is obtained and the original morphology is preserved. In the diluent-free homogeneous process, acetylated chains are soluble in the reaction medium consisting of acetic acid and a catalytic amount of sulfuric acid. Consequently, the cellulosic substrates are found to undergo substantial morphological changes upon extensive acetylation. Cetin, *et al.*¹⁶² decorated the CNC surface with acetyl groups by using carbonate to catalyze the transesterification of vinyl acetate. In this study, only the nanocrystal surface was functionalized, leaving the original dimensions and crystallinity intact. The rate and degree of acetylation was determined by diffusion. Upon prolonged reaction time, nanocrystals showed a higher amount of acetylation, smaller size, and a lower percentage of crystallinity. Bulota and co-workers used acetic anhydride for the acetylation of mechanically isolated NFC¹⁶³. They demonstrated that nanofibers with a greater degree of substitution remarkably influenced the properties of the prepared polylactic acid–acetylated NFC composite. The measured contact angle increased from 33° for non-acetylated nanofibers to 115° for those that had been acetylated, showing a large increase in hydrophobic

character. Yuan, *et al.* developed a facile surface esterification that has low reagent consumption¹⁶⁴. The group used aqueous alkenyl succinic anhydride emulsions as a template. The obtained derivative was found to possess a highly hydrophobic character. In a recent work by Missoum, *et al.* the feasibility of using ionic liquids as a reaction media to carry out the esterification of NFCs was reported¹⁶⁵. Co-solvents 1-butyl-3-methyl-imidazolium-hexafluorophosphate and acetic anhydride were successfully employed, allowing the original NFC morphology and crystallinity to be preserved.

These chemical acetylation methods use expensive and/or corrosive chemicals, which raise concerns over the sustainability of the whole process. Recently, acetylation of nanofibrillated cellulose using acetic anhydride as an acyl donor has reported using enzyme lipase from *Aspergillus niger*¹⁶⁶. Enzymatic acetylation on NFC yielded much higher hydrophobicity (contact angle of $84\pm 9^\circ$) compared to chemical acetylation (contact angle of $33\pm 3^\circ$)¹⁶⁶. Transesterification of cellulose using acylating agents such as vinyl propionate and vinyl acrylate can make the surfaces of nanocellulose hydrophobic as demonstrated by increased contact angles¹⁶⁷⁻¹⁷⁰. Acyl modification of hydroxyethylcellulose has been reported in the presence of β -galactosidase from *Aspergillus oryzae*. Surface modification has also been performed using succinic anhydride, vinyl stearate, vinyl acetate, and vinyl acrylate through transesterification in N,N-dimethylacetamide (DMAc) using lipase from *Pseudomonas cepacia*.

5.2.2 Etherification

Etherification forms a widely used chemical pretreatment method that facilitates cellulose defibrillation to prepare nanosized NFC. The process involves the carboxymethylation of cellulose fibers, which proceeds by first activating the fibers with an aqueous alkali hydroxide,

such as NaOH, and then converting the hydroxyl groups to carboxymethyl moieties with monochloroacetic acid or its sodium salt¹⁷¹. Drawbacks include the use of toxic halocarbons and sometimes increasing the hydrophilicity of the resulting NFCs. Etherification has been used to graft cationically charged species onto a CNC surface, such as epoxypropyltrimethyl ammonium chloride (EPTMAC)¹⁷². Alkali-activated hydroxyl moieties along the cellulose backbone reacted via a nucleophilic addition to the epoxide of EPTMAC. Stable aqueous suspensions with thixotropic gelling properties were obtained.

5.2.3 Silylation

Silane surface modification is a simple way to increase the hydrophobicity of a hydrophilic cellulose surface. Alkyldimethylchlorosilanes are generally used for the purpose of silylation⁹. Gousse and co-workers studied the rheological properties of NFC after a mild silylation proceduring using isopropyl dimethylchlorosilane¹⁷³. The silylated NFC possessed inherent flexibility and the rheological properties of their suspension in methyl oleate showed a marked shear thinning effect. Similarly, Anderson, *et al.*¹⁷⁴ successfully used chlorodimethyl isopropylsilane to silylate the surface of NFCs. The NCFs kept their morphological integrity at a moderate degrees of substitution (between 0.6 and 1), and could stabilize water-in-oil emulsions. Zhang, *et al.* recently reported the use of flexible silylated nanocellulose sponges to remove oil from water¹⁷⁵. High porosity ($\geq 99\%$) functional materials were fabricated by freeze-drying aqueous suspensions of nanofibrillated cellulose, containing various quantities of methyltrimethoxysilane sols. The silylated NFC sponges displayed an unprecedented flexibility compared to conventional inorganic porous materials. In addition, the sponges exhibited hydrophobic and oleophilic properties, which were perfectly adapted to remove dodecane spills

from water surfaces. Moreover, these materials showed excellent selectivity and recyclability. Silylation is a multi-purpose functionalization method.

5.2.4 Urethanization

Reaction between isocyanate and the surface hydroxyl groups of nanocellulosic materials entails the formation of covalent bonds, *i.e.* a urethane linkage between the two, thus urethanization can serve as an alternative to esterification. Urethanization, carbonylation and carbamation¹²³ are a few synonyms reported in the literature for the process. In a study conducted by Siqueira and co-workers, the surface modification of CNC and NFC by *n*-octadecyl isocyanate was studied and found to enhance hydrophobicity¹⁷⁶. The degree of substitution for isocyanate-grafting was 0.07 for CNC and was 0.09 for NFC. The dispersability of modified CNCs and NFCs in organic solvents was improved upon isocyanate grafting. In a recent study by Biyani, *et al.*, isocyanate-mediated coupling was used to decorate CNCs with hydrogen-bonding ureidopyrimidone¹⁷⁷. In this reaction, CNCs reacted with a stoichiometric amount of 2-(6-isocyanatohexylaminocarbonylamino)-6-methyl 4[1H] pyrimidinone in DMF at 100 °C, using a catalytic amount of dibutyltindilaurate. The ureidopyrimidone functionalized CNCs were incorporated into ureidopyrimidone functionalized telechelic poly(ethylene-co-butylene), yielding light-healing capabilities with superior mechanical properties.

5.2.5 Amidation

A carbodiimide-mediated reaction is the most common way to amidate cellulosic surfaces. The reaction usually targets the carboxylic groups of pre-oxidized nanocellulose substrates. The most commonly used carbodiimide for nanocellulose amidation is *N*-ethyl-*N*-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDAC). The favorable pH range is between 7 and 10 for the amidation of nanocellulose substrates. Celia, *et al.* covalently attached β -cyclodextrin to amine-modified nanocellulose via amidation¹⁷⁸. The β -cyclodextrin

functionalized nanocellulose could then act as an adanofloxacin sorbent in the selective fluorimetric detection of this antibiotic in milk.

5.3 Polymer grafting on cellulose

Grafting polymers onto cellulose is an excellent way to modify the chemical and physical properties of the material¹⁷⁹. Polymer-cellulose composites have been synthesized to stabilize nanocellulose, for abrasion and wear resistance, for shape-retaining materials, to change the hydrophilicity/hydrophobicity of the surface and the sorbancy, and to obtain elasticity, stimuli-responsive materials, ion exchangers, electrolytes, thermal resistance, and self-cleaning surfaces (Fig. 12). Polymer-grafted cellulose combines good mechanical properties with good biocompatibility and low degradability, thus such materials have been used in surgical repair¹⁸⁰. Polymer grafting has been performed using different methods that can be divided into three categories (Fig. 13): *grafting-to*, *grafting-from* and *grafting-through*. In the grafting-to approach, purified and well-characterized polymers or peptides are attached to the cellulose, typically by coupling the reactive end group of the polymer to the hydroxyl groups of the cellulose backbone. A wide variety of polymers, (*e.g.* polypropylene, polystyrene, poly(lactic acid), and poly(caprolactone) to mention a few) can be grown and attached to the cellulose, as long as there is a linkable functionality. In the grafting-from method the cellulose is first functionalized with an initiator and then monomers are polymerized directly from the surface. This method can achieve higher polymer densities than when grafting-to, but it is difficult to characterize the resulting polymers, and the polydispersity of the polymers can be higher than in the grafting-to approach. When applying grafting-through, the cellulose is first functionalized with polymerizable species, such as with vinyl-bearing molecules. The functionalized cellulose is then

mixed with a co-monomer and the polymerization is initiated. Among these methods, grafting from is the most popular method to date^{4,181}, with focused reviews on ring-opening polymerization¹⁸², controlled radical polymerization grafting methods¹⁸³ and the colloidal stability of grafted nanocellulose¹⁸⁴.

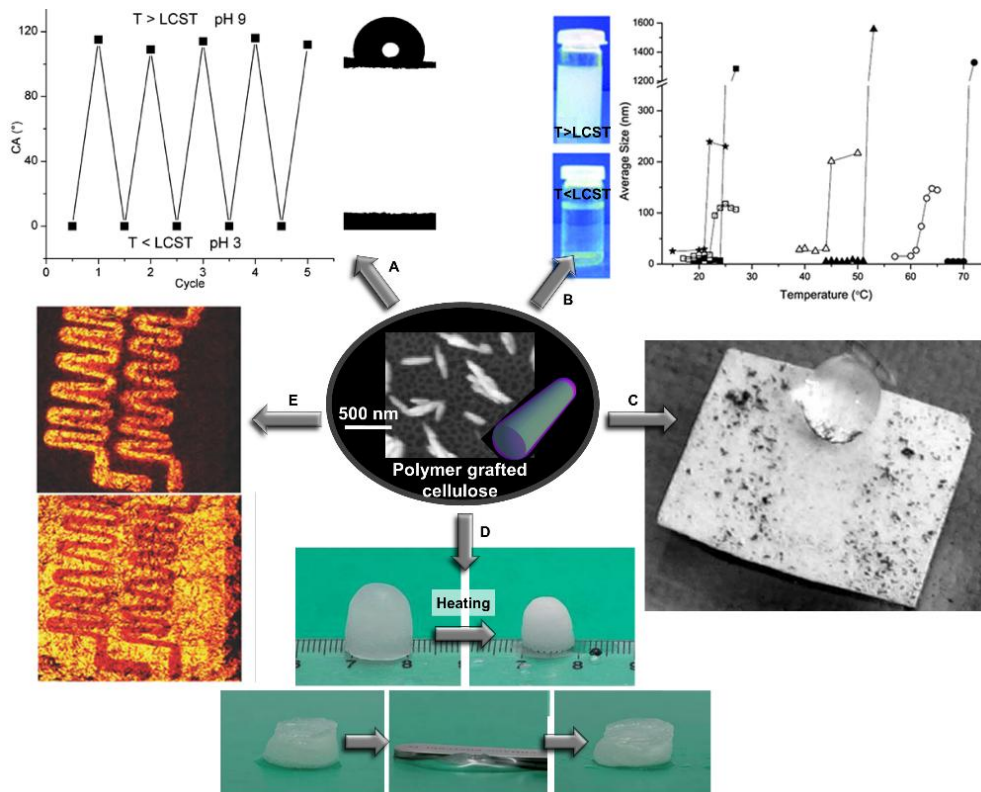


Figure 12: Nanocellulose has been functionalized with polymers for a large variety of applications (adapted with permission from ref. 185, Copyright 2011, American Chemical Society). Examples include A: Temperature and pH responsive sorbancy (adapted with permission from ref. 186, Copyright 2008, American Chemical Society), B: Temperature responsive micelle formation (adapted with permission from ref. 187, Copyright 2011, Royal Society of Chemistry), C: Self-cleaning by a superhydrophobic surface (adapted with permission from ref. 188, Copyright 2006, Royal Society of Chemistry), D: Temperature responsive volume

changes and high elasticity (adapted with permission from ref. 189), and E: ToF-SIMS image of a patterned nanocellulose-fluoropolymer surface (adapted from ref. 190). Images reproduced with permission.

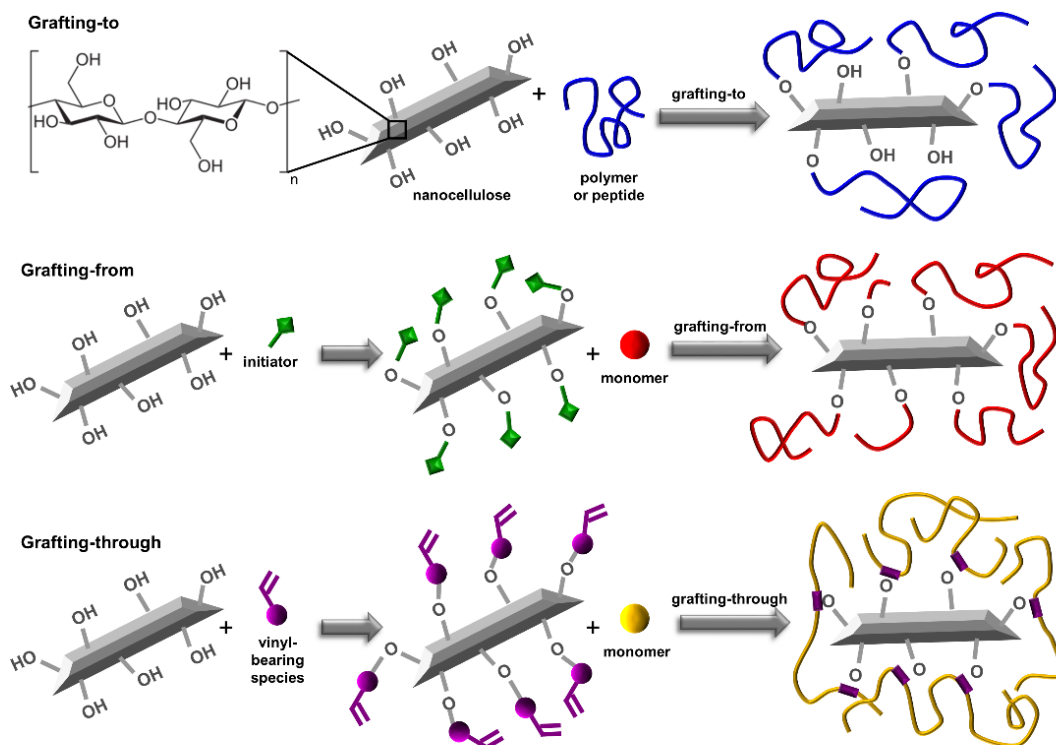


Figure 13: Depiction of grafting-from, grafting-to and grafting-through of polymers to a nanocellulose surface.

Functionalizing nanocellulose with polymers may also proceed *via* electrostatic interaction or macromolecular physisorption to produce the desired effect. As an example, modified spruce O-acetyl galactoglucomannans with a low-degree of oxidation was readily and irreversibly physisorbed to nanofibrillated cellulose in water¹⁹¹. Galactoglucomannan-functionalized

cellulose can improve the tensile strength of paper and can be more readily modified with bioactive molecules than non-modified cellulose.

When a covalent attachment is desired, grafting-to using atom transfer radical polymerization (ATRP), free radical, reversible addition-fragmentation chain transfer (RAFT) and ring-opening polymerization are often applied. The desired end product determines which polymerization method should be used. ATRP is a free-living radical polymerization applied to styrenes, (meth)acrylates, (meth)acrylamides and acrylonitriles. RAFT is another free-living radical polymerization used for the same set of monomers and also for vinyl esters and vinyl amides. RAFT has an additional advantage in that its end group can be easily reduced to a thiol¹⁹², providing a functionality that can be further modified. Ring-opening polymerization is used for cyclic monomers (epoxides, lactones, lactams) and can be achieved using radical, anionic or cationic initiators. Thus ring-opening polymerization is preferred for the production of mechanically reinforced biocompatible polymers¹⁹³.

In grafting-to, it is possible to use classical methods to attach the polymer or peptide to the cellulose surface. For example, cellulose was modified at the C₆ position with thiocarbonylthio species, which were then used as a substrate for a hetero Diels–Alder reaction with diene-containing fluorinated polymers and peptide sequences via both thermal and photochemical activation (Fig. 12E)¹⁹⁰. The photochemical conjugation was used in combination with a mask to spatially control the regions of functionalization.

5.3.1 Atom transfer radical polymerization (ATRP) grafting-to synthesis

A variety of polymers have been grown from cellulose surfaces using ATRP and the lower copper consumption variant, activators regenerated by electron transfer (ARGET) ATRP¹⁹⁴. The

first ATRP report, appearing in 2002, described the reaction of surface hydroxyl groups with 2-bromoisobutyryl bromide, which was used to initiate the ATRP polymerization of methyl acrylate¹⁷⁹. The resulting cellulosic materials were extremely hydrophobic, having a contact angle of 133°.

CNC has been grafted with poly(methyl acrylate) to produce materials dispersible in tetrahydrofuran, chloroform, dimethylformamide, and dimethyl sulfoxide, in contrast to non-modified CNCs¹⁹⁵. A 1,10-carbonyldiimidazole-mediated esterification reaction with the cellulose generated a macroinitiator, which was then used to polymerize methyl acrylate. The polymerization was initiated by Cu(0) coming from copper wire, decreasing copper consumption.

Superhydrophobic cellulose substrates (contact angle >170°) were prepared by growing poly(glycidyl methacrylate) from a cellulose surface functionalized with an ATRP initiator¹⁸⁸ (Fig. 12C). Pendant hydroxyl groups along the acrylate backbone were post-functionalized with pentadecafluorooctanoyl chloride to highly fluorinate the polymer. These materials combined hydrophobicity with surface roughness to achieve the lotus-leaf affect. The hydrophobic/hydrophilic character of functionalized cellulose was used to demonstrate the livingness of a grafted polymer on the cellulose surface¹⁹⁶. First poly(methyl acrylate) was grafted-from the cellulose using ATRP, a second block of 2-hydroxyethyl methacrylate was then grown. The first block rendered the cellulose very hydrophobic, but the second block returned water absorbency to the material.

Hydroxypropyl cellulose was grafted with methyl methacrylate and hexadecyl methacrylate using the grafting-from approach¹⁹⁷. The rheological properties were then studied, showing that the hydroxypropyl cellulose-polymer composites were significantly different from both the

hydroxypropyl cellulose and the polymers alone. The hydroxypropyl cellulose could easily orient itself in the direction of flow, whereas the composite demonstrated complex viscosity. The polymer chains in the composite behaved as if they were entangled or lightly crosslinked, which was not the case for the free polymer.

Temperature and pH stimuli responsive cellulose surfaces were created by grafting with *N*-isopropylacrylamide and 4-vinylpyridine homo- and block copolymers (Fig. 12A)¹⁸⁶. The hydrophobic/hydrophilic character could be reversibly altered by adjusting the temperature and the pH. The responsive behavior could be fine-tuned by adjusting the length of the individual blocks.

Liquid crystalline biofibers were pursued by grafting nanocellulose with 11-(49-cyanophenyl-40-phenoxy)undecyl acrylate, a monomer used to form liquid crystalline polymers. Poly[11-(49-cyanophenyl-40-phenoxy) undecyl acrylate] and poly(methacrylate)-block-[11-(49-cyanophenyl-40-phenoxy)undecyl acrylate] were grafted from cellulose using ATRP, rendering the cellulose hydrophobic¹⁹⁸. The polymerization of methacrylate prior to 11-(49-cyanophenyl-40-phenoxy)undecyl acrylate allowed the second block to attain a narrower distribution in molecular weight, as methacrylate is more flexible and less sterically encumbered.

Cellulose has been grafted with thermo-responsive polymers with a lower critical solution temperature (LCST) tunable between 27 and 73 °C, achieved by modifying the feed ratio of the monomers (oligo(ethylene glycol) methyl ether methacrylate and di(ethylene glycol) methyl ether methacrylate) (Fig. 12B)¹⁸⁷. The LCST was slightly lower when the polymer was bound to the cellulose surface, compared to the free polymer, but the LCST was still tunable. Moreover, the grafted cellulose could form micelles in solution, ranging from 20-40 nm. These thermo-

responsive, biocompatible, stealthy cellulose materials could be interesting for biomedical applications.

ATRP grafting-to cellulosic surfaces has been so well developed that research in this area is now turning towards commercialization. Hydrophobic poly(methylmethacrylate) has been grafted-from a variety of different cellulose surfaces using industrially friendly conditions¹⁹⁹. That is, the solvent-free solution was not deoxygenated before the ARGET ATRP polymerization, minimal washing was required to remove physisorbed polymer, the solution could be recycled for a second cycle and no sacrificial initiator was needed. The reaction required 3 h and was performed between 40 and 80 °C.

5.3.2 Free radical grafting-to synthesis

Cellulose nanocrystals were incorporated into thermoresponsive poly(N-isopropylacrylamide) cryogels (Fig. 12D)¹⁸⁹. Both cellulose that was physically adsorbed and covalently bound, by modifying the surface with polymerizable species, was studied. The physically adsorbed nanocrystals were more hydrophilic and thus it was possible to homogeneously incorporate larger loadings. However, the covalently bound nanocrystals generated gels demonstrating faster diffusion, due to the pore structure, and a higher degree of swelling. When heated above the LCST of the polymer (above 32 °C), the gel reversibly shrunk. The addition of cellulose nanocrystals to the gel allowed the gel to recover its form after compression, in contrast to the pure polyacrylamide gels.

5.3.3 Reversible addition-fragmentation chain transfer (RAFT) grafting-to synthesis

Soluble cellulose was synthesized using RAFT to polymerize acrylic monomers²⁰⁰. A macro chain transfer agent was created by attaching dithioesters to the primary alcohol at the C₆ position of the cellulose backbone, followed by polymerization of either ethyl acrylate or N-isopropylacrylamide.

Poly(2-(dimethylamino)ethyl methacrylate) was grafted from a cellulose surface using RAFT²⁰¹. The polymer chains could be cleaved from the cellulose using acidic conditions, allowing the polymer to be characterized and compared to polymer grown freely in solution. The same procedure and characterization had been applied to polystyrene grafted onto cellulose, showing that the molecular weight of the polystyrene is narrow, but the grafting density and coverage can be improved²⁰².

RAFT has also been used to grow antimicrobial polymers from cellulose surfaces. Alkyl bromides with 8, 12 or 16 carbon atoms were used to quaternize poly(2-(dimethylamino)ethyl methacrylate) chains on the cellulose surface in order to add cationic charges²⁰³. These materials were then tested for antibacterial activity against *Escherichia coli* by incubating bacterial solutions in the presence of the hybrid cellulose materials. It was found that the non-modified and 1-bromooctane quaternized polymer-grafted cellulose displayed the highest antibacterial activity. The longer alkyl chains increased the hydrophobicity of the cellulose, and thus decreased the interaction between the material and bacteria in solution.

5.3.4 Ring-opening polymerization grafting-to synthesis

In an effort to make nanocomposites for tissue engineering repair, biomedical implants, and packing, Li, *et al.* grafted biocompatible polymers with tunable biodegradability from cellulose fibers via ring-opening polymerization²⁰⁴. The surface hydroxyl groups of the cellulose were

activated with Sn(Oct)₂ and then used to open *L*-lactide and ϵ -caprolactone monomers. NIH3T3 cell adhesion and proliferation were greater in the nanocomposite than in pure polyesters. The tensile storage modulus of the nanocomposite was 650 times greater than the polyesters alone, due to intermolecular hydrogen bonding and the entangled cellulose chains. The mechanical properties of the nanocellulose composite were in no way impacted by the molecular weight of the polymer, though the monomer feed ratio and the nanocellulose content did influence tensile strength and Young's modulus.

In a similar poly(caprolactone) grafted nanocellulose material, higher molecular weight was found to have a large effect on the mechanical properties²⁰⁵. Short (8, 100 Da), medium (16, 400 Da) and long (26, 800 Da) polymer chains were grown from microfibrillated cellulose with either 3 or 10 wt% cellulose content. For comparison, the composites reported by Li, *et al.* had a molecular weight of 8,400 Da with 7.4 wt% cellulose content²⁰⁴. The effect of the molecular weight of the grafted polymer was particularly pronounced for high loadings of cellulose. Thus it seems that the type of nanocellulose influences the trends and the resultant properties of the nanocomposite.

5.3.5 Post-polymerization grafting-from

Poly(styrene) and poly(*t*-butyl acrylate) were grafted-from oxidized cellulose microcrystals using an amidation reaction that coupled terminal amines on the polymers with the carboxylic acid groups of the cellulose substrate¹⁸⁵. A grafting density of 60-64 wt% was achieved, which was sufficient to allow the nanocomposite to be soluble in toluene and acetone. The cellulose microcrystals were not degraded by the functionalization method. This method could be applied to a large variety of polymers.

6. Nanocellulose-based materials

The need for sustainable alternatives to conventional petroleum-based materials triggers a growing demand for bio-based materials for applications in all areas of the industry. Nanocellulose has been incorporated into many types of materials, both in pure and composite forms.

6.1 Nanocellulose as a templating agent

The use of nanocellulose as a templating agent has been reviewed recently²⁰⁶⁻²⁰⁸. As explained above, CNCs exhibit chiral nematic properties^{24,38}. Self-assembly can be preserved and translated upon drying or spin coating of such solutions, forming iridescent and birefringent films²⁰⁹. An in depth study of the drying effects has been published by the Vignoli group²¹⁰. The chiral nematic phases, also called cholesteric phases, observed in the CNC solutions can be described as the superimposition of planes in which all CNC rods are directionally parallel, while the overall direction of the rods from one plane to the next is tilted²⁴. This results in helicoidal structures, acting as a 1D photonic structure able to reflect polarized light with a wavelength corresponding to the pitch of the CNC structures. These phases were shown to be tunable using a magnetic field²¹¹. These phases have been used as templates in several schemes in order to afford ordered nano- and mesostructured materials²⁰⁷. The MacLachlan group developed a method to use this pattern to template silica morphology by evaporation- induced self- assembly of CNCs with silica precursors to obtain composite films with chiral nematic structures. The removal of CNC afforded chiral nematic mesoporous silica²¹², featuring iridescence (Fig. 14). Interestingly, the reflected color of the obtained films could be tuned between the UV and the IR region, by varying the concentration of the alkoxy silane precursor. Organosilica, in the form of ethylene-

bridged mesoporous silica were also synthesized using this method to afford flexible and iridescent films²¹³. In another scheme, the chiral nematic CNC/silica composites were pyrolyzed before silica was removed by alkaline treatment²¹⁴. This resulted in glassy black films composed of freestanding mesoporous carbon. Graphitic C₃N₄ was also produced in a similar fashion for application in H₂ evolution²¹⁵. CNC has also been used as a hard template to form porous hematite by casting a sol containing CNC and an iron salt, which then gelled upon drying²¹⁶. Mesoporous titania can not be produced by the same method, yet CNC structured silica was used as a template in itself to cast TiO₂ with chiral nematic ordering²¹⁴. The chiral nematic structure of CNCs was also applied to the development of soft films. By crosslinking latex nanoparticles with CNC upon synthesis, the Kumacheva group produced a soft film while preserving the CNC photonic properties²¹⁷. Chiral plasmonic films were also made using CNCs as templates. In this case, gold nanorods were incorporated into a CNC chiral nematic phase. The resulting materials obtained by slow drying still featured chiral order, resulting in chiral photonic crystal properties with circular dichroism²¹⁸. Self-assembled CNCs have also been incorporated into polymer matrices, where tactoid formation and dynamics were observed by scanning electron and confocal optical microscopy^{219,220}.

Mesoporous metal oxides prepared *via* CNC templating offer an excellent entry into highly catalytic materials. TiO₂-coated nanocellulose materials with high porosity possess photocatalytic activity, demonstrating potential in water purification^{221,222}.

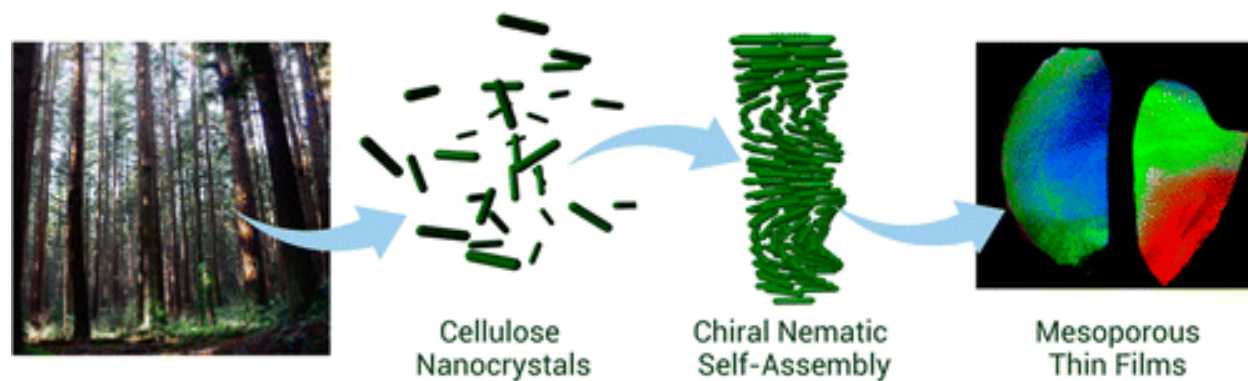


Figure 14: From cellulose nanocrystals chiral nematic self-assembly to the formation of mesoporous materials. Reproduced with permission from ref 207, Copyright 2014, American Chemical Society.

6.2 Hydro- and aerogels of nanocellulose

The field of hydro- and aerogels of nanocellulose has been extensively reviewed by Cranston and coworkers in 2017²²³. The preparation, physicochemistry, properties, morphologies and applications of nanocellulose-reinforced foams and aerogels have been recently reviewed²²⁴. These types of materials are being intensely investigated because nanocellulose is a particularly suitable building block to form gels, because of its combined lightweight and toughness. The hydrophilic surface of these nanocelluloses allows them to serve as building blocks in hydrogels, where they can be cross-linked via hydrogen bonding, covalent bonding or ionic interactions into three-dimensional networks with a large array of different metals, organic species and polymers.

Hydrogels are highly hydrated chemically or physically cross-linked networks that can be produced from nanocellulose alone, or in hybrid structures with additional polymers. Surface functionalization and self-assembly processes can be used to fine-tune the properties of the hydrogel. CNCs gel in water above a concentration of 10 wt%²²⁵. Controlling the ionic content of water changes CNC gelation behavior, as CNC is itself a charged species²²⁶. Gelation could

even be switched, through the addition of imidazoles to the CNC aqueous suspension²²⁷. The CNC suspension turned from a gel (produced from bubbling the solution with CO₂) to a liquid after N₂ gas exposure. CNCs physically or chemically modified with polymers improved the hydrogel properties. For instance, CNCs were used to reinforce polyvinyl alcohol hydrogels^{228,229}. Such systems were prepared with a CNC content up to 7 wt% and showed excellent resistance against microorganisms²³⁰. In another scheme, CNCs were cross-linked with poly(oligoethylene glycol methacrylate) via hydrazone. Hydrogels were made by freeze casting, and by varying the temperature and composition of the hydrogels, different anisotropic structures could be obtained (Fig. 15)²³¹.

CNFs, as longer and more flexible forms of nanocellulose, are more amenable in their pure form to the formation of hydrogels. CNFs create more elastic gels than CNCs. CNFs will afford such structures at concentration ranges of 0.05 to 6 wt %²²³. Hydrogels of CNF have been used as a starting material to spin fibers with excellent strength²³². CNCs, with their high rigidity and relatively low anisotropy, are well suited to act as templates for aligned structures (*e.g.* artificial muscle-like materials) while providing toughness and flexibility²²³. With collagen, for instance, this afforded networks with mechanical properties similar to tendon and ligaments and excellent biocompatibility²³³. CNCs and CNFs can be combined to tailor the pore structure of a material²³⁴.

Aerogels are highly porous and light. They are the counterpart of hydrogels with gas in place of liquids. The mechanical properties of CNCs allow the formation of aerogels with much improved mechanical resistance compared to inorganic oxide based systems²³⁵. They feature high surface areas, with values up to 605 m²/g²³⁶. A seminal example of a pure CNC aerogel was produced by simple CNC aqueous solution sonication followed by solvent exchange with ethanol

and supercritical CO₂ drying²³⁶. Aerogel mechanical properties could be improved by chemical crosslinking aldehyde-modified CNCs with a hydrazide²³⁵. Such aerogels feature low density, absorbance²³⁵, insulation²³⁷ and supercapacitor properties²³⁸. Aerogels were also created with imprinted periodic structures based on CNCs²³⁹.

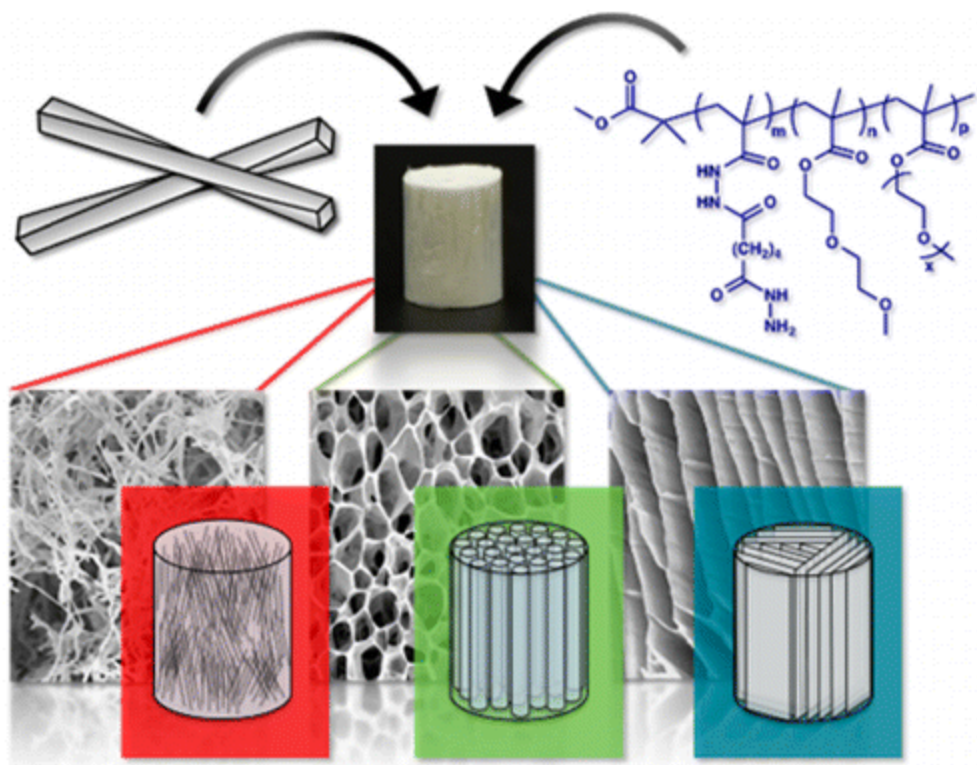


Figure 15: Poly(oligoethylene glycol methacrylate)/CNC hybrid hydrogels produced by freeze-casting, featuring direction dependence. Reproduced from reference 231, Copyright 2016, American Chemical Society.

The mechanical properties of nanocellulose aerogels can be improved either chemically or through processing, *e.g.* through freezing-solvent exchange-ambient drying²⁴⁰. For example, TEMPO-modified CNFs were processed into an aerosol and post-synthetically cross-linked with methylene diphenyl diisocyanate²⁴¹. The cross-linking improved the thermal stability and the

strength of the aerogel. It also changed the hydrophobicity, rendering the material suitable for chloroform separation from water. TEMPO-oxidized CNFs have been shaped into aerogel microspheres using polyamide-epichlorohydrin resin as a crosslinker²⁴². These aerogels were capable of adsorbing 120 g/g H₂O and could be used to extract phenol and copper. They were easily recovered and regenerated by simply squeezing and rinsing the microspheres.

Graphene oxide-nanocellulose composites have been formed into aerogels^{8,243} and membranes²⁴⁴. The pore structure of the composite allows for a good flux while maintaining excellent strength and flexibility.

6.3 Nanocellulose-nanocarbon composites

Nanocellulose has been combined with nanocarbons, *i.e.*, carbon quantum dots, carbon nanotubes and graphene-related materials, to add functionality to cellulose-based materials (Fig. 16). In doing so, nanocellulose possesses attractive properties previously mentioned: biocompatibility, biodegradability, non-toxicity, and excellent mechanical properties particularly for use in cloths: durability, flexibility, soft texture, breathability and deformability. Thus, nanocellulose is typically used as a support for nanocarbons, which are otherwise difficult to process into either a material or a free-standing substrate due to difficulties with aggregation and processing. Nanocellulose/nanocarbon composites have much higher mechanical strength than polymer/nanocarbon materials²⁴⁵. Nanocellulose is inexpensive compared to carbon nanotubes and graphene-related materials. By doping cellulose with nanocarbons, a percolation threshold can be reached, rendering the entire fabric electrically conductive for a fraction of the price of the pure nanocarbon material. The chemistry previously developed, such as surface modification techniques to increase cellulose solubility²⁴⁶, have been applied to the fabrication of the

cellulose-nanocarbon composites, but it has also been possible to create stable dispersions without such pre-treatments thanks to favorable interactions between the nanocarbon and the cellulose which interrupt the tendency for both cellulose and nanocarbons to auto-aggregate²⁴⁷. Cellulose nanocrystals can also be used to stabilize the surface of polymer latexes^{248,249}, for example through a Pickering emulsion²⁵⁰. Most applications envisaged for nanocarbon-nanocellulose materials require mechanically robust materials with electrical conductivity, with biocompatibility being often a desirable quality. The composite materials will now be presented, separating nanocarbons into carbon quantum dots, carbon nanotubes and graphene-related materials.

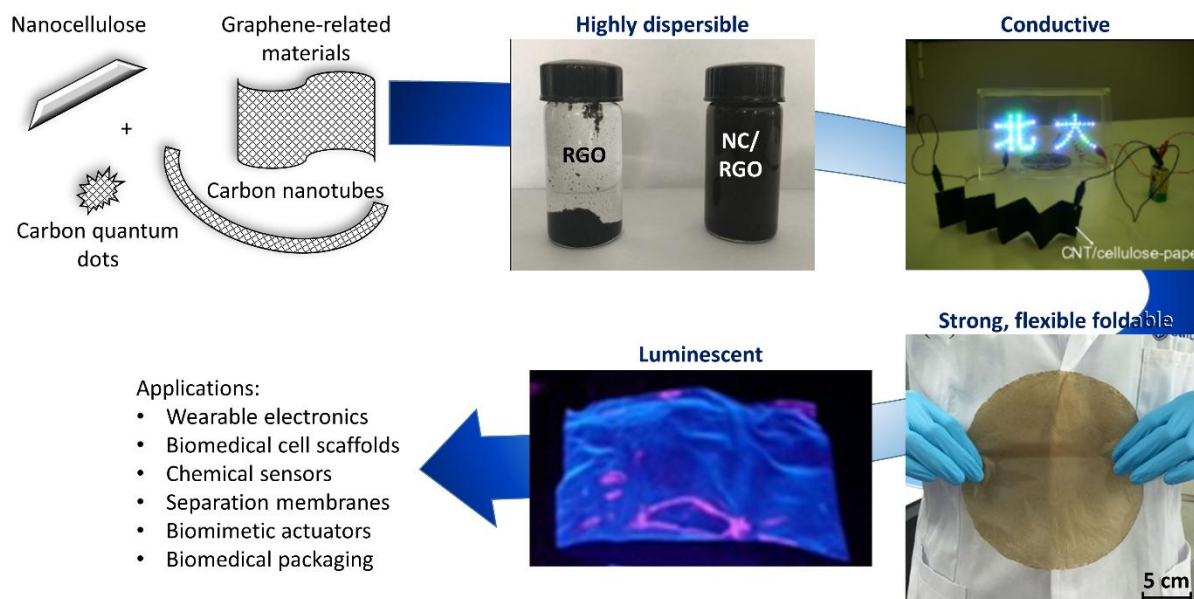


Figure 16: Nanocellulose in many different forms has been combined with carbon nanomaterials such as carbon quantum dots, carbon nanotubes and graphene-related materials. The composite materials are typically produced as flexible, durable films or fabrics, thanks to the high dispersibility of the cellulose-nanocarbons that can stay stable in suspension for days or weeks (adapted with permission from ref. 251, Copyright 2016, Elsevier). Graphene-related materials

and carbon nanotubes add electrical conductivity to these composites (adapted with permission from ref. 252, Copyright 2008, Elsevier). The excellent, flexible mechanical properties of nanocellulose and nanocarbons is preserved upon their combination (adapted with permission from ref. 253, copyright Creative Commons (<https://creativecommons.org/licenses/by/3.0/>)). Carbon quantum dots render the composite luminescent (adapted with permission from ref. 254, Copyright SpringerLink). These properties recommend such composites for application in wearable electronics, sensors, biomedical uses and ecological packaging.

6.3.1 Nanocellulose-carbon quantum dot composites

Carbon quantum dot research began in 2004 and has been an intense area of research ever since because carbon quantum dots are fluorescent, non-toxic and readily water-dispersible²⁵⁵. Moreover, carbon quantum dots can be obtained from a host of different sources, from food, to standard petro-chemicals to cellulose. The optical properties of carbon quantum dots are intriguing because different studies often produce contradictory results. For instance, carbon quantum dots have been synthesized from microcrystalline cellulose using an ionic liquid, 1-butyl-3-methylimidazolium chloride, as a catalyst²⁵⁶. These carbon quantum dots exhibited *excitation-dependent* fluorescence emission behavior. Carbon quantum dots with *excitation-independent* fluorescent properties have been synthesized from the same precursor, microcrystalline cellulose, but using harsher conditions, that is a concentrated solution of sulfuric acid and higher temperature (200 °C instead of 100 °C)²⁵⁷. Perhaps the excitation-independent behavior is a sign of a more homogeneous batch of carbon quantum dots. The quantum yield of the excitation-independent carbon quantum dots was higher (32%) than that of the excitation-dependent materials (4.7%). Much work to understand the phenomena behind the optical

properties of carbon quantum dots remains, but in the meantime a couple of efforts have been made to incorporate carbon quantum dots into materials.

A cellulose fabric was pyrolysed under argon at 1000 °C to produce a conducting carbon cloth²⁵⁸. This cloth could be used to produce hydrogen and oxygen through water electrolysis. Because of the highly disordered structure and the high conductivity of the cellulose cloth, hydrogen generation could be performed using low voltages (0.2 V). At low voltage only hydrogen was produced, where above a threshold voltage both hydrogen and oxygen were liberated. During electrolysis carbon quantum dots of 5-7 nm were produced within the cloth which exhibited excitation-dependent fluorescence. In contrast to the cellulose cloth, the graphite anode did not form carbon quantum dots, even at higher applied voltages.

Self-standing cellulose/carbon quantum dot composite films were prepared which demonstrated transparency and photoluminescence²⁵⁴. A regenerated film of microcrystalline cellulose was prepared and then dipped into a solution of pre-prepared carbon quantum dots. The maximum photoluminescent intensity occurred at 419 nm with long-afterglow luminescence that lasted for over 10 minutes. By adding carbon quantum dots to the regenerated cellulose film, the film became softer, but still demonstrated excellent mechanical properties.

6.3.2 Nanocellulose-carbon nanotube composites

Carbon nanotubes have excellent mechanical strength, high electrical and thermal conductivities, high stability and high aspect ratios. They increase the mechanical strength of the cellulose composite and the composite becomes conductive as long as there are a sufficient number of junctions between the dispersed carbon nanotubes. Carbon nanotubes and cellulose have a high affinity for one another, making them natural partners in composite materials. IR

spectroscopy has shown that the interaction between carbon nanotubes and cellulose is noncovalent and nondestructive²⁵⁹. Carbon nanotubes are notoriously difficult to disperse in water and organic solvents; however, their mixture with cellulose nanocrystals allows them to be readily dispersed in water²⁶⁰. Similarly, Raman spectroscopy shows that carbon nanotubes disrupt the intra- and intermolecular hydrogen bonding between native cellulose strains that are responsible for its typical insolubility in water²⁴⁷. Cellulose-carbon nanotube mixtures remained as stable aqueous suspensions for months at pH 6 to 10. A more recent investigation has shown that a fluctuation in the counterion species on the nanocellulose surface induces polarization in the sp² network of the nanocarbon²⁶¹. The higher the surface charge on the nanocellulose, the better the interaction with the nanocarbon and the better the dispersive qualities.

Carbon nanotube-cellulose composites have been predominately investigated as conductive papers^{252,262,263} and conductive fibers for wearable electronics²⁵⁴, with one report of an aerogel²⁶⁴. Individual carbon nanotubes are prone to wrap around the cellulose fibers, forming a pulp that can be cast into a paper with uniform electrical conductivity using standard papermaking technology²⁵⁴. The composite paper had electromagnetic interference shielding efficiencies superior to metal-printed circuit-boards. Moreover, by adding carbon nanotubes to cellulose, the tensile strength and the stiffness of the paper increased, producing a strong, flexible material. The increase in ductility is thought to be due to having both short and long entangled objects: the cellulose nanocrystals prevent the carbon nanotubes from aggregating, thus preserving junctions in the extensive nanotube network²⁴⁶.

Cellulose-carbon nanotube composites have been used as foldable, lightweight, self-standing scaffolds for both titania²⁶⁵ and polyaniline²⁶⁶ for use as supercapacitor electrodes and as biomimetic actuators and biosensor. Polyaniline and carbon nanotubes are excellent materials for

conducting electrodes, but their combination yields poor films due to problems with carbon nanotube aggregation²⁶⁷. Cellulose is an excellent support, where the cellulose and carbon nanotubes are premixed and then aniline is polymerized from the surface of these two materials to form a porous composite. By adding polyaniline, the electrode gains a larger integrated cyclic voltammetric area and a larger specific capacitance²⁶⁸. If this polymer-carbon composite is further doped with ClO_4^- and Cl^- ions, the surface conductivity is increased by an order of magnitude, creating a low power consumption actuator²⁶⁹. Low power consumption actuators could be used in microwave-driven biological devices.

6.3.3 Nanocellulose-graphene-related material composites

Graphene has extraordinary electronic transport properties and high electrocatalytic activities. Cellulose-graphene composites are highly porous, with excellent shape retention. For instance, these composites can retain encapsulated polymers, such as polyethylene glycol, above the polymer's melting point and while under compression²⁷⁰.

Flexible electrodes and flexible supercapacitors are the major targeted application of cellulose-graphene materials. Nanocrystalline cellulose-graphene membranes have impressive resilience, flexibility and mechanical strength²⁷¹, stimulating interest in these composites for wearable electronics. As with cellulose-carbon nanotubes, cellulose-graphene-related materials composites have been studied both on their own and after incorporation of an electroactive polymer. The nanocellulose delivers the needed tensile strength, the graphene oxide a high electrical conductivity, and the polymer a pseudocapacitance. The application of nanocellulose/graphene/polymer systems as supercapacitors are discussed in more detail in Section 7.7.

Bacterial cellulose and graphene oxide were organized into stacked layers in order to build ion permeation membranes that selectively retained large molecules and positively charged ions²⁷². These composite membranes showed resistance to mechanical stress up to 64.5 MPa, which is twice the tensile strength of either cellulose or graphene oxide membranes alone. The composite was stable in water and could selectively separate organic and inorganic ions due to the size of the porosity and the charge of the graphene oxide. More recently it has been demonstrated that a graphene/BNC composite can be directly produced by culturing the bacteria (*Gluconacetobacter hansenii*) with graphene flakes²⁷³. This method produced highly entangled BNC and graphene with excellent mechanical properties, electrochemical properties and cycling stability.

Graphene oxide-cellulose composites have been made as sensitive and selective solvent sensors, based on detecting a change in capacitance upon sorption²⁷⁴. The adsorption of ethanol, acetone, toluene, chloroform and n-hexene could all be distinguished from one another based on the relative capacitance change. A similar study measured the resistivity of reduced graphene oxide-cellulose-latex composites, showing a strong and cyclable response to toluene and chloroform, but an insensitivity to dimethylformamide and acetone²⁵¹. The percolation threshold was half that of other graphene composite materials.

Biosensors and scaffolds using electrical stimulation have been envisioned using graphene-related materials. However the hydrophobicity of this class of carbon material is problematic. By designing a cellulose-graphene composite not only is the hydrophobicity addressed, but the mechanical properties are also improved. Graphene oxide films were functionalized with bacterial cellulose fibers, reducing the contact angle from 93 to 14°²⁷⁵. These hydrophilic films

were then used as supports for cell adhesion, growth and proliferation. The composite had much better cellular response than the graphene film alone.

In another scheme, CNCs were used as a additive to help improve dispersion of carbon fibers with graphite in order to achieve high conductivity²⁷⁶.

Through these examples, it is clear that nanocarbons and nanocellulose are highly compatible, increasing the mechanical properties over the individual components and yielding excellent properties in domains ranging from electrical conductivity, to ion permeability, to chemical sensing. The role of the cellulose is always the same: to provide a strong, flexible scaffold for the nanocarbon, allowing the desirable properties of the nanocarbon to be integrated into a non-toxic, environmentally friendly device.

6.4 Nanocellulose-organic polymer matrices

Nanocellulose has been widely applied as a filler to reinforce polymer composites. The role of the interfacial layer on the mechanical reinforcement has been explored in depth. The assembly occurs *via* hydrogen-bonding of parallel chains between the native cellulose and crystalline domains. Due to this structure and the high surface area of the composites, if load is effectively transferred to the hard reinforcing phase, then the modulus of the composite is similar to that of randomly orientated rigid CNC with high strength and modulus²⁷⁷.

Nanocellulose and organic polymeric materials form composites with a complex network of inter- and intramolecular hydrogen bonds, excellent mechanical properties and the ability to assemble themselves into a tight, high-strength and high-stiffness structure. Nanocellulose has been used to reinforce a wide range of polymer matrices, such as poly(styrene-co-butyl acrylate)²⁷⁸, poly(vinyl acetate)²⁷⁹, poly(ethylene oxide-co-epichlorohydrin)²⁸⁰, poly(styrene-co-

butadiene)²⁸¹, polyurethane²⁸², and epoxy resins²⁸³. A number of methods such as compression molding²⁸⁴, freeze drying, hot pressing²⁸⁵, and solution impregnation²⁸⁶ are employed for the preparation of these organic composites, however, casting is the most common technique used²⁸⁷⁻²⁸⁹. Fig. 17 exhibits the recent reports of nanocellulose-based organic polymer composites and their different applications.

It can be difficult to obtain a homogeneous composite when nanocellulose is added to a viscous polymer either in solution or in a melt. However, nanocellulose can be easily homogeneously dispersed in the much less viscous monomer solution. Hees, *et al.* first impregnated the nanocellulose with bisiminopyridine iron(II) complexes, an excellent catalyst for ethylene polymerization at low pressures²⁹⁰. High density poly(ethylene) was then grown from the nanocellulose, forming a homogeneous composite with superior properties to melt cast high density poly(ethylene) and nanocellulose.

Both the reinforcing phase and reinforced matrix are composed of cellulose in all-cellulose composites²⁶. They exhibit excellent interfacial compatibility and are fully biocompatible and biodegradable, in addition to being lightweight, with high strength and high stiffness. In these composites, the matrix is dissolved and then cellulose is precipitated, whereas the reinforcement is composed of undissolved or partly dissolved cellulose microstructures or nanostructures. In order to prepare all cellulose composites, two different strategies are typically employed: (1) The two-step method²⁹¹⁻²⁹⁴, in which a solution of cellulose obtained by complete dissolution of a portion of cellulose is reinforced with some additional cellulosic material. (2) The one step method^{295,296}, where a partial (or selective) dissolution of cellulosic material forms a matrix phase *in situ* around the remaining fiber core.

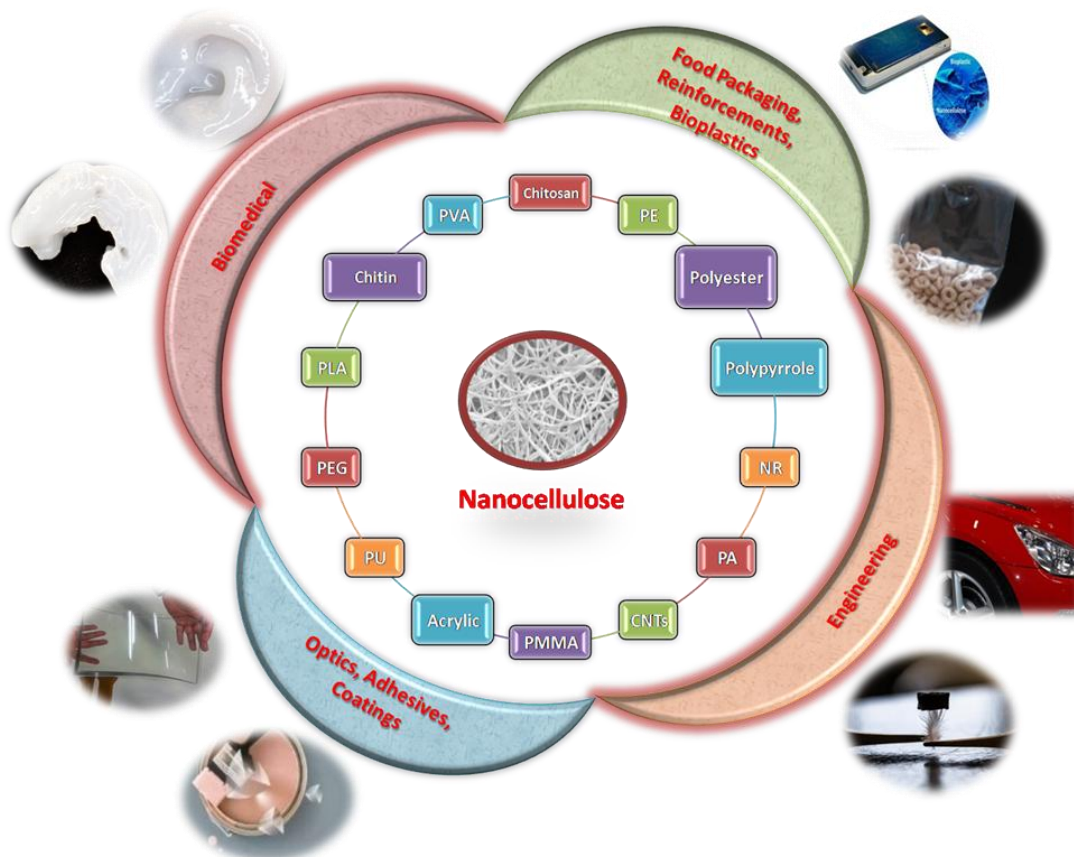


Figure 17: A schematic representation of the recent reports of nanocellulose-based organic polymer composites and their applications.

Thermal, mechanical and optical properties are enhanced in the composites formed by incorporating nanocellulose into the polymer matrix. For example, in a recent work, Tan, *et al.* prepared a homogeneous dispersion of cellulose nanofibers in waterborne acrylic coatings with improved properties and equivalent transparency²⁹⁷. The composite coatings showed a maximum 500% improvement in Young's modulus, a two-fold improvement in hardness and a 35% reduction in abrasion loss as compared with those of neat coating. Both thermosets (epoxy,

polyurethane) as well as thermoplastic polymers (PE, PP, PPC, PVA, PLA, and PEO) have been reinforced with nanocellulosic materials to obtain quality products¹⁸⁰.

Previously we discussed the interest of nanocellulose-polyaniline-graphene related materials composites, but the simple nanocellulose-polyaniline composite is also interesting as a conductive material. Polyaniline alone is brittle, rigid, has poor processability, and easily aggregates into large particles^{298,299}. Nanocellulose is an ideal candidate to reinforce polyaniline. It can provide greater interfacial area and strong interactions with the matrix. These tunable electrically conducting biocomposites have potential applications in anti-static, electrochromic devices, electromagnetic interference shielding, sensors, electrodes, and storage devices. Relatively, high specific capacitance of about 161.9 F/g could be achieved for the NC/polyaniline composite, benefitting from the large electrochemical activity of polyaniline and a good range of structural stability due to the synergistic effects in the bionanocellulose. Chen and co-workers have published a series of papers on the *in situ* preparation, and the electro-analytical studies of polyaniline-nanocellulose composites³⁰⁰⁻³⁰³. In general, the thermal stability and conductivity of nanocellulose increased upon loading with polyaniline. The significant increase in conductivity results from the dense coverage of tiny polyaniline particles on the surface of cellulose nanowhiskers and the formation of an interconnected network. The high conductivity of the NC/polyaniline composite attributes to the homogenous formation of a polyaniline layer on the surfaces of the cellulose nanowhiskers.

Lee, *et al.* have reported the interfacial polymerization of aniline from bacterial cellulose. This method does not use any template or surfactant molecules, while the BC serves as a support. The stiffness and brittleness of polyaniline is compensated by the more ductile cellulose³⁰⁴.

The nature of the interaction between CNCs and polymeric materials has been further studied by the group of Ikkala using cryo transmission electron microscopy³⁰⁵. Dendronized glycopolymers featured multivalent interactions with CNCs and polymer wrapping.

6.5 Nanocellulose-inorganic nanoparticle composites

Organic-inorganic hybrid nanomaterials often have improved physicochemical properties including thermal, mechanical and optical properties, and conductivity, due to the synergetic effect of the combined physical and chemical interactions between the organic and inorganic components^{277,306}. Incorporation of cellulose nanowhiskers and nanofibers as an organic reinforcing agent in various matrices for the development of composite materials has led to the preparation of novel materials³⁰⁷. For instance, nacre-like iridescent films were prepared by infiltrating nanocellulose layers with CaCO_3 ³⁰⁸. Cellulose-metal nanocomposites, in general, show excellent antimicrobial activity, good chemical and biosensing abilities (for instance, DNA biosensors)³⁰⁹; protein adsorption properties, biodegradability, exhibit enhanced mechanical properties and good electrical and electronic conductivity (10^{-6} to 10^3 S/cm)^{310,311}.

Mineral nanoparticle-reinforced, metal nanoparticle-reinforced, metal/mineral nanoparticle-reinforced and nanofiber-reinforced polymer matrix nanocomposites have been reported using cellulose. Nanocellulose has been combined with a diverse set of inorganic nanoparticles: oxides (*e.g.* Fe_2O_3 , ZnO , SnO_2 , TiO_2 , Ag_2O , CuO), zeolites, clays, including montmorillonite, other layered silicates, such as vermiculite and mica and talc, halide nanoparticles (*e.g.* AgCl), metal nanoparticles (*e.g.* Au , Ag , Cu , Fe , Pt , Pd , Ni , Se , Ru , Ag-Au , Cu-Pd), quantum dots (*e.g.* CdS , ZnSe , CdSe/ZnS), and nanometal-metaloxide blends ($\text{Cu-Co/Fe}_2\text{O}_4$, Ag/ZnO , Fe/SnO_2 , $\text{Ag/Ag}_2\text{O}$, Ag/TiO_2 , aminosilica-coated $\text{Yb-NaYF}_4/\text{Er}$)³¹²⁻³¹⁹. A schematic representation of the

various types of organic-inorganic hybrid materials of nanocellulose with inorganic materials with corresponding applications is shown in Fig. 18.

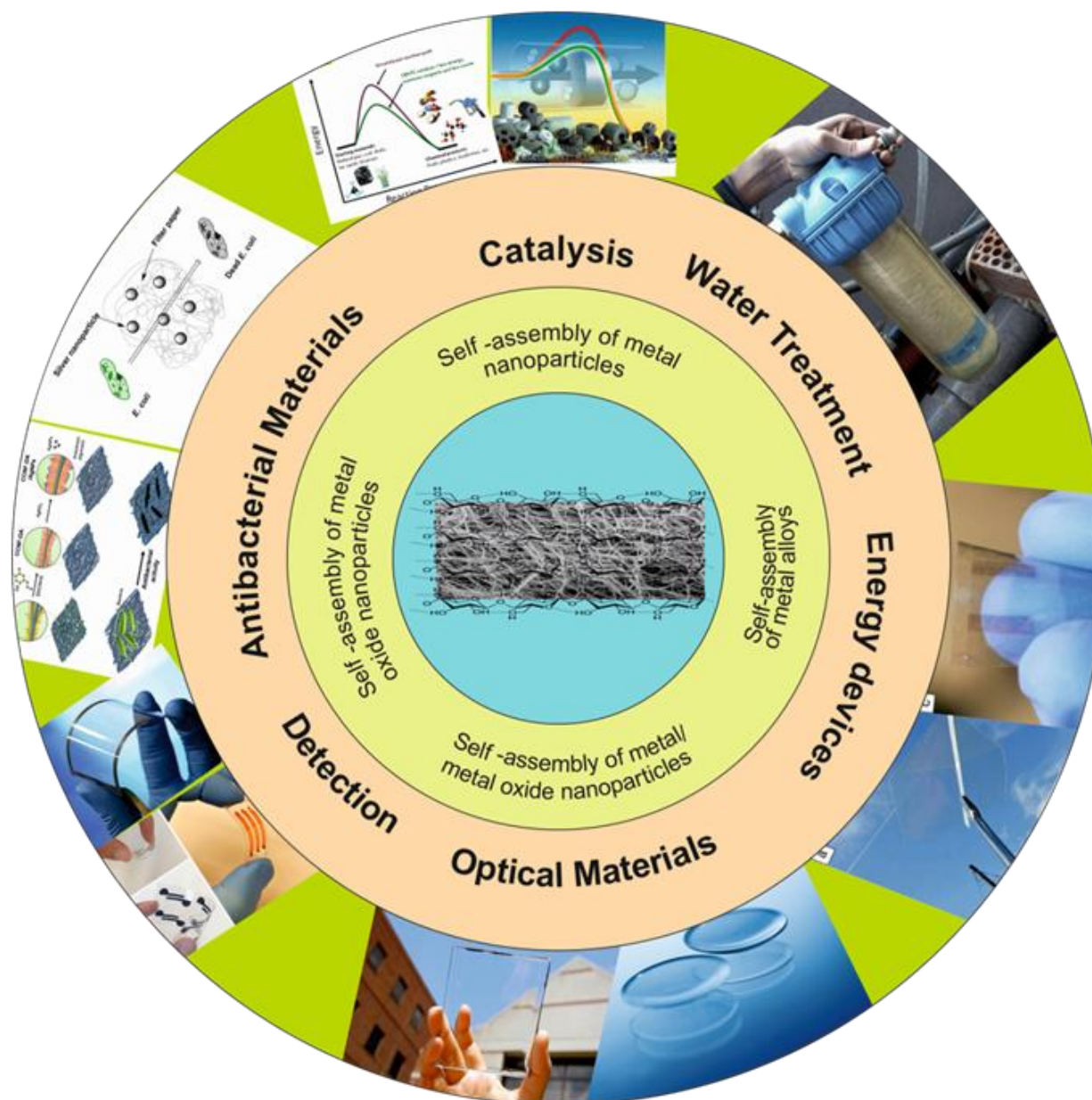


Figure 18: Various types of hybrid materials result from combining nanocellulose and inorganic materials. The possible applications depend in large part on the properties of the inorganic component, with nanocellulose providing structure and mechanical properties.

There are technical challenges to incorporate cellulose nanoparticles into a hybrid material, as an effective composite requires a good integration of the filler particles into the matrix. Matrix incorporation becomes more difficult when dry cellulose nanoparticles are needed, for instance, during their introduction into hydrophobic polymeric matrices. In general, cellulose nanoparticle production, using either microorganisms or extraction, are performed in aqueous media. Drying cellulose nanoparticles *via* lyophilization can result in their agglomeration³²⁰. In conventional methods of polymeric composite production, mixing the filler and polymeric matrix occurs in the melted state. In order to obtain good nanocellulose dispersion, the methods of nanocomposite production must occur in aqueous media, which effectively avoids the drying of cellulose nanoparticles after extraction/production.

The most common methods to prepare nanocellulose-inorganic hybrid composites include liquid phase deposition, layer-by-layer deposition, doping casting ionic liquid/cellulose dispersions, and atomic layer deposition. In the case of a metal nanoparticle-nanocellulose hybrid composite, three approaches are usually applied for synthesis *via* reduction using (a) an external agent, (b) a reducing functional group introduced onto the nanocellulose surface, and (c) the intrinsic reductive properties of nanocellulose hydroxyl and aldehyde groups³²¹⁻³²³. In a unique example, by combining CNCs with Ag wire in the presence of light, the CNCs were able to grow small, catalytically active Ag nanoparticles from their surface³²⁴. The light is thought to be responsible for dissolving the Ag wire, providing a certain concentration of Ag⁺ ions in solution. The CNC surface hydroxyl groups are oxidized to carbon-oxygen double bonds while reducing the silver on the surface. Ruthenium nanoparticles, which are notoriously difficult to produce using common RuCl₃ as a precursor, were formed through a combination of CNC surface and chemical oxidation³²⁵.

7. Properties and applications of nanocellulosic materials

Many factors influence the properties of nanocellulosic materials: the maturity of the fibers, the origin of the plant matter, their chemical composition, the separation process employed, defects in the fibers (*e.g.* pits and nods), and the environmental conditions in which the plant was grown. The mechanical, optical and gas barrier properties of nanocellulosic materials have been well studied, bringing them to a mature stage in terms of their applications (Fig. 19). A number of reviews go into great detail about the applications of nanocellulose^{3,326,327}, for example as supports for metal nanoparticle catalysts³¹³, in printed electronics³²⁸, in devices and energy applications³²⁹, in textiles³³⁰ and in biomedicine^{331,332}. We present the current state of the art in optimized nanocellulose properties and how these properties have been applied, illustrated with the most exciting recent examples.



Figure 19: The applications of nanocellulosic materials range from paper to energy harvesting materials.

7.1 Mechanical reinforcement

Compared to glass fibers, low density nanocellulose fibers have high tensile modulus strength, with a Young's modulus around 70 GPa³³³ at a density around 2.6 g/cm³. Nanocellulose is commonly used in composites with the aim of replacing glass fibers. For comparison, Kevlar³³⁴ has a Young's modulus between 60–125 GPa and a density of 1.45 g/cm³, and steel boasts a modulus of 200–220 GPa with a high density of 8 g/cm³. However, when specific Young's modulus is used, which accounts for density, nanocellulose measures 65 J/g for microfibrils and 85 J/g for nanocrystals, whereas steel provides just 25 J/g. Thus when the weight of a material is of importance, the mechanical properties of nanocellulosic materials should be used in preference to steel in reinforced polymer composites. The fiber dimensions, fiber aspect ratio, the volume fraction of the cellulosic matter, the fiber orientation, its adhesion to the matrix and an effective interfacial stress transfer all affect the properties of a cellulosic fiber-reinforced nanocomposite.

Nanocellulose was originally attractive as reinforcements in composites due to the high stiffness and strength of the cellulose crystals and fibers. Due to environmental concerns, nanoscale cellulosic materials have been used as fillers and reinforcements in place of synthetic fibers. The larger surface area, superior mechanical properties and lower occurrence of defects compared to micron sized additives make nanocellulose a better candidate for incorporation into reinforced composites. As reinforcements in polymer matrices, nanocellulosic materials have successfully replaced many of the conventional reinforcements due to their low cost, low density, biodegradability and the fact that they come from a renewable resource. Classical paper made from wood pulp can be transformed into a high strength paper by incorporating bacterial nanocellulose into the composition³³⁵. Hervy, *et al.* recently suggested that a high loading of

nanocellulose in reinforced epoxy composites would produce materials with “greener credentials” than the best bio-derived polymers on the market³³⁶. He, *et al.* introduced microcrystalline cellulose and dialdehyde cellulose to reinforce epoxidized soybean oil, creating a thermosetting polymer system³³⁷. The dialdehyde cellulose was well-dispersed in the epoxidized soybean oil polymer. As there was a favourable interaction between the filler and the matrix, the resulting composite possessed high toughness and thermal stability. The increased storage modulus and glass transition temperature indicated that the cellulose fillers impart stiffness to the composites. The acetylation of CNC showed to help mechanical reinforcement of polyester-based nanocomposites.³³⁸ Table 4 lists a literature survey of the CNCs, CNFs and BCs used to reinforce composites.

Nanocellulose fibers are added to cement to decrease shrinkage during drying, to increase sound absorption and to produce a more environmentally friendly, less hazardous material. Such composites are an alternative to asbestos. However, nanocellulose-cement matrices are less durable due to the hydrophilicity of the cellulose component and its lower chemical stability. Moreover, the cement and the cellulose components can lose adhesion with time, leading to crack formation. Two composites preparation methods were used: 1. cellulose fibers were coated with bacterial nanocellulose and 2. bacterial nanocellulose was injected into the cement composite as a gel³³⁹. Depending on the way in which the bacterial nanocellulose was incorporated, the surface basicity, degree of hydration, surface roughness and fiber mineralization were favorably impacted.

Table 4: Recent literature of CNCs and CNFs as reinforcement materials.

Composite	Preparation method	Measure of filler loading	Advantages/Properties of composites formed	Applications	Reference
Reduced graphene (rGO)/bacterial cellulose composite	Solution incorporation of GO into BC and in-situ reduction of graphene oxide (GO) incorporated to BC by hydrazene	Variable wt% of rGO nanoparticles formation in the medium	Enhanced thermal stability, average conductivity, decreased hydrophilic property increase in the contact angle, tensile strength, and Young modulus.	NEA	4a
APS-CNF waterborne acrylic resin/polyester blend	Solvent casting	0.08–0.48 wt % APS: Range of compositions including 5, 10, 15, 20 wt% CNF	High transparency, 500% improvement in Young’s modulus, two-level improvement in hardness, and 35% reduction in	HVA	297

abrasion loss.

CNC/Carbon nanotube/natural rubber composite	Latex assembly technique	CNT@CNC concentration was kept constant while concentration of NR was altered	Very low electrical conductivity, high resistivity, sensitivity and reversible resistance properties.	NEA	4b
CNC/PMMA composite	Solution casting	0, 2, 3, 5, 8, 10 wt% CNC	Enhanced storage modulus, lower T _g , good optical transmittance.	NEA	30
Tunicate-CNC- COOH/polyimide composite	Solution casting	0-13.33 wt% CNC	Lower shrinkage during aging, lower density, high thermal stability and higher porosity.	LVA	4c
Magnetic CNC/poly(lactic acid) nanocomposite films	Solvent casting followed by oven	1-3 wt% CNC, Fe ₃ O ₄ nanoparticles	Enhancement in T _g , elastic modulus and tensile	LVA	4d

drying (~51 wt% loading) strength.
adsorbed onto CNC

CNC/poly(D,L-lactide)	Solvent casting	0, 2, 10, 17 wt% CNC	Increased storage modulus, rise in melting temperature, increase in Young's modulus	HVA	25
Polyvinyl alcohol/ poly(D,L-lactide co- glycolide)	Solvent casting	0, 0.5, 1, 2, and 5 wt% CNC	Increased elongation properties and Young's modulus, exhibited good transparency.	NEA	4e
CNC-polyacrylamide	Solvent casting	0.1,0.2,0.4,0.6 vol% CNC	Provided viscoelastic character to the composites.	NEA	4f
CNF/epoxy biocomposite	Solvent casting	0, 15, 30, 50 vol% CNF	High strength, modulus, ductility, moisture stability.	HVA	4g
TEMPO-CNF/chitosan biocomposite	Solvent casting	0, 5, 10, 15, 20, 25 wt% Tempo-CNF	Enhanced barrier properties, strength, transparency, thermal stability, flexibility.	HVA	288, 4h

CNF/carbon nanotube papers	Vacuum-assisted self-assembly technique.	0.1 wt % CNF:0, 0.5, 2, 3.2, 4.5 wt% CNT	Flexible, improved mechanical strength, dielectric energy storage capability.	NEA	4i
TEMPO-CNF/Waterborn PU coatings	Solvent casting	0, 0.1, 0.5, 1, 2, 3, 5 wt% CNF	Improved mechanical properties, pencil hardness and adhesion strength.	HVA	4j

Polyhydroxyalkanoate / bacterial cellulose composites	Melt processing technique	3 wt% BC	High biocompatibility mechanical properties and thermal stability.	NEA	4k
Polycaprolactone (PCL)/ bacterial cellulose composites	<i>In situ</i> production of composite by supplementing the BC culture medium with PCL powder	Variable wt% of PCL	High biodegradability and biocompatibility, good thermal stability, and improved mechanical properties.	NEA	4l
Poly(vinyl alcohol)/ bacterial cellulose composites	<i>In situ</i> bioproduction of BC/PVA composite by <i>Gluconacetobacter</i>	0 to up to 14 wt% of bacterial cellulose	High biodegradability and biocompatibility, excellent mechanical, thermal and dimensional properties as well as moisture stability	NEA	4m, 4n
Poly-3-hydroxybutyrate/ bacterial cellulose	Impregnation of bacterial cellulose	10-90 wt % bacterial cellulose	High biodegradability and biocompatibility,	NEA	4n, 4o

composites	into the poly(3-hydroxybutyrate)		transparency, improved thermal stability, increase in the mechanical properties		
Hydrogen peroxide oxidized BC or periodic acid oxidized BC /chitosan/alginate composites	Dry fabricated bio-film	Various amounts of chitosan and alginate	Higher elongation, rehydration, swelling ratios, and water vapor transmission, improved calcium retaining capacity	NEA	4p
CNF-Poly(vinyl alcohol) composite films	Solution impregnation/ unidirectional freeze-drying/ Electrospinning	Variable amounts of CNF from 1 to 54 wt% CNF	Biodegradable, high visible light transmittance, improved mechanical properties, high water resistance, and dimensional stability	NEA	4m, 4q
CNF-Poly(vinyl alcohol) composite films	Solution impregnation	32 to 54 wt% CNF	High visible light transmittance, improved mechanical properties	NEA	286

¹HVA = High volume applications, NEA=Novel and emerging applications, LVA=Low volume applications

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Foams, hydrogels and aerogels are lightweight materials with a particular need for mechanical reinforcement. CNCs and CNFs have formed a focal point as mechanical stabilizers for these materials (See Section 6.2). Foams can be mechanically stabilized with nanocellulose filler, however their morphology is altered³⁴⁰. Typically, the pore sizes within the foam become smaller and more polydisperse as the nanocellulose acts to nucleate wall formation. By changing the surface chemistry of the nanocellulose filler, it can be a highly desirable foam stabilizer³⁴¹.

7.2 Barrier properties and packaging

Most conventional materials used to package food are non-degradable petrochemical-based polymers, creating considerable environmental impact. The low permeability of cellulose, which is enhanced further by the nanoscale dimensions and highly crystalline nature of cellulosic nanoparticles, and their ability to form a dense percolating network due to hydrogen bonds are desirable properties for filtration and packaging, especially food packaging³⁴². Thus since 2015, prolific growth has occurred in nanocellulose research for packaging applications, as demonstrated in three reviews published in 2017³⁴³⁻³⁴⁵. Nanocellulosic materials³⁴⁶, including nanocellulose in reinforced forms³⁴⁷, have been widely used in such applications. Oxygen permeability³⁴⁸ and water vapor transmission³⁴⁹ are two well-investigated areas in this regard. Water³⁵⁰ and gas permeability³⁵¹ is reduced when cellulose is nanosized because of the dense crystalline structure of the nanoparticles. Cellulose nanocrystal coatings on plastic films reduce friction in flexible packaging while retaining the optical properties of the coating³⁵². Nogi, *et al.* showed that a densely packed film of MFC is optically transparent, because a tight fiber packing with small interstitial spacing poorly scatter lights³⁵³. However, the degree of transparency was related to the processing conditions. Nogi's group prepared optically transparent cellulose based nanopapers with a range of transmittance³⁵⁴⁻³⁵⁶.

Cellulose nanofibers form biodegradable coatings and films alone or in combination with inorganic fillers, such as clay or calcium carbonate. These films can replace the non-degradable plastic coatings used in packaging³⁵⁷. The use of nanocellulosic materials for packaging has arisen due to an intensive search for bio-based food packing materials, taking into consideration efficiency, food safety and environmental consciousness.

Food packaging requires gas impermeability, particularly oxygen. Cellulose is hydrophilic in nature and thus absorbs water when immersed or exposed to moisture. The oxygen barrier properties of nanocellulosic materials have been studied, revealing that NFC films were sufficiently impermeable³⁵⁸. Hydrophilicity clearly compromises the use of nanocellulosic materials in applications requiring materials with water and gas barriers, thus for packaging the surface is modified to increase the hydrophobicity of the material. Polymer grafting onto nanocellulosic surfaces is typically used for packaging.

Researchers have demonstrated packaging strategies in which cellulosic materials are employed in a layered system (sandwiched or the so called multilayer packaging films). In this case, the cellulosic materials are isolated from the humid environment and hence protect the materials inside from the effects of moisture³⁵⁹⁻³⁶³. A recent patent by Schade *et al.* describes the use of a multiplayered structure in which a layer of NFC is protected by water-resistant plastic layers³⁶⁴. Very high resistance to oxygen could be maintained, even at high humidity, by coating CNF films with wax. Polyethyleneimine (PEI) functionalized NFC and PEI/carboxymethyl cellulose have oxygen permeabilities of 0.34 and 0.71 $\text{cm}^3 \cdot \mu\text{m}/\text{m}^2 \cdot \text{day}^1 \cdot \text{kPa}^1$ at 23 °C and 50% relative humidity, respectively, which is in the same range as poly(vinyl alcohol) and ethylene vinyl alcohol deposited on PLA. Fig. 20 shows a schematic cross sectional view of the multilayer packaging films. Polymer films with a MFC coating were prepared and examined as a means to produce good barrier materials^{365,366}. Polymers having desirable and complementary properties to nanocellulose can be combined into a single platform.

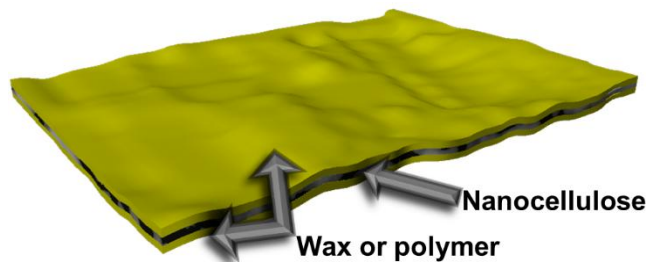


Figure 20: Schematic representation of the sandwiched thin film structures in which a nanocellulose film, which offers high resistance to oxygen permeation when dry, is sandwiched between a pair of water-resistant layers.

However, it is not always desirable to create a hydrophobic film, although it is always necessary for food packaging to form an excellent barrier to water and oxygen. This has been achieved by silylating the surface with (3-aminopropyl)trimethoxysilane, showing desirable barrier properties even at 95% relative humidity³⁶⁷. However, functionalizing the surface with hexamethyldisilazane increased the hydrophobicity of the film while completely destroying the oxygen-barrier properties. In an alternative approach, hydrophilic TEMPO-oxidized nanocellulose was crosslinked with 0.1-0.5 wt% polyamide epichlorohydrin resin³⁶⁸. These films kept excellent visible transparency and their mechanical properties in a humid environment. Typically humidity disrupts the intermolecular hydrogen bonding between cellulose chains, but the crosslinking effectively maintained the film structure.

In another study, the nanocellulose acted itself as the cross-linker, being used as reinforcing filler in chitosan films³⁶⁹. The surface of the nanocellulose was decorated with aldehyde groups, which readily reacted with the chitosan to cross-link the film. This improved the film stability in water and its tensile strength, but at the expense of the elongation at break point. Yao, *et al.* recently reported the preparation of CNF-montmorillonite composites using dopamine as a

linker³⁷⁰. Interfacial adhesion between the matrix and the reinforcing materials is important for mechanical and barrier performance, especially under high humidity conditions. Dopamine is conjugated to cellulose nanofibrils and hence it acts as an effective linker between CNF and montmorillonite. Such nanocomposites showed excellent gas barrier properties at high relative humidity (95%).

Nanocellulosic materials are widely used to prepare nanopapers exhibiting high strength, large surface area, transparency, foldability and low thermal expansion coefficients. Nanocellulosic materials have been extensively reported for the production of transparent films, and aerogels, exhibiting extraordinary mechanical, thermal, and optical properties. Nanocellulose-ZnO-carbon dots composite films were synthesized and have proven to act as excellent UV-blocking protective shields, thanks to excellent transparency of CNCs³⁷¹. Starch-based coating formulations have been filled with CNF and zinc oxide in order to create antibacterial coatings on paper. The coated papers showed bactericidal activity against gram-positive and gram-negative bacteria³⁷². Bacterial adhesion to CNF films and TEMPO-oxidized CNF films is low³⁷³. Bacterial adhesive ability was largely increased by treating TEMPO-oxidized CNF films with polyelectrolytes, showing the importance of surface chemistry in either augmenting or diminishing material interactions with bacteria. The excellent air-barrier and antimicrobial activity of nanocellulose coatings has been reconfirmed by El-Samahy, *et al.*³⁷⁴.

7.3 Medical applications

Nanocellulose is interesting for biomedical materials because of its mechanical properties, nanofibrous network and its natural source, which is increasingly important for consumers with

regards to health care products. Thus, applications for nanocellulose in hydrogels, threads and scaffolds have been developed (Fig. 21).

Despite extensive research in the area of biomaterial synthesis for bone engineering applications, researchers are looking for a material with osteoconductive and osteoinductive properties and a surface structure closer to the natural extracellular matrix for improved cell/material interactions. Bacterial cellulose has emerged as an effective biopolymer and extensively used as a matrix for the synthesis of biomaterials for tissue engineering and regenerative medicine applications due to its high mechanical properties, bio and cyto compatibilities, and low cytotoxicity^{62,67,375}. Recently, Saska and co-workers showed that a nanocellulose-collagen-apatite composite associated with osteogenic growth peptide can be effectively used for bone regeneration³⁷⁶.

Nanocellulose has been found to be non-cytotoxic and thus has been proposed as a tissue culture medium to support cell proliferation³⁷⁷. In a recent work reported by Petreus, *et al.*¹²⁴, hydrosoluble phosphorous acid-functionalized cellulose was evaluated for cytotoxicity and for use as a tissue scaffold material. Phosphorous acid-derivatized cellulose was obtained by reacting microcrystalline cellulose with a molten mixture of phosphorous acid and urea. The obtained water-soluble films were subjected to cell compatibility studies and found to exhibit good cytocompatibility due to their non-toxic nature. However, a more recent report has found that cellulose nanocrystals induced an inflammatory response and were capable of entering cells, where nanofibrillated cellulose were relatively toxic³⁷⁸. Thus the size and shape seem to have a large influence on the cytotoxicity and inflammatory response to nanocellulose. The surface chemistry has also been shown to have a large effect on inflammatory response³⁷⁹.

Modified nanocellulosic materials are particularly pertinent to bone and tissue engineering thanks to nanocellulose's biocompatibility, mechanical properties and compatibility with other biological materials such as collagen and apatite. Phosphorylated nanocellulose has been studied as a biocompatible material as scaffolds for bone regeneration. Once implanted, phosphorylated cellulose promotes calcium phosphate precipitation, upon which the material closely resembles bone. The products obtained by Granja, *et al.* were crystalline monoesters, which swelled in water, and which could be sterilized with gamma irradiation without being significantly damaged. In another study, a hybrid composite for bone regeneration was constructed through the covalent attachment of collagen to a bacterial cellulose matrix³⁷⁶. Carbonate apatite and osteogenic growth peptide were incorporated into this composite in order to form a bone-like material capable of encouraging supported cell growth.

Wounds present a risk of infection and thus promoting healing can avoid more serious health problems. Nanocellulose threads have been decorated with human stem-cells in order to accelerate healing³⁸⁰. These threads could be prepared with the patient's own cells a week before surgery to avoid an immune reaction. To keep the threads moist, they were treated with glutaraldehyde. Nanofibrillated cellulose has been crosslinked with calcium ions to form a hydrogel for wound-healing dressings³⁸¹. The hydrogel is nontoxic and noninflammatory. It retained a desirably moist environment to promote healing. Zander, *et al.* recently reported using metal cation cross-linked nanocellulose hydrogels as tissue engineering substrates³⁸².

Poly(vinyl alcohol)-based hydrogels containing nanocellulose have been proposed for ophthalmic applications as these composite materials are soft and flexible, yet mechanically strong (see Fig. 21a). They can also be transparent and can have a water content of up to 90%³⁸³. When films of the poly(vinyl alcohol)-nanocellulose composites were subjected to strain, they

underwent a reorganization of the nanocellulose alignment, visualized via birefringence measurements.

A double membrane hydrogel composed of alginate and CNC shows great promise for the targeted release of antibiotic drugs via controlled swelling mechanisms.³⁸⁴ CNF films have also been used for the loading and controlled release of active substances³⁸⁵. Dong, *et al.* proposed modified CNCs for targeted drug delivery of chemotherapeutics³⁸⁶. CNC-chitosan hydrogels produced via a solvent-free process have also been proposed for stomach specific drug delivery due to their mechanical properties and pH sensitive drug delivery characteristics³⁸⁷. A transdermal drug delivery system has been proposed by constructing a membrane via the radical polymerization of *N*-methacryloyl glycine within the entangled strands of bacterial cellulose.³⁸⁸ The resulting transparent membranes (see Fig. 21c) had excellent tensile properties thanks to the incorporation of the bacterial cellulose. This composite was non-cytotoxic and demonstrated pH sensitivity and sustained drug release.³⁸⁸

Viral filtration is a critical step in biological purification and in microbiological water quality monitoring. Nanocellulose-based filters are the only 100% unmodified natural polymer filter that features a virus removal efficiency equal to that of synthetic or semisynthetic polymers including polyvinylidene difluoride (PVDF), cuprammonium-regenerated cellulose, cellulose acetate, and polycarbonate as well as ceramic filters³⁸⁹. Recently, nanocellulose based systems have been used as virus removal membranes. Pristine highly crystalline cellulose nanofibers and cross-linked nanocellulose-based papers have been shown to remove highly pathogenic viruses including, aichi virus, human enterovirus, bovine viral diarrhea virus, hepatitis A virus, hepatitis C virus, rotavirus A, and xenotropic murine leukemia virus³⁹⁰⁻³⁹². The pore-size distribution of nanocellulose can be tailored through suitable physical/chemical approaches, for the design of

virus retention filter paper and size-exclusion nanofiltration. Such viral filters provide essential protection against airborne viral particles. Junter and Lebrun exclusively reviewed nanocellulose-based virus-retentive filters towards a range of viruses³⁹³. CNC could also be applied to virus inhibition, for example to inhibit HIV. Zoppe, *et al.* reported CNC-based systems as viral inhibitors (alphavirus infectivity)³⁹⁴. In addition to drug delivery applications, CNC-based biosensors for human neutrophil elastase detection have been reported³⁹⁵.

Nanocellulose-based 3D bioprinting may revolutionize the field of tissue engineering and regenerative medicine as the 3D bioprinter is able to dispense materials while moving in X, Y, and Z directions, enabling the bottom-up engineering of complex structures³⁹⁶. Porous hydrogels have been printed by forming a printable paste out of fibrillated nanocellulose, alginate and glycerin³⁹⁷. Although further research is required to improve the mechanical properties, these printed hydrogels show a glimpse of an exciting future.

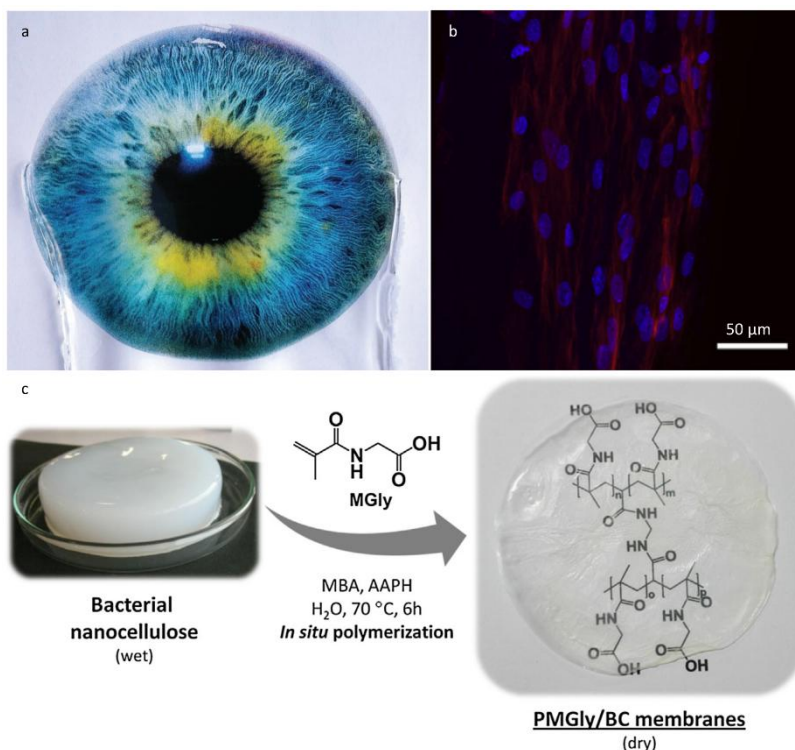


Figure 21: (a) A transparent nanocellulose-poly(vinyl alcohol) hydrogel destined for ophthalmic applications covers the lower half of the image of an eye (adapted with permission from ref. 383, Copyright 2017, Royal Society of Chemistry). (b) Cells attached to a NFC thread (adapted with permission from ref. 382, Copyright 2014, American Chemical Society), (c) The preparation of a membrane for transdermal drug delivery out of bacterial nanocellulose and poly(*N*-methacryloyl glycine) (adapted with permission from ref. 388, Copyright 2017, Elsevier).

7.4 Sensing and biosensing

Protecting human health and ensuring well-being requires the detection of various molecules in the environment, including small molecules, macromolecules and biomolecules³⁹⁸. The world sensor market is projected to grow at an annual rate of more than 10%, reaching \$20 billion by 2020, which is driven by intensified global manufacturing competition and advances in pollution prevention, health care and biomedical applications. Sensors for health care and biomedical applications are of increasing importance. Key areas in the biomedical field include chemical sensors for consumer health monitoring (*e.g.*, for glucose and cholesterol), for home use, biocompatible materials for use with implants and prostheses³⁹⁹. Sensors also play a role in preventing accidental fire explosions, atmospheric environmental testing, and the industrial production of poisonous and harmful gases.

Nanocellulose-based materials possess photonic, colloidal and surface properties making them very attractive sensors, as discussed in a recent review⁴⁰⁰. Pure bacterial cellulose films produced by using, for instance, wild type and recombinant *Komagataeibacter xylinus* (*K. Xylinus*) is shown to have a significant intrinsic piezoelectricity, thus this type of nanocellulose could be incorporated into piezoelectric sensors.⁴⁰¹ Their non-toxic properties are also particularly attractive to biosensing. Nanocellulose is being tailored and applied extensively in

clinical/medical diagnostics, environmental monitoring, food safety, forensics, physical/mechanical sensing, labeling and bioimaging applications. A recent review by Golmohammadi and co-workers systematically analyzes how nanocellulose is being tailored and applied in (bio)sensing technology⁴⁰².

Flexible and ultrathin substrates supporting microelectronic components have potential applications in developing persistent physiological and health monitoring devices by providing biosensors and bioelectronics that can be invisibly integrated onto or into the human body. A bio-based device has been developed which consists of a thin film organic electrochemical transistor fabricated on a thin, porous microbial nanocellulose membrane as a self-adhering bioelectronic decal that can collect, transmit and interrogate a bio-fluid⁴⁰³. For instance, soy protein could be crosslinked to CNC to afford robust films with pliable electromechanical properties for applications in sensing.⁴⁰⁴ The porous and hydrophilic nanocellulose substrate is highly permeable to liquids and gases and it also allows efficient vertical fluid delivery (wicking) of analytes entering the bottom surface to the sensing electronics above, thereby reducing the analyte delivery time (Fig. 22). The use of an organic electrochemical transistor decal simplifies the fabrication and operation, while the nanocellulose provides the required mechanical properties and permeability. Multiple devices have been fabricated on one substrate and can easily be peeled from the backing substrate by simply moistening the nanocellulose sheet, and re-attached to any surface, as shown in Fig. 22. A cellulose nanocrystal/polyvinylpyrrolidone composite film was designed, featuring iridescent properties to allow distinguishing between similar organic solvents.⁴⁰⁵

Nanocellulose-based organic/inorganic hybrid nanocomposites are of interest for (bio)sensing of different analytes including gases, biomarkers, drugs, proteins, DNA, pathogens,

toxic and hazardous compounds; even in real samples, including environmental, biological or clinical samples. Functionalized nanocellulose colloidal properties can be used to interact with biomolecules, as shown recently by the Thielemans group using albumin⁴⁰⁶. Silver nanoparticles were coated on nanofibrillated cellulose in order to obtain a surface enhanced resonance spectroscopy (SERS) platform for the detection of pesticides⁴⁰⁷. In SERS, the presence of a coinage metal enhances the typically weak Raman signal *via* the surface plasmon resonance antenna effect. These CNC/silver hybrids formed a 3D fiber network able to increase surface roughness, an established mechanism for SERS effect optimization^{408,409}.

TEMPO-oxidized nanocellulose has been used to form a hydrogel to support fluorescent carbon quantum dots⁴¹⁰. This hybrid material was used to monitor the fluorescent quenching upon detection laccase enzymes. The nanocellulose hydrogel matrix increased the intensity of the fluorescent signal without shifting the excitation or emission wavelengths. This was attributed to the better dispersion of the carbon quantum dots in the hydrogel than in the absence of nanocellulose thanks to a favorable interaction between the support and fluorophore surfaces. TEMPO-oxidized nanofibrillated cellulose was also used as a platform for immobilizing a sensing biomolecule, C-phycoerythrin, which acted as an effective biosensor for copper ion detection⁴¹¹.

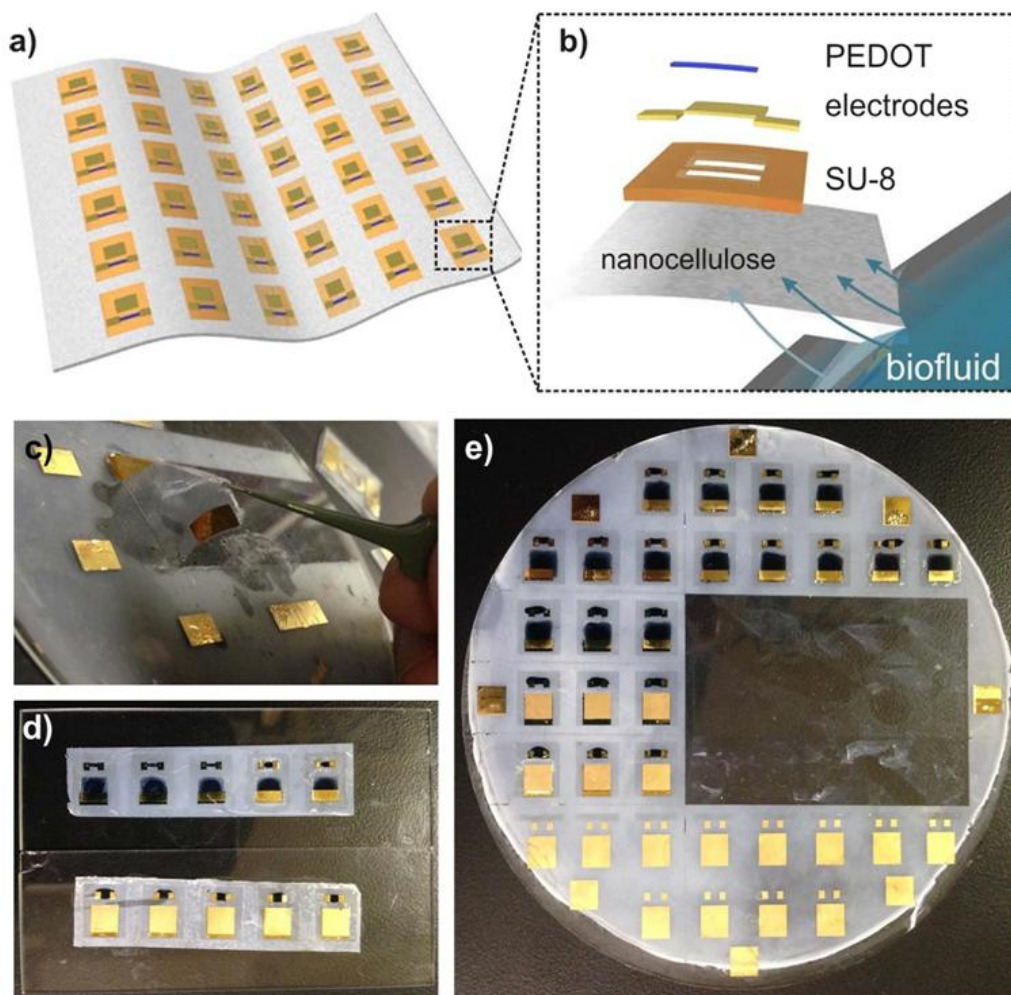


Figure 22: Schematic representation of the bioelectronic decal and lamination. (a) Illustration of bioelectronic decal composed of a sheet of nanocellulose containing multiple organic electrochemical transistors; (b) Expanded schematic of a single organic electrochemical transistor decal. Biofluid, *e.g.* sweat, will be vertically wicked within the decal, due to the porous and hydrophilic nanocellulose substrate. The biofluid will be transported to the gate electrodes and PEDOT:PSS layer on top. (c) Removal of the decal from the backing glass wafer after fabrication. (d) Laminated organic electrochemical transistor decals on glass and (e) the original wafer from which they were peeled. (Reproduced with permission, ref 403, Copyright 2017, Nature Publishing Group).

7.5 Electronic and engineering applications

The most significant future optoelectronic application for nanocellulosic materials is that of lightweight, flexible supercapacitors. Nanocellulose provides the needed mechanical support for freestanding and flexible materials, and is combined with a conductive material-typically a polymer-to provide high volumetric capacitance. The most common conductive polymers used are polypyrrole, polyaniline and poly(ethylenedioxythiophene). Nyström, *et al.* prepared CNF-based electro-active composites by coating cellulose fibrils with polypyrrole⁹¹. In addition to being electro-active, this composite was also conductive and could store energy. An optimization of the polypyrrole/nanocellulose system yielded a material with a nearly ideal pseudocapacitive response⁴¹².

Recently CNF was used as a precursor for carbon nanofibers, producing an anode for sodium-ion batteries⁴¹³. CNF has been also used in organic light emitting diodes by coating the cellulose with an indium tin oxide film⁴¹⁴. Conductive nanocellulosic papers are promising materials for the development of flexible electronics, as they are lightweight, and have good thermal and chemical stability. For instance, CNC and silver have been 3D printed with high resolution into conductive tracks, reducing the quantity of silver needed⁴¹⁵. CNCs have been reported in composite electronics with tin oxide layers for flexible organic field effect transistors⁴¹⁶.

Metal oxide-nanocellulose materials have also been investigated as thermally insulating electrical materials. The production of a ZnO-TEMPO-oxidized nanocellulose film showed an order of magnitude reduction in thermal conductivity compared to the ZnO film alone⁴¹⁷. Unfortunately the electrical properties of the hybrid film were not reported.

Nanopapers have been used as templates to produce electronic materials⁴¹⁸. Nanocellulose films exhibit improved conductivity⁴¹⁹, taking advantage of a dense nanocellulose packing and minimal porosity compared to traditional papers treated with conductive material. Nanocellulose substrates have been used as the host matrix for metals (Au, Ag, Pd, and Ni), minerals ($\text{Ca}_x(\text{PO}_4)_y$, CaCO_3 and montmorillonite), and carbon (carbon nanotubes and graphene) nanomaterials^{420,421}.

The electroluminescent properties exhibited by cellulose-based systems are promising for achieving transparent and flexible light-emitting papers⁴²². Nanofibrillated cellulose with luminescent phosphorous on a silver nanowire coated polyvinylidene difluoride membrane showed electroluminescent properties and can be used as the active component in optoelectronic devices⁴²³. This provides the foundation for the commercialization of viable, flexible and transparent light-emitting papers.

7.6 Energy conservation and production

The field of nanocellulose-based materials for electrochemical energy storage has been recently reviewed⁴²⁴. Nanocellulose is incorporated into composite materials both to conserve and to generate energy. For instance, paraffin@CNF core-shell materials have been prepared for thermal regulation, absorbing solar heat during hot periods for release when the temperature lowers⁴²⁵. The nanocellulose provided a high strength matrix, where paraffin would not have formed an easily manipulable paper on its own. However, by far the main application of nanocellulose in energy applications is its use as a (super)capacitor due to its high permanent electric dipole moment, lightweight, good mechanical properties, good optical transparency, and its minimal porosity, thermal expansion coefficient, and air permeability⁴²⁶. The reader interested

in supercapacitors based on cellulose is directed to a complete and specialized review of the topic⁴²⁷. In charge storage devices, nanocellulose is typically combined with a nanocarbon and a conductive polymer to produce a high specific capacitance that well exceeds that of nanocarbon-based materials without nanocellulose⁴²⁸. Metal-free, all organic supercapacitors using nanocellulose cost less than 10% of commercial units, while maintaining half of the specific capacitance⁴²⁹.

In pursuit of supercapacitors, polypyrrole was polymerized from the surface of cellulose, and then graphene oxide sheets were incorporated into the material⁴³⁰. There was excellent contact between the polypyrrole and the graphene, yielding good conductance and high capacitance. Because the ion diffusion pathways were short, the active-sites were highly accessible and thus the composite paper did not require a current collector, a binder or other additives. Previously cellulose and graphene oxide were combined before polymerizing pyrrole within the pores of the composite⁴³¹, yielding a supercapacitor with excellent electrical conductivity and volumetric capacitance. These two methods differ only in that the order in which the polymer is added was reversed. They seem to yield similar morphologies and similar properties. Better results were obtained for a composite consisting of aniline polymerized around bacterial cellulose fibers that were then infiltrated with graphene sheets⁴³². An aerial capacitance of 6.15 F/cm^2 was achieved and an energy density of 0.17 mW h/cm^2 . These values are at least three times higher than other polyaniline/carbon materials and demonstrated better cycle performance, indicating the important role of the cellulose component in supporting a conductive graphene network. A similar material has been reported using CNF instead of BNC⁴³³. By polymerizing aniline from the nanocellulose surface, the surface area of the polymer was increased and an excellent surface coverage was obtained. This material displayed an excellent balance between power and energy

density. The compatibility between cellulose and graphene-related materials is no doubt responsible for a lower degree of graphene aggregation and thus higher electrical performance, a fortunate side effect of adding nanocellulose as a means to augment the mechanical properties of the composite. By introducing polyaniline into a reduced graphene oxide (RGO)/nanocellulose composite enhanced both thermal stability and conductivity. Microscopic evaluation of the ternary composites shows that PANi nanoparticles formed a spherical shape over the RGO/NC template, which in turn increased the thermal stability of the composite⁴³⁴.

A LiCoO₂/multiwall carbon nanotube/NCF paper was produced with a higher energy density than other currently reported freestanding electrodes, thus such a composite is enticing as a flexible battery⁴³⁵. The lightweight, low volume composite was fabricated by mixing the LiCoO₂, carbon nanotubes and NCF in solution and casting a membrane. This paper had a capacity of 216 mAh/g at 4.7 V, and a volumetric energy density of 720 mAh/cm³.

One final exciting prospect for nanocellulose-based materials is the capture of minute quantities of energy that were previously too small to harvest. This is the concept behind many wearable and bioelectronics nanodevices. The first nanocellulose triboelectric nanogenerator has been developed where a power density of 8.1 $\mu\text{C}/\text{m}^2$ can be generated from a light mechanical force of 16.8 N (Fig. 23)⁴³⁶. To build the nanogenerator, a BNC film was sandwiched between two copper films that acted as current collectors. The lower copper layer also acted as a friction source when pressed in contact with the BNC film. An electrical potential is created upon the release of the two pressed surfaces in friction. When the BNC film and copper film are pressed together, they develop oppositely charged surfaces in order to compensate for differing surface energy and other physical properties. Upon release, current flows through an external circuit to reestablish the resting equilibrium state of the BNC and lower copper film.

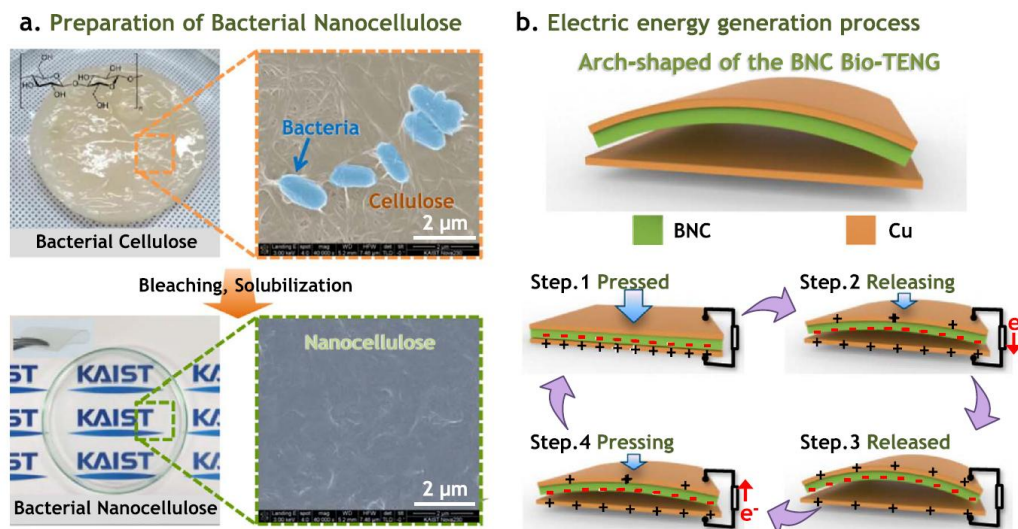


Figure 23. (a) BNC is regenerated and solubilized to form a flexible and transparent film. (b) Energy is generated using mechanical force. A copper foil is used as a current collector and a source of friction with the BNC layer. Reproduced with permission from ref. 436, Copyright 2017, Elsevier.

7.7 Adsorption, separation, decontamination and filtration

Nanocellulose composites may find application in water^{437,438} and air purification⁴³⁹, catalytic degradation of toxic organic compounds⁴⁴⁰, adsorbents for oil contamination⁴⁴¹, repellents^{442,443}, sensors for waterborne pathogens⁴⁴⁴ and high performance energy conversion devices⁴⁴⁵. Nanocellulose as an adsorbent for environmental remediation has been recently reviewed⁴⁴⁶. Typically nanocellulose is valued in adsorption and separation due to its high hydrophilicity as well as its morphology and mechanical properties to form supports and membranes.

Nanocellulose based systems have been used in chromatographic columns for the separation of chiral enantiomers, necessary to pharmaceutical, clinical, food, and environmental science. Various chromatographic techniques have traditionally been used to separate chiral enantiomers,

including high pressure liquid chromatography, gas chromatography, supercritical fluid chromatography, and capillary liquid chromatography. However, these techniques are not ideal due to long analysis times and the use of highly expensive chiral stationary phases. Consequently, capillary electrochromatography, especially open tubular capillary electrochromatography, has evolved as an effective alternative with a chiral stationary phases, suitable for one-pair enantiomer separation. Nanocellulose with the ability to transform into a chiral liquid-crystalline phase at a critical concentration and with tunable hydrophobicity and hydrophilicity can be used as a valuable chiral stationary phase⁴⁴⁷. Nanocellulose crystals modified with 3,5-dimethylphenyl isocyanate were used as a tubular column capillary for enantioseparation. They demonstrated good column lifetime, stability, repeatability over many cycles and applicability for many enantiomer pairs⁴⁴⁸.

Nanocellulose materials appear in water purification technologies due to their high water permeability, high surface area, good mechanical properties, and versatile surface chemistry. A recent study by Tato and co-workers demonstrated the efficiency of nanocellulose metalized with Ag and Pt nanoparticle composites in the form of thin film composites under forward osmosis water treatment⁴⁴⁹. This composite showed higher water fluxes and solute rejections for wastewater samples.

Nanocellulose membranes have been prepared as adsorbents for Ag⁺, Cu²⁺ and Fe³⁺ metal ions. The native nanocellulose had pores that were too small and fibers that were too dense to allow fast water permeation through the membrane⁴²⁴. By functionalizing the membrane with TEMPO, the surface roughness, and consequently filtration time, improved. It seems that in the TEMPO functionalized nanocellulose system, the metal ions are first coordinated by the carboxylate groups, and then upon drying the copper assembles into clusters or aggregates⁴⁵⁰.

Nanocellulose has also been functionalized with 1,2,3,4-butanetetracarboxylic acid to improve pollutant adsorption⁴⁵¹. The high density of carboxylic acids and the possibility to use multiple carboxylic acids to complex heavy metals substantially increased the adsorption capacity for Pb(II). In a study by Liu, *et al.*, enzymatically phosphorylated nanocellulose adsorbents removed metal ions (Ag^+ , Cu^{2+} and Fe^{3+}) from an aqueous model of industrial effluents¹³³. Phosphorylation was found to significantly improve the functionality and sorption behavior of nanocellulose. Phosphorylated nanocellulose was able to remove above 99% of the Cu^{2+} and Fe^{3+} . Specificity for a particular analyte can be designed with a careful consideration of the surface chemistry. CNF surface modification with dopamine provided a high affinity for Cr(VI), where Fe(III) cross-linked CNFs adsorbed As(V) better than other surface functionalities⁴⁵².

Mautner, *et al.* employed phosphorylated nanocellulose papers to remove copper from aqueous solution⁴⁵³. H_3PO_4 was used as the phosphorylating agent. The functional groups appearing on the nanopaper surface readily adsorbed higher concentrations of copper ions than the phosphate groups located within the nanopaper interior. Fig. 24 shows a photograph of phosphorylated nanocellulose papers after copper adsorption. A blue region on the surface of the nanopaper indicates that the nanopaper surface contains Cu(II) ions, proving the capability of phosphorylated nanopapers to remove copper. The nanopapers could be easily regenerated by washing with 0.1 M H_3PO_4 , releasing the adsorbed copper.

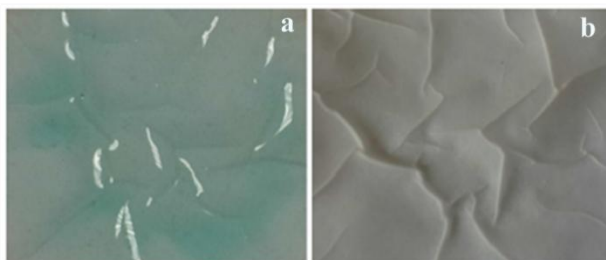


Figure 24: (a) Photographic image of the top view of a CNF-P nanopaper after copper adsorption tests. The turquoise haze on the surface of the nanopaper shows adsorbed copper ions. (b) CNF-P top-view of the regenerated nanopaper via copper desorption using 0.1 M H₃PO₄. (Reprinted with permission from ref. 453, Copyright 2016, Springer).

Nanocellulose membranes and aerogels have been used to purify air. MFC films were found to be excellent CO₂ barriers, allowing CO₂ to be efficiently separated from N₂ and CH₄, even under high humidity⁴⁵⁴. TEMPO-oxidized cellulose nanofibrils were dispersed in *tert*-butyl alcohol and then freeze-dried to form an aerogel⁴³⁹. This aerogel had a high surface area (300 m²/g) and an interconnected, but tortuous macroporosity. These aerogels proved to be efficient air filters with insignificant pressure drops. These simple cellulose nanofibril-based materials can be used for air filtration as they performed better than conventional filters.

Nanocellulose can be used as a coating in self-cleaning surfaces. To this effect, solid surfaces have been coated with a CNF monolayer through a simple physical deposition⁴⁴³. The excellent hydration of surface polar groups strongly inhibits hydrophobes from adsorbing on the surface and also effectively removes hydrophobes, if they adsorb, upon action with water. The surface is then free from oils, ranging from viscous engine oil to polar *n*-butanol⁴⁴³. The self-cleaning function is correlated to the unique molecular structure of the CNF, in which abundant surface polar carboxyl and hydroxyl groups are uniformly, densely, and symmetrically arranged to form a polar corona on a crystalline nanocellulose strand.

AgNPs-BC nanocomposites have been widely used to remove bacterial contamination. For instance, due to the high water holding capacity and high biocompatibility, they have been used in wound dressing materials with improved antimicrobial activity, the development of

antibacterial food-packaging materials^{455,456}, bactericidal paper for water remediation⁴⁵⁷ and nanocomposites for laundering^{458,459}. They are efficient substrates for substrate enhanced Raman scattering (SERS) and used in water-treatment^{460,461}.

7.8 Catalysis

Interest towards green methods has advanced steadily in the field of catalysis. Metal and metal oxide nanoparticles have been used as catalysts for waste water purification, esterification of long chain fatty acids in biofuel production, decontamination and chemical production^{462,463}. Ag, Au, Pd, Pt, Cu, Ru, Cu-Pd, CuO-nanocellulose hybrid composites have all been studied for catalytic applications^{458,464,465}. CNC was functionalized with Pd nanoparticles under a reducing atmosphere for catalytic hydrogenation and Heck coupling reactions⁴⁶⁶. CNC was compared to Al₂O₃ and C supports, showing that the CNC had equivalent or higher activity than the other supports while requiring less Pd, resulting in 90% conversion. The surface of the CNC seemed to actively participate in the catalytic reactions. Cellulose sponges prepared by double cross-linking cellulose with γ -glycidoxypropyltrimethoxysilane and polydopamine was used as a support for Pd nanoparticles. This recyclable catalyst was successfully applied to the heterogeneous Suzuki and Heck cross-coupling reactions. Palladium leaching was negligible and the catalyst could be conveniently separated from the reaction mixture and reused⁴⁶⁷. These novel materials show excellent turnover frequency compared to conventional polymer-supported metallic NPs, and the strategy provides for a more efficient use of noble metals by using our abundant natural bioresources as a support. The higher efficiency stems from the improved dispersity in nanoparticle size and in their improved coverage on the surface of the support⁴⁶⁷. Pd functionalized CNCs have been shown to induce enantioselectivity (up to 65% ee) during ketone

hydrogenation reactions, which is thought to be through multiple hydrogen bonding between the CNC surface and the substrate⁴⁶⁸.

TEMPO-oxidized CNF has been demonstrated as an ideal support for copper ions to prepare catalytic material via the Huisgen click reaction⁴⁶⁹. Similarly, silver⁴⁶³, magnetite⁴⁶² and gold nanoparticles have been incorporated onto nanocellulose supports to produce composite structures with excellent catalytic activity.

7.9 Fire retardants and thermal stability

Phosphorylated cellulose provides a rare combination of good thermal stability and low flammability. Native cellulose and most of its derivatives can be characterized by low thermal stability and high flammability, burning without charring⁴⁷⁰. Flame retardants based upon halogens, phosphorus, nitrogen, metal ions, and nanofillers have been used⁴⁷¹, the most effective being halogen-based. But, the use of halogen-based flame retardants has both health and environmental consequences, as halogens are toxic compounds that leach from the polymer matrix into the environment, accumulating in living beings. In addition, they can release toxic gases upon combustion. Phosphorus-based compounds favor the formation of char instead of combustible volatile species. In intumescent flame retardants, a char layer is formed due to the reaction between the flame retardant (*e.g.* phosphorous acids and their salts) and the carbon source. This layer of char insulates the material, retarding the spread of fire⁴⁷². Cellulose, with its high carbon composition, can be used to act as a carbon source in intumescent flame retardants. In many cases, external flame retardants are used, for example diammonium hydrogen phosphate and ammonium sulfate⁴⁷³. Attaching a flame retardant, such as phosphate groups, to cellulose via covalent bonding has certain advantages over external flame retardants. Covalently attached

groups demonstrate lower chemical leaching over time as the char forms while burning. This char acts as a thermal insulator and protects the surrounding polymer from further decomposition. Chemically modified cellulose bearing charged phosphoric acid groups can enhance the properties of nanocellulosic materials by working as a char-forming agent. Imparting flame retardancy to cellulose fibrils will make these materials safer commercial products.

Sirviö, *et al.* studied the thermal properties of phosphonated nanocellulose⁴⁷⁴. In this work, phosphonate functional groups were introduced to nanocellulose using bisphosphonate compounds via a periodate oxidation followed by reductive amination. Depending on the oxidation degree, either bisphosphonate nanofibrils or nanocrystals were obtained. Compared to mechanically produced NFC, bisphosphonate nanocellulose possessed good thermal stability and char-forming abilities, even with a low degree of substitution (0.22–0.32 mmol g⁻¹). Bisphosphonate nanocellulose can potentially be used as a composite reinforcement and a char-forming agent.

Ghanadpour, *et al.* recently worked on phosphorylated cellulose nanofibrils as renewable nanomaterials that are intrinsically flame retardant (Fig. 25)¹³⁶. The phosphorylation of cellulose-containing pulp fibers was achieved using (NH₄)₂HPO₄ in the presence of urea, and the resulting material was subjected to high-pressure homogenization to obtain phosphorylated CNFs. For the first time, cellulose nanofibrils were prepared from phosphorylated fibers using no other pretreatment, yielding fibrils with widths of approximately 3 nm and lengths between 500 and 1000 nm. The thermal stability and flame retardant properties of nanopaper sheets prepared from phosphorylated CNFs were largely improved compared to those of unmodified pulp fibers and filter paper, as shown in Fig. 25. The nanopaper sheets showed self-extinguishing behavior

during flammability tests and did not ignite under a heat flux of 35 kW/m^2 . Fibrous forms of this material could be used in sustainable, environmentally-friendly flame-retardant composites and nanocoatings.

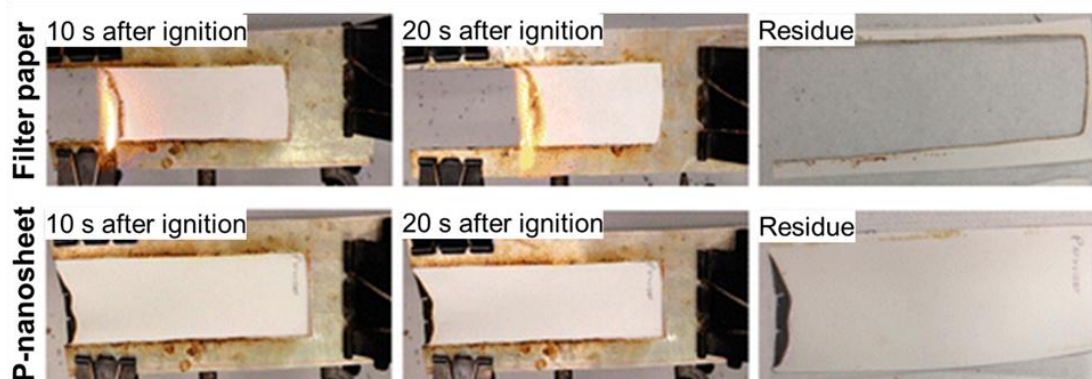


Figure 25: Snapshots of filter paper (top) and P-nanosheet (bottom) taken at fixed times during the flammability test. (Reprinted with permission from ref. 136, Copyright 2015, American Chemical Society).

Surprisingly the formation of a graphene-nanocellulose composite also has flame resistance, due to the fact that the peak of heat release rate is 25% lower for the composite than for CNFs alone⁸. This composite material was more resistant to combustion than polymeric foams with halogenated fire retardants.

Although phosphorylation is the current best surface modification technique to increase thermal stability, several other functional groups perform the same role. Esterification with benzoyl and pivaloyl esters, esters without α -hydrogens, increases the thermal stability from decomposition of nanocellulose at $230 \text{ }^\circ\text{C}$ to above $300 \text{ }^\circ\text{C}$ by preventing depolymerization⁴⁷⁵. Functionalization with thermally stable, long chain amides was able to increase the onset temperature of thermal decomposition by $90 \text{ }^\circ\text{C}$ ⁴⁷⁶. The key is to use thermally stable functional groups.

8. Future perspectives

Phosphorylation of nanocellulose is expected to open new areas of research, particularly in catalysis. Traditionally, liquid acids like H_2SO_4 , HF or Lewis acids such as ZnCl_2 and AlCl_3 have been used as catalysts in homogeneous catalysis. However, these are highly corrosive and highly hygroscopic, making them difficult to handle. Under the reaction conditions, these reagents are converted to toxic materials. The standard workup procedure for these reagents involves neutralization followed by water quenching, which prevents them from being used again and leads to substantial quantities of aqueous waste. Since the reagents are irreversibly lost during the workup process the overall atom efficiency of the process becomes very low, which means that the use of homogeneous catalysts is not an environmentally acceptable process⁴⁷⁷⁻⁴⁷⁹. Moreover, their thermal stability is also poor. Heterogeneous catalysis can overcome the drawbacks of homogeneous catalysis. But a significant problem associated with heterogeneous catalyst is the poor reactivity as a function of surface area⁴⁸⁰. On the contrary, in the case of homogeneous catalysts, each catalytic entity can act as a single active site which makes homogeneous catalysts intrinsically more active and selective compared to traditional heterogeneous catalysts⁴⁸¹. Homogeneous and heterogeneous catalysts have their own set of advantages and disadvantages. To overcome the drawbacks of each, one can aim to heterogenize homogeneous catalysts on p-nanocellulose, so as to combine the high activity and selectivity of homogeneous catalysts with the recyclability of heterogeneous catalysts.

The presence of negatively charged phosphate groups on nanocellulosic surfaces provides the capability to immobilize the Lewis acids used for homogeneous catalysts, such as ZnCl_2 , AlCl_3 , FeCl_3 so as to obtain these homogeneous catalysts in the heterogenized forms. Reactions such as

Friedel-Crafts acylation and alkylation, acetalization of aldehydes and ketones, and Beckmann rearrangement of aldoximes can be efficiently performed using the proposed p-nanocellulose-Lewis acid immobilized catalysts. This possibly offers a new way to perform such synthetically important reactions under heterogeneous conditions, while eliminating the tedious workup associated with homogeneous catalysts. The heterogenization also increases the sustainability of the catalytic process. The ability of p-nanocellulose to adsorb catalytic metals like Fe, Ag and Cu may one day be used to catalyze reactions employing these metals, for instance, oxidation reactions using Fe and Cu, and the Heck reaction using Ag.

In this era of increasing environmental concern, sustainability and renewability are taken into account in the early stages of scientific research. Thus nanocellulosic materials stand to potentially replace conventional packaging materials, fire retardants, catalysts, adsorbents, and mechanical reinforcement materials. We expect that gelation methods for phosphorylated nanocellulose and their applications in various domains of life will be a topic of intense study in the coming years.

9. Conclusions

The word cellulose brings the image of a tree to mind, so it is natural to conjure images of carpentry and wood-based composites when thinking of cellulose-based materials. Nanocellulose, that is cellulose broken into nanometric objects, is interesting for two main reasons: 1. It can be sourced from a wide range of natural materials, including biomass. Managing biomass could transform waste into a valuable product. Moreover, plant waste is often burned, thus processing it avoids air pollution. Thus environmental management encourages its use. 2. It has a number of excellent properties and thus can be incorporated into a variety of materials. Nanocellulose has been studied not only for applications in packaging, films and

paper, but also for much more surprising domains: biomedicine, microelectronics, optics, catalysts and *even flame retardants*. The broader and more versatile properties originate from the size and chemistry introduced by scaling down to the nanometer. The nanostructure, and thus the properties, depends on many factors, the cellulose source (*i.e.* cellulose nanocrystals, nanofibrillated cellulose or bacterial nanocellulose), the degradation treatment applied (*i.e.* mechanical, chemical, enzymatic or a combination of these), and the surface chemistry.

Nanocellulose is abundant, renewable, non-toxic and biodegradable. Although nanoscale cellulose has many new properties, it does not lose the excellent mechanical properties exhibited by bulk cellulosic materials, such as high strength and high elasticity modulus. Thus, nanocellulose has been put to use as nanoscale reinforcement materials for polymers. Nanocellulose-enriched polymer nanocomposites were found to be more efficient and have better mechanical properties than those produced using conventional micro- or macrocomposite materials. The hydrophilic nature, which poses a limit to some applications of nanocellulose, can be overcome using surface modification techniques. Carboxymethylation, amidation, esterification, etherylation, silylation, sulfonation and phosphorylation are surface modifications performed on nanocellulose, with the aim of altering the properties and extending their applications. Nanocellulose can also be functionalized with polymers using the grafting-to, grafting-from or grafting-through methods.

Nanocellulose has been used in a diverse range of composites, combined with nanocarbons (graphene-related materials, carbon nanotubes and carbon quantum dots), polymers, and inorganic materials (oxides, ceramics, metals and alloys). It is rather difficult to create homogenous inorganic-nanocellulose composites due to compatibility issues. Nanocellulose markedly improves organic materials, thus the most promising composites are nanocarbon or

polymer based composites. Nanocellulose and nanocarbons are highly compatible. Though both types of materials are notoriously difficult to disperse, their combination creates dispersions that are stable for months. The thermal and mechanical properties and the transparency of nanocellulose-polymer composites are well above that of the polymer alone. Nanocellulose is added to composites as a support material, as it retains its flexibility and excellent mechanical properties upon their integration into a composite.

Phosphorylation of nanocellulose received particular emphasis in this review, because it marks an area rich with potential and needing further research. Different methods for phosphorylating cellulose have been discussed. Phosphorylated nanocellulosic materials are produced using more environmentally friendly methods than other popular functionalization techniques. But the real interest in exploring these materials lies in their unique properties. Nanocellulose-phosphate supports will be explored to heterogenize homogeneous catalysts as a means to create recyclable, sustainable catalysts with high activity and selectivity. Furthermore, gelation methods for phosphorylated nanocellulose and their applications in various domains of life will be intensively studied to produce the next generation of biological implants, adsorbents and flame retardants.

Biographies

Bejoy Thomas studied chemistry at the University of Bangalore (India) and received his doctoral degree in physical chemistry from Cochin University of Science and Technology (CUSAT) in 2005 (India). After working for some time in NMR spectroscopy at the Indian Institute of Science (India) as a senior research fellow, he moved to Germany as a DFG postdoctoral fellow at the Institute of Chemical Technology, University of Stuttgart. Later on he moved to Paris and

worked as a postdoctoral associate at the Laboratoire de Chimie de la Matière de Condensée de Paris (LCMCP), UPMC-P6 until 2011. He is an assistant professor in Chemistry at Newman College, Thodupuzha, India since 2011. He has diverse research interests and the main themes include chemistry of nanocellulose, self-assembly of amphiphilic biopolymers, eco-design of materials, catalysis for the biomass conversion to value added chemicals, synthesis of hierarchical zeolites, ordered mesoporous materials, surface science, catalysis, and in situ NMR spectroscopy of working catalysts.

Graduated from Newman College (India) with a B. Sc in Chemistry, Midhun C. Raj completed his masters in Chemistry at the School of Chemical Sciences, Mahathma Gandhi University (India) 2014. Currently aspiring to be a research scholar under Dr. Bejoy Thomas, his research interests include areas of materials science and synthesis of bio-nanomaterials. He is currently working on nanocellulose based materials; synthesis and characterization. Isolation, surface functionalization, and templating applications of nanocellulose towards the eco-design of materials like SiO₂ form his research interests.

Athira K.B, a full-time researcher in the group of Dr. Bejoy Thomas, has completed under graduate (2013) as well as graduate school in chemistry (2015) at Newman College- Thodupuzha (India). She has talent for exploring multiple areas of chemistry viz, biomaterials, organic synthesis, material chemistry, surface science, catalysis, and nanoscience. Synthesis of amphiphilic biosurfactants, self-assembly, eco-design of materials, nanocellulose based composite materials-possessing potential end-user applications is the targeted vision of her studies.

Rubiyah, M. H. received her masters' from the School of Chemical Sciences, Mahatma Gandhi University (India) in 2009. Later she worked as project assistant at the Institute for Integrated Programmes and Research in Basic Sciences (IIRBS), Mahatma Gandhi University for a short period. She successfully completed the prestigious National Eligibility Test (NET) examinations conducted jointly by the Council of Scientific and Industrial Research and University Grants Commission, Government of India. She started her doctoral studies under Dr. Bejoy Thomas in 2016. Her areas of research include nanocellulose, self-assembly of biopolymers, eco-design of materials, especially mesoporous silica, catalysis for biomass conversion to value added chemicals.

Jithin Joy received his masters' degree in pure Chemistry from Mahatma Gandhi University (India) in 2008. He is engaged in doctoral studies in the School of Chemical Sciences, Mahatma Gandhi University in the area of nanocellulose-based polymer nanocomposites since 2011. He is a visiting student fellow to Clemson University, South Carolina in USA. In 2010, Jithin received the prestigious research fellowship administered jointly by the Council of Scientific and Industrial Research and University Grants Commission of the Government of India. He is an assistant professor in Chemistry at Newman College, Thodupuzha, India since 2016. He has many publications in reputed journals and conference proceedings to his credit. He is a co-author of several book chapters, peer-reviewed publications, and invited presentations.

Audrey Moores completed her PhD at the Ecole Polytechnique, France in 2005 with Prof. Pascal Le Floch. She conducted a post doctoral fellowship at Yale University under the guidance of

Prof. Robert H. Crabtree. She is now an associate professor in the Department of Chemistry at McGill University. She serves as an associate editor for ACS Sustainable Chemistry and Engineering, a member of the advisory board of the Green Chemistry Institute of the American Chemical Society and the scientific director on the board of Green Center Canada, an Ontario-based tech transfer company. She is also an associate director of the Facility for Electron Microscopy Research (FEMR) at McGill and co-leader of the McGill Sustainability Systems Initiative, Materials theme, a McGill-based research center on sustainability science. She is a leading expert in the field of catalysis using metal, metal oxide and biomass-based nanomaterials, with a special emphasis on sustainable processes and use of earth-abundant starting materials. Specifically, she has made an important discovery towards the use of iron for significant hydrogenation and oxidation catalytic reactions and replace noble metals as catalysts. In 2007 she was awarded a Canada Research Chair in Green Chemistry, which was renewed in 2012. She also received a Discovery Grant Accelerator in 2018 by the Natural Sciences and Engineering Research Council of Canada.

Dr. Glenna L. Drisko is a full-time researcher for the CNRS, specializing in nanoparticle synthesis. She obtained a Junior Chair position through the LabEx AMADEus to launch a research program in silicon particle synthesis and assembly. She defended her PhD in 2010 from The University of Melbourne where she studied morphological control of sol-gel derived materials using organic templates. She spent 3 years as a post-doctorate researcher in the Collège de France studying the self-assembly hybrid thin films and solution synthesis methods to core-shell hybrid particles. In a second post-doc at the Laboratoire de Chimie de Coordination, she acquired synthetic skills in metal-organic precursor decomposition to form inorganic

nanoparticles. She is passionate about discovering synthetic mechanisms and self-assembly. She received a L’Oreal-UNESCO For Women in Science award in 2016 and ever since she has been an ambassador in the classroom to promote science equality and science education for young children.

Clément Sanchez is a professor at the Collège de France and chair of the “Chemistry of Hybrid Materials”. He was Director of the *Laboratoire de Chimie de la Matière Condensée de Paris* (UMR 7574, University of Pierre and Marie Curie-Collège de France-CNRS) (1999-2013). He did a large part of his career at the CNRS where he was Director of Research and he was also Professor at l’Ecole Polytechnique. He is specialised in the field of nanochemistry of nanostructured porous and non-porous transition metal oxide based gels and porous and non-porous hybrid organic inorganic materials shaped as monoliths, microspheres and films. He also studies the properties of hybrids and inorganic nanomaterials looking for applications in the domains of energy, environment, biomaterials and health. For more details please check:

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<https://scholar.google.fr/citations?user=vM9snnEAAAAJ&hl=fr>

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