



Recent Developments of Nanocellulose and its Applications in Polymeric Composites

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Abstract

Recently, nanocelluloses have gained great interest as naturally derived biobased nanometer-sized reinforcement in diverse technological areas due to the excellent mechanical properties, biodegradability, biocompatibility, high specific surface area, and rich hydroxyl groups for extensive chemical modification. However, the extraction of nanocellulose from cellulosic biomass and its dispersion in the matrix is still a substantial challenge since its inherent hydrophilicity and difficulty in dispersion inside hydrophobic matrix. This paper presents an overview of recent developments in nanocellulose research, highlighting its extraction routes, surface modification and its applications in polymeric composites. Literature shows that the morphologies and performances of nanocellulose depends on the source of the cellulosic materials and the processing parameters. Although nanocellulose is derived from seemingly fragile plants or organisms, it can be used as the reinforcement material or the main component to fabricate high value-added cutting-edge materials or devices, such high-performance nanocomposites, multifunctional hydrogel, conductive filaments, medical dressing, and energy storage material.

Keywords: Cellulose nanofibrils; Cellulose nanocrystals; Surface modification; Natural biopolymer; Nanocellulose-based nanocomposites.

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1. Introduction

With the overexploitation and depletion of petroleum-based resources and serious environmental deterioration, the application of renewable and sustainable biomasses in novel functional polymeric composites has gained increasing

interest in academia and industry area. Cellulose is one of the most abundant renewable biomass materials and has been used as an energy source, directly used materials and the primary carbon source for the burgeoning renewable emerging functional composites for millennia.^[1-3] It can be extracted from various botanical sources, fungi and marine organisms and has a wide range of applications in papermaking, coating, cosmetic and pharmaceutical industries due to its renewability, non-toxicity, biodegradability, biocompatibility and environmental-friendly. Cellulose is synthesized in certain living organisms such as plants, bacteria and animals, mainly through photosynthesis and microbial synthesis, and is therefore considered to be the main raw material for energy and chemical industry in the future. In essence, cellulose is a natural polysaccharide, mainly composed of glucose units linked by 1,4- β -glycosidic bonds, and has numerous free active hydroxyl groups on the surface at the C2, C3, and C6 positions which lead to strong hydrogen bonds between the linear cellulose molecular chains.^[4-6] Cellulose also possesses excellent physicochemical and mechanical properties and extensive chemical modification, making it as an excellent bio-filler for synthetic or natural polymer. Even though

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cellulose is an excellent bio-filler with many beneficial features, its application in high value-added fields is still limited due to its inherent hydrophilicity, poor solubility and infusible processability.^[7,8]

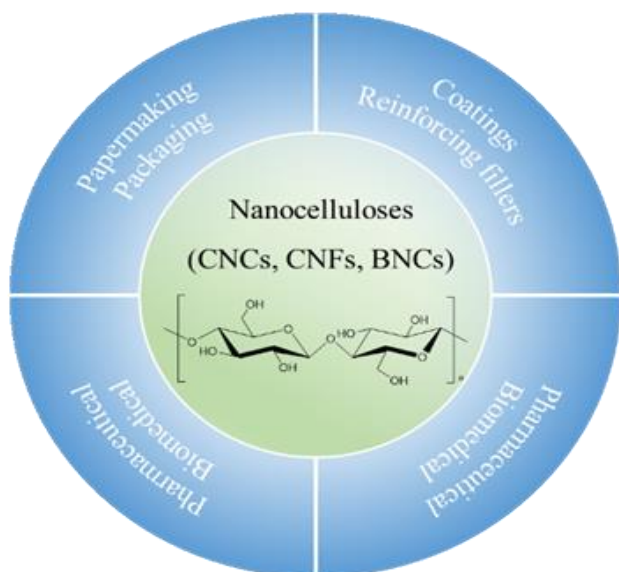


Fig. 1 Applications of nanocelluloses.

In recent years, it has become a major trend to extract structured materials with nanoscale dimensions from cellulose to develop various high value-added biocompatible composites and commercial cellulose derivatives. Such cellulose-based nanostructured material generally referred to as nanocellulose has at least one dimension of 1–100 nm and can mainly divided into three types according to raw material, manufacturing process and fiber morphology, namely cellulose nanofibrils (CNFs), cellulose nanocrystals (CNCs), and bacterial nanocellulose (BNC).^[9,10] CNFs and CNCs are essentially smaller polysaccharide aggregates compared to micro-cellulose and can be obtained via top-down deconstruction from macroscopic cellulose. CNFs are filamentous fragments distributed with amorphous and crystalline segments. CNCs are rigid rod-like crystalline fragments of cellulose, which can be obtained by selectively removing the amorphous domains in elementary fibrils through acid hydrolysis. BNC is microbial cellulose typically synthesized by bacterial microorganisms, commonly known as a bottom to up fabrication process. All types of nanocellulose are typical anisotropic one-dimensional elongated shape and contain abundant hydroxy groups on their surface.^[11] Therefore, nanocellulose not only inherits the basic performances of cellulose, but also exhibits many fascinating new physicochemical properties at the nanoscale, such as high elastic modulus, excellent mechanical strengths and stability, biocompatibility, extensive chemical modification, *etc.*, which is beneficial to promote the high value-added applications (as displayed in Fig. 1) of nanocellulose in biosensors, energy storage devices, pharmaceutical, biomedical, water filtration, environmental remediation, assisted dispersion of inorganic nanoparticles, aerogel, hydrogels and so on.^[6,12-19]

However, there are still some substantial challenges for the application of nanocellulose. Although nanocellulose can be manufactured via various physical, chemical, and biosynthesis methods, these processes still involve harsh chemical treatment, non-universal equipment or specialized raw materials. Therefore, a sustainable, efficient and environmentally friendly processing technique for the commercial production of nanocellulose is urgently needed in order to reduce the production costs and price. Nanocellulose can be used as a bio-based nanofiller to reinforce the polymeric composite required excellent biocompatibility and low toxicity. But it easily trends to aggregate due to its high inherent hydrophilicity and surface effect, generally making it poorly dispersed in the matrix and impairing the performance of composites. In addition, the irreversible keratinization for nanocellulose may occur upon drying, which may result in difficulty in obtaining dry nanoparticles or product defects.^[20]

The objective of this paper is to present a brief summary on the extraction and modification of nanocellulose, and their recent applications in polymeric composites including nanocellulose-based polymeric nanocomposites, nanocellulose-based hydrogels, and nanocellulose-based filaments.

2. Extraction of Nanocelluloses

Nanocellulose is essentially smaller elementary fibrils aggregates with at least one dimension in nanoscale as compared to cellulose. In fact, cellulose is a semicrystalline polymer with crystallinities ranging from 65 to 95%, depending on the source. Structurally, linear homopolymer chains of glucose units mainly form highly ordered elementary fibrils that are packed into microfibrils and eventually into larger macroscopic cellulosic structures. Therefore, nanocellulose can usually be obtained via top-down deconstruction from macroscopic cellulose through chemical treatment or mechanical exfoliation. The hierarchical structure of cellulose in plant-based biomass and the schematic illustration of the formation for nanocelluloses through top-down method is shown as Fig. 2a. Cellulose is derived from biomass feedstocks and the plant-based lignocellulosic materials are generally considered to be a ubiquitous source of cellulose. Plant-based natural fiber mainly consists of cellulose (40%-50%) and non-cellulose substance, such as hemicellulose (20%-30%), lignin (20%-30%), and other extractives. By removing their non-cellulose components, plant-based cellulose can be extracted and further reduced in size to obtain highly ordered fibrils in nanoscale, mainly comprising both cellulose nanofibrils (CNFs) and cellulose nanocrystals (CNCs).^[21] And especially, bacterial cellulose fibrils are naturally in nanoscale, *i.e.*, bacterial nanocellulose (BNC), about 20–100 nm in diameter.

Cellulose nanofibrils (CNFs), also known as nanofibrillated cellulose, are a type of flexible and elongated nanocellulose with a diameter of 5-50 nm and a length of several micrometers. CNFs are long entangled nanofibrils

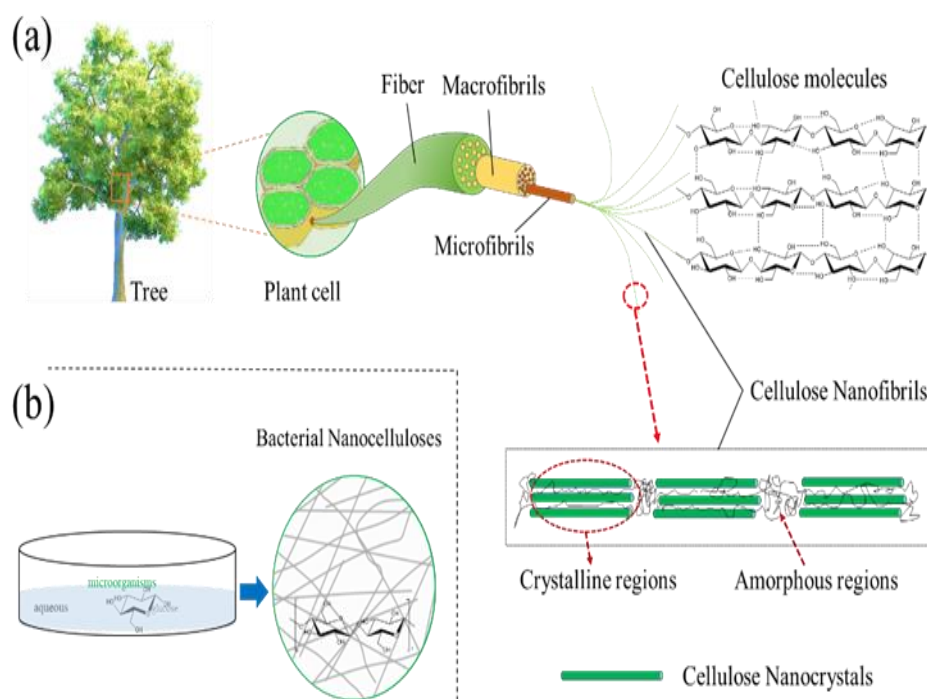


Fig. 2 Schematic illustration of the formation for nanocelluloses. (a) The hierarchical structure of cellulose in plant-based biomass (top-down), (b) Bacterial nanocellulose cultured from cellulose-synthesizing bacteria (bottom-up).

containing both crystalline regions with highly ordered fibrillar architectures and disordered amorphous regions, making them both rigid and tough. Cellulose nanofibrils are commonly fabricated from cellulosic feedstocks extracted from various botanical sources, via mechanical or chemo-mechanical processes, as displayed in Fig. 3. The key to this approach is to generate a critical pressure in the center of fibrous materials through powerful mechanical force, which can break the interactions between cellulose fibers and facilitate the crack propagation process along the longitudinal direction from oriented fibers, resulting in the formation of nanofibrils. High-pressure homogenization is one of the efficient and commonly used mechanical treatment for the formation of cellulose nanofibrils from cellulose slurry. In this process, a diluted cellulose pulp suspension is forced through a impacting and homogenizing valve under high pressure and high velocity, which makes the material undergo strong shearing and impacting action induced by continuous and rapid opening and closing of the valve, resulting in the delamination of nanofibrils from cellulose fibers. Similar to utilizing a homogenizer, a microfluidizer can also be used to generate cellulose nanofibrils by repressing the cellulose suspension into z-molded chambers where can induce higher shearing force to promote the mechanical delamination of the strands. The dimension distribution of nanocellulose obtained by microfluidization is narrower than that produced by other mechanical processes. High-power ultrasonication has additionally been used to generate nanocellulose, mainly utilizing the hydrodynamic powers from the ultrasound gear to weaken to interaction between cellulose filaments, which is considered a more beneficial approach for biomedical

applications because of the non-involvement of any toxic chemicals during manufacturing. In addition, cryocrushing, balling milling, micro-grinding, steam explosion, and electrospinning approaches are also used to generate nanocellulose. However, the purely mechanical process consumes more energy and processing time due to the intense network of hydrogen bonds and a greater number of passes. Thus, the mechanical defibrillation is commonly coupled with some chemical pretreatments or surface modifications to reduce the energy consumption, such as enzymatic hydrolysis, catalytic oxidation using 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), and partial carboxymethylation.^[22,23]

Cellulose nanocrystals (CNCs), also called as cellulose whiskers, are rigid rod-like nanoparticles with typical dimensions varying from 2 to 50 nm in diameter and 50 to 500nm in length depending on the cellulosic source, crystallinity of cellulose, and isolation process. Generally, CNCs can be obtained through acid hydrolysis process, which the cellulose is exposed to an acidic environment under controlled temperature and processing time, depending on the type and concentration of acid. The amorphous regions of cellulose fibers are selectively dissolved via acid hydrolysis, leaving only the rod/needle-like crystalline fragments. In a typical acid-induced hydrolysis process, the most readily accessible glycosidic linkages within the disordered regions of microfibrils are cleaved and disrupted under a suitable acid environment, while the crystalline regions can remain intact due to their high resistance to acid attack. The inorganic acids such as sulphuric acid (H_2SO_4), hydrochloric (HCl), phosphoric (H_3PO_4), and hydrobromic acids (HBr) or a mixture of inorganic and organic acids are widely used to

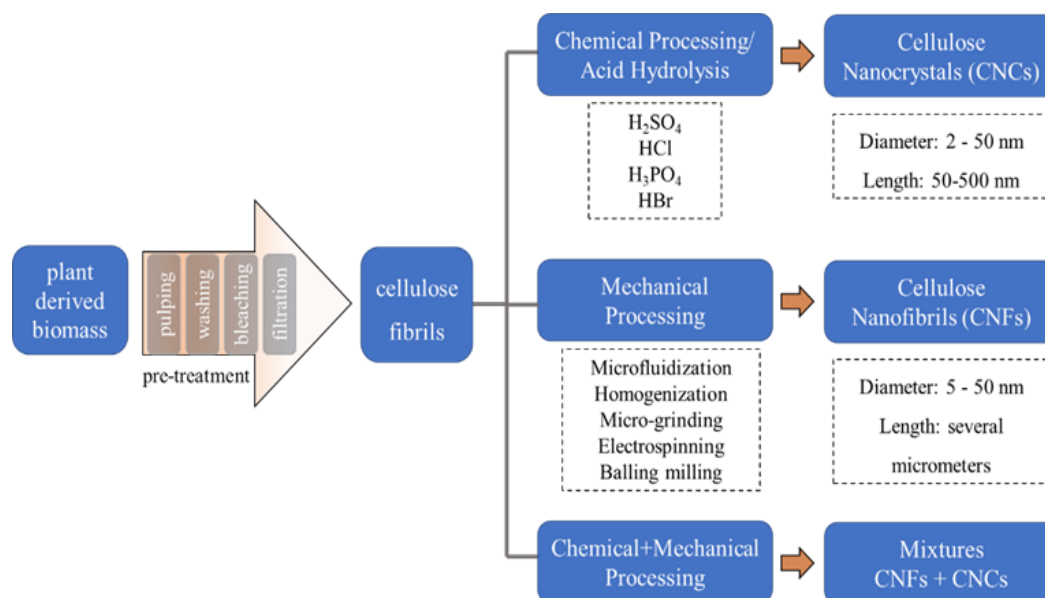


Fig. 3 Common routes of CNCs and CNFs extracted from plant-derived biomass.

fabricate CNCs.^[5] In general, hydrolysis of cellulose with sulfuric acid at a concentration of about 65 wt% in a temperature range from 45 to 60 °C is the most common procedure for producing CNCs, and the obtained nanocrystals can form colloidally stable aqueous suspensions due to the esterification process of anionic sulphate ester groups (OSO_3^-) with hydroxyl groups on cellulose surface which imparts electrostatic stability. The HCl hydrolysis generates more reactive hydroxyl groups on CNCs surface, and the obtained CNCs display limited colloidal stability due to the presence of low-density surface charges. The crystallinity and morphology of CNCs are greatly affected by cellulose source, acid concentration, acid hydrolysis time and temperature, as well as pretreatment conditions.

Bacterial nanocellulose (BNC) is a nanoscale form of microbial cellulose and consists of ribbon-like nanofibrils with diameters varying from 20 to 100 nm and lengths up to several micrometers. In contrast to CNFs and CNCs, which are extracted from macroscopic crude cellulose or cellulosic feedstocks via a top-down deconstruction strategy, the formation of BNC is a bottom-up approach and it is

synthesized by bacterial microorganisms in aqueous culture media containing a sugar source (as shown in Fig. 2b).^[24,25] Fermentation and purification are essential processes to synthesis BNC. In the fermentation process, the glucose is polymerized inside the bacterial body into linear chains, then the glucan chains form crystals and arranges in a hierarchy in fibers through hydrogen bonds and van der Waals forces, resulting in the formation of ribbon-shaped BNC nanofibers. By controlling the fermentation parameters, the length of BNC can be adjusted to nano or macro regimes. The obtained BNC can further be modified to crystalline or fibrillar form combined with external treatments. Although CNF and BNC are similar in diameters and morphologies (as displayed in Fig. 4), BNC can be better differentiated from plant-derived CNFs by considerably higher crystallinity (80-90%) and its excellent chemical purity without impurities such as lignin, hemicellulose, or pectin. Indeed, biological process is considered a better strategy to obtain nanocellulose than the chemical and mechanical treatments, which makes it more suitable for applications in biomedical field.

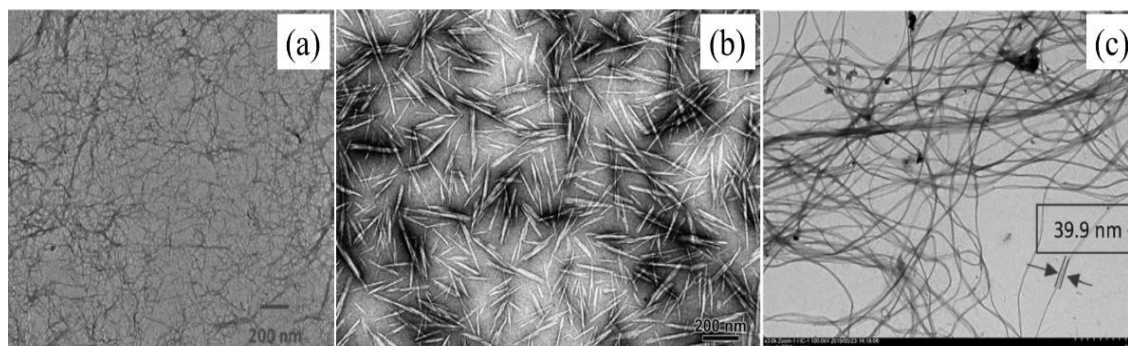


Fig. 4 TEM micrographs of different nanocelluloses. (a) CNFs obtained from kapok. Reproduced with the permission from [26], Copyright 2015 Springer Science Business Media, LLC. (b) CNCs extracted from ramie fibers. Reproduced with the permission from [27], Copyright 2008 Royal Society of Chemistry. (c) BNCs synthesized from banana peel waste. Reproduced with the permission from [28], Copyright 2020 The Author(s).

3. Surface modification and functionalization for nanocelluloses

Although nanocellulose has various advantages, there are also some limitations or drawbacks, such as poor thermal stability, absorption of moisture, incompatibility with hydrophobic polymers, and poor redispersion, which greatly restrict its application in polymeric composites. Nanocellulose has higher specific surface area and a large number of hydroxyl groups (OH) on its surface, which results in the hydrophilicity of nanocellulose surface and its strong self-aggregation due to the strong inter- and intra-molecular hydrogen bonds between hydroxy groups. Therefore, it is difficult to uniformly disperse nanocellulose in most conventional non-polar polymeric materials. And it should be noted that the reactive groups on nanocellulose surface may lead to poor thermal stability and dimensional stability of the samples. However, taking another perspective, the abundant reactive groups on nanocellulose surface provide various available routes for the desired modifications, which mainly aims to reduce the aggregation and differences in polarity of nanoparticles. The surface modifications in nanocellulose could enhance its compatibility, dispersibility, and related performance and raised its potential for a variety of high value-added applications. In general, the modifications of nanocellulose include structural adjustment of nanocellulose and functional modification of hydroxyl groups present in its structure. The commonly used chemical modification procedures (as shown in Fig. 5) to establish the covalent connection with reactive groups on nanocellulose surface include esterification, silylation, amination, oxidation, sulfonation, carboxymethylation, polymer grafting, and so on.^[5,29-33]

3.1 Esterification

Esterification is the most well-known and simplest method to reduce the hydroxyl density of nanocellulose, while acetylation of nanocellulose is the most commonly used esterification reaction. The basic mechanism of acetylation is to replace the hydroxyl groups on nanocellulose with acetyl groups, generally by introducing ester groups through condensation of carboxylic acid group (COOH) and alcohol group (OH). In practical synthesis process, acid anhydrides or acyl chlorides are often used as an acyl donor in the presence of a small amount of either sulfuric or perchloric acid as the catalyst. CNC can be modified with different length chains of acid anhydrides in the presence of H_2SO_4 , and the reaction between acid anhydride and hydrogen in the alcohol group of CNC can be confirmed successfully.^[34] The polarity of nanocellulose can be tailored by changing the reaction parameters, so that it can be dispersed in solvents of different polarities. Anionic groups, such as sulphate, carboxylic acid group, and phosphate groups are commonly introduced to the surface of CNCs or CNFs to improve the charge repulsion, leading to form stable aqueous suspensions with mostly of individual fibrils and few aggregates.^[31,35,36] For the acetylation of nanocellulose, the formation of acetyl groups reduces the hydroxyl density and minimizes the water absorption, which can reduce the degradation by hydrolytic cleavage and increase the thermal stability of acetylated nanocellulose.^[37] Agustin *et al.*^[38] used four different esters (acetyl, myristoyl, benzoyl, and pivaloyl) to modify the wood-derived CNFs and found that the esterification could significantly improve the thermal stability of nanofibers, probably due to the high degree of esterification of the amorphous regions of nanocellulose.

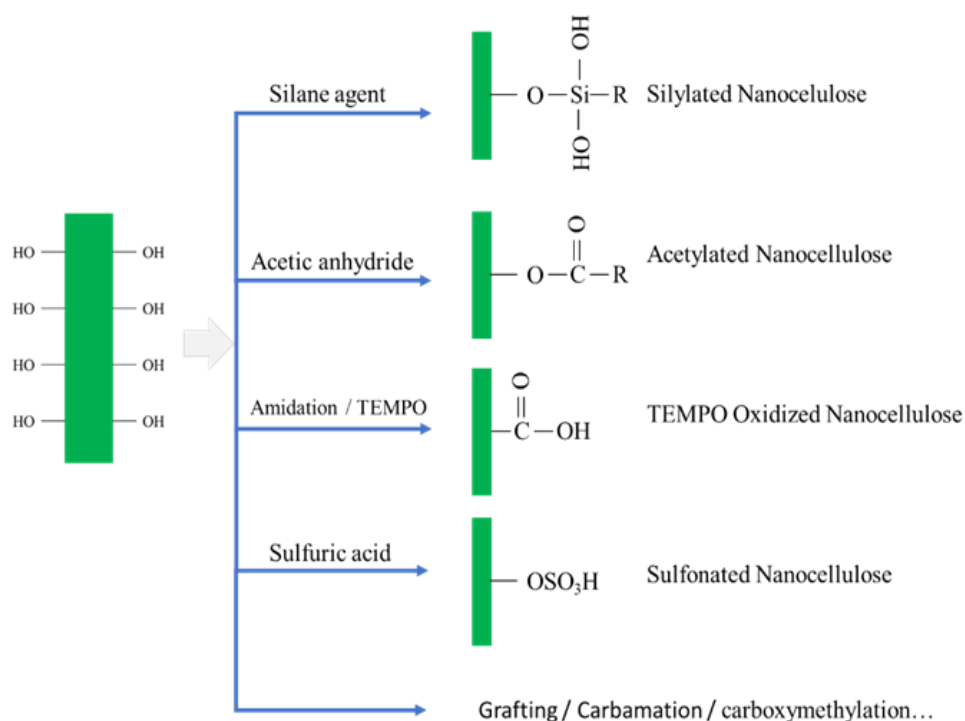


Fig. 5 Schematic diagram of most commonly used chemical modification techniques for nanocelluloses.

3.2 Silylation

Silylation is a simple and promising method to increase the hydrophobicity of nanocellulose surface by introducing hydrophobic alkyl moieties, which is conducive to improve its compatibility with non-polar matrices. Silylation is a surface modification technique based on the reaction of hydroxyl groups on nanocellulose with alkoxysilanes or polysiloxane. Many silane derivatives such as hexamethyldisilazane (HDMS),^[39] 3-aminopropyltriethoxysilane (APTES),^[40] trichloromethylsilane (TC),^[41,42] and 3-methacryloxypropyltrimethoxysilane (MPS)^[43] have been used to fabricate unique silylated nanocellulose. Generally, the silylation of nanocellulose includes several necessary stages. Silane is first hydrolyzed in aqueous solution to form silanol, which can be adsorbed on the surface of nanocellulose through hydrogen bonding, eventually forming the unique silylated surface through covalent bonding. Alkylation modification can effectively improve the dispersibility of nanocellulose in organic solvents of low polarities such as tetrahydrofuran (THF) and improve the interfacial interaction with the hydrophobic matrix. The degree of alkylation on nanocellulose surface is increased directly proportional to the silane ratio in the reaction. However, excessive substitution on the surface of nanofibers will destroy the crystalline regions of nanofibers, resulting in a decrease in the strength of nanocellulose. Therefore, the optimal process is essentially a compromise between the extent of silylation and the preservation of nanocellulose morphology. To address this challenge, the silylation process is commonly carried out by using diverse types of silylating agents and different reaction parameters. Goussé *et al.*^[29,36] used several types chlorosilanes as silylating agents to modify CNCs and CNFs, and found that the silylated CNCs and CNFs were dispersible in various organic solvents of low polarity and the morphological integrity of them has been well preserved, through a mild silylation protocol with using less reagents and shorter reaction times. Moreover, it is interesting to find that the excessive silylation conditions were less disruptive to CNFs as compared to CNCs, possibly due to the presence of abundant reactive groups on the surface of CNFs. The silylated nanocelluloses exhibit enhanced hydrophobicity, compatibility, thermal stability and mechanical strength and extend their applications in biomaterials, coatings, optical devices, food packaging, and polymer reinforcement.^[32,44]

3.3 Amidation

Amidation is one of the most common surface-modification routes to obtain functionalized nanocellulose with hydrophobicity and enhanced surface activity.^[5,35] The amide linkage can be formed by a reaction between amine and carboxylic moieties. However, there are no carboxy groups on the surface of nanocellulose in general and the carboxy groups are also introduced through pre-oxidized treatment such as TEMPO-mediated oxidation.^[22] These carboxylate groups can be used as efficient platform to assemble metal ions or

alkylammonium ions by ion exchange to obtain nanocellulose with different functionalities.

3.4 Sulfonation

Sulfonation esterification can impart anionic surface charge on the surface of nanocellulose. Sulfonation occurs naturally during sulfuric acid hydrolysis to form sulfate half-esters by substituting the hydrogens on the hydroxyl groups on the nanocellulose surface. The sulfate esters on the surface of CNCs or CNFs allows the formation of colloiddally stable suspensions by suppressing the formation of hydrogen bonds through electrostatic repulsion. Carboxymethyl groups can be introduced via carboxymethylation to create ionic surface on nanocellulose, generally rendering the surface negatively charged.^[45]

4. Applications of nanocellulose in polymeric composites

4.1 Nanocellulose-reinforced polymer nanocomposites

4.1.1 Dispersion of nanocelluloses in the matrix

Nanocellulose is a desirable and reliable bio-nanofiller due to its excellent characteristics such as high stiffness, high strength, on-toxicity, biocompatibility, and renewability. Nanocellulose has been widely used as reinforcement and can be compounded with various polymers such as polyolefin, polyester, thermoplastic elastomer, rubber, epoxy resin, and so on. Similar to inorganic nanoparticles such as graphene, carbon nanotubes, nano-titanium dioxide, *etc.*, nanocellulose has a high specific surface area and nanometer-sized in at least one dimension. However, the extremely small size and great surface activity of nanocelluloses make them easy to agglomerate with each other, thereby weakening the reinforcing effect of nanoparticles on their polymer nanocomposites. Therefore, as compounded with polymers, several issues include the dispersion of nanocellulose in the matrix and the compatibility of nanocellulose with the polymer must be addressed. The dispersion morphology of nanocellulose in the polymer matrix is closely related to its processing method, mainly including solution casting and melt compounding. The compatibility of nanoparticles with the matrix affects the dispersion of nanoparticles and directly determines the physicochemical properties of nanocomposites, which can be tuned by surface modification.

For solution mixing, nanocellulose is required to form a stable suspension solution in a good solvent of the target polymer to be compounded. Surface modification can reduce the density of active groups on the surface of nanocellulose, thereby reducing its agglomeration, which is beneficial for it to form a stable suspension and dispersion system in solution. Germiniani *et al.*^[46] prepared poly(ϵ -caprolactone) (PCL) / neat CNCs nanocomposites by combining solvent exchange and solvent casting which avoided using any additives or chemical modification and the CNCs exhibited good dispersion and random distribution, as showed in Fig. 6e. Dunlop *et al.*^[47] used the tunicate sourced CNCs as reinforcements to mix with polyvinyl alcohol (PVA) in

aqueous solution and confirmed that the cellulose nanocrystals have been well dispersed in PVA. As mentioned earlier, the hydrophilicity or hydrophobicity of nanocellulose can be tuned by surface modification, depending on the nature of solvent of the polymer in the composite. Gwon *et al.*^[48] used diisocyanate (TDI) to modify CNCs in order to overcome the limitation in nonpolar solvent systems. The authors confirmed the well-dispersed of TDI-modified CNCs in PLA matrix even with the increase of their loading levels and a schematic diagram of the dispersion mechanism is displayed as Fig. 6a. Shi *et al.*^[49] prepared carboxylated CNFs by TEMPO-oxidized process and fabricated the composite films of poly (ethylene oxide) (PEO) and carboxylated CNFs by successive solution casting and drying. The results show that the individual CNFs were well dispersed in the PEO matrix without significant agglomeration and the composite films were still transparent even with the addition of 20% CNFs. Wang *et al.*^[50] developed an environmentally friendly antimicrobial film by incorporating silver nanoparticles (AgNPs) into bacterial nanocellulose (BNC) and followed mixing with 3 wt% polyvinyl alcohol (PVA) in aqueous solution. The AgNP/PVA/BNC films exhibited higher oxygen barrier capacity with slightly improved water vapor permeability. Hydrophobic modification can improve the stable dispersibility of nanocellulose in organic solvents. Song *et al.*^[51] firstly hydrophobically modified CNFs by free radical polymerization with hydrophobic monomer and composited it with PLA in tetrahydrofuran (THF) solution. The obtained CNF/PLA composites were then applied on paper surface via a cast-coating process and enhanced the water vapor barrier property of paper. Hendren *et al.*^[52] synthesized high-density polyethylene (HDPE)/CNCs nanocomposites through in situ dispersion and polymerization. CNCs aerogels were prepared first by freeze-drying and loaded with metallocene catalysts, and then the polymerization of ethylene was conducted in toluene solution with using catalyst-bound CNCs as catalyst. The aspect ratios of nanocelluloses and their dispersed morphologies in polymer matrix are the key factors affecting the performances of composites. Obviously, nanocelluloses can be well dispersed in the polymer matrix by solution mixing, but its addition amount should not be too high, otherwise it will cause agglomeration.

The melt compounding of polymer and nanocellulose is an important method for the large-scale preparation of their nanocomposites. For melt processing, homogeneous dispersion of nanocellulose in the melt of polymer is a challenge, since the viscosity of the melt is much higher than that of the solution. In this process, the interaction between nanoparticles is disrupted by mechanical force, so that they can be uniformly dispersed in the polymer matrix. Menezes *et al.*^[53] modified CNCs by grafting organic acid chlorides with different aliphatic chains and fabricated the low-density polyethylene (LDPE)/CNCs nanocomposites by melt mixing with a twin-screw extruder. The CNCs content is ranging from 0 to 15 wt%. A superior level of dispersion and significant

improvement in elongation at break was observed when sufficiently long chains were grafted on the surface of CNCs by an esterification reaction. Nazrin *et al.*^[54] prepared SPCNC-reinforced TPS/PLA blend bionanocomposite by melt blending with an internal mixer. Sugar palm crystalline nanocellulose (SPCNC) was first dispersed through sonication in advance of starch gelatinization, obtaining SPCNC-reinforced thermoplastic sugar palm starch (TPS) by solution casting. SPCNC-reinforced TPS was well dispersed within PLA phase, leading to a quicker diffusivity but reducing maximum water uptake for the bionanocomposites. Chihaoui *et al.*^[55] used lignocellulosic nanofibers (LCNFs) from date palm waste to reinforce polyethylene glycol (PEG)-plasticized polylactic acid (PLA). PLA/PEG/LCNF nanocomposites were fabricated by one-step melt processing with an extruder. LCNFs exhibited a homogeneously distributed and entangled network within the PLA/PEG matrix and resulted in greatly increasing on toughness.

As stated in the previous, a uniform dispersion and distribution of nanocellulose within polymer matrix can significantly affect the performances of the obtained nanocomposites. Generally, the nanocomposites fabricated with solution casting exhibited better reinforcing effects than the melt-mixed nanocomposites, mainly due to the formation of uniform dispersion and rigid cellulosic networks during casting. Mokhena *et al.*^[56] prepared polyethylene/CNCs nanocomposites by melt mixing and solution casting and compared the dispersion of CNCs in the matrix through different processing (as shown in Figs. 6b-d). The solution mixed nanocomposites showed a stronger reinforcing effect, probably because a rigid cellulosic network was formed during the process of solution mixing. The finer nanocellulose-based products such as membranes, scaffolds, and microspheres can be obtained by solution methods. Nonetheless, the melt processing route is very suitable for the large-scale production of bulk reinforced products, especially in the case of large amounts of nanocellulose. The dispersion state of nanoparticles in the melt can also be improved by flow-field induced dispersing and surface modification.^[57-59] However, the strong shearing effect of the processing may reduce the nanocellulose retention length, which is not conducive to the construction of the payload transport network.

4.1.2 Mechanical performances of nanocomposites

Nanocelluloses can significantly enhance the physicochemical performances of its nanocomposites with polymers when the dosage is very small, due to the surface effects in nanoscale and abundant reactive groups on the surface. Nanocelluloses can form a strong reinforcing network throughout the entire composite structure by solution casting or melt-mixed processing. As the material subjected to loading, the reinforcing networks inside the block act as a stress-transfer medium, which can absorb the stresses and inhibit the formation of cracks, ultimately resulting in increasing the overall stiffness and ductility of the composite. During the

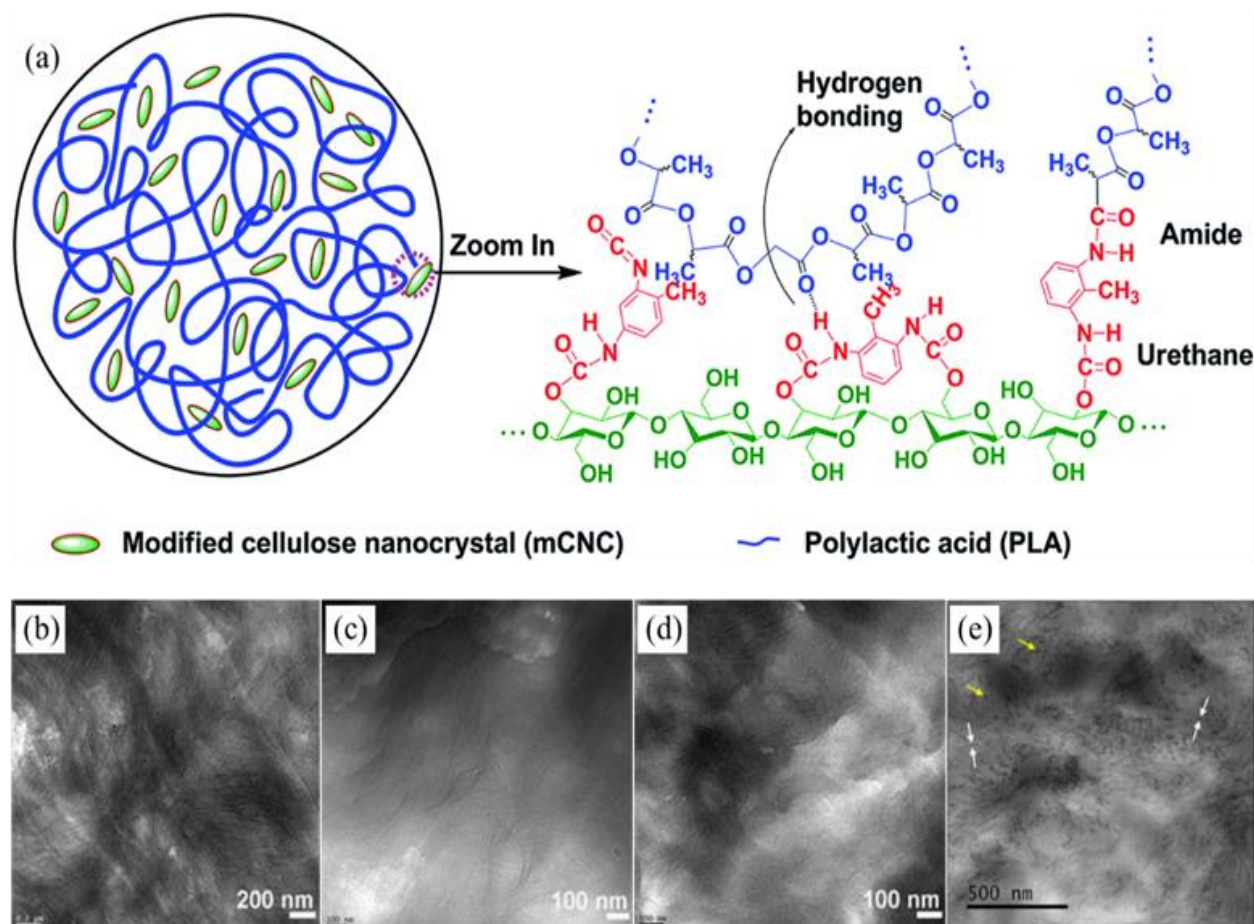


Fig. 6 (a) Schematic diagram of the dispersibility of mCNC in PLA matrix and interfacial interactions between mCNC and PLA, Reproduced with the permission from [48], Copyright 2016 The Royal Society of Chemistry. (b-d) TEM images of HDPE/sisal whiskers nanocomposites, Reproduced with the permission from [56], 2014 Society of Plastics Engineers; (b) untreated melt mixed 95/5 w/w HDPE/sisal, (b) VTES-treated melt mixed 95/5 w/w HDPE/sisal, and (c) untreated solution mixed 95/5 w/w HDPE/sisal. (e) TEM image of PCL/CNC25 through solvent processing, Reproduced with the permission from [46], Copyright 2018, Springer Science Business Media, LLC.

crack development process, nanofibers can span across the crack and anchored on both sides of the crack in the early stage, they are fractured or pulled out from the matrix when tensile stresses have reached their critical point. Theoretically, the presence of nanocellulose in the polymer matrix can absorb the stresses at any point and in any direction. The proper dosage and good dispersion are the keys to building an effective reinforcement network within the polymer matrix. As previously explained, the researchers constructed a three-dimensional network inside the PCL matrix through a special procedure without any additives or chemical modification.^[46] The PCL/CNCs nanocomposites displayed significant mechanical reinforcement, reaching a 155% Young's modulus increase at 25 wt% CNC content. Mokhena *et al.*^[56] confirmed that a good dispersion of whiskers and interaction with the polymers can be achieved through surface modification and the tensile performances of the nanocomposites were improved upon the addition of the whiskers. Hendren *et al.*^[52] made catalyst-loaded CNCs well dispersed in HDPE by in-situ polymerization without sacrificing interfacial characteristics. The results show that the reinforced nanocomposites exhibited

a significant increase in Young's modulus compared to commercially produced PEs.

The enhanced interface between nanocellulose and the matrix can improve the ability of the nanocomposites to resist destruction. Therefore, a strong interfacial interaction often leads to a manifold increase in the tensile strength and elastic modulus of nanocellulose reinforced composites. Sakakibara *et al.*^[60] proposed to tune the interface between CNFs and HDPE by the rational design of polymer dispersants based on the surface free energy and glass transition temperature and achieved both a uniform dispersion of CNF and greatly improved mechanical properties of CNF-reinforced HDPE nanocomposite by using a suitable dispersant. Jamaluddin *et al.*^[33] modified the surface of CNFs by introducing acetyl group and subsequently compounded the acetylated-CNFs with PLA matrix by solution casting. The compatibility of CNFs with PLA has been improved through esterification modification and the nanocomposites exhibited higher tensile strength and higher hydrophobicity than neat PLA. However, excessive interface interaction may result in a reduction in the elongation at break and increases brittleness of the

nanocomposites.^[61]

4.2 Nanocellulose-based hydrogels

Hydrogels are usually three-dimensional networks of hydrophilic polymer chains, or colloidal gels with water as the dispersion medium. Nanocellulose-based hydrogels are a class of composite hydrogels based on nanocellulose and polymers. The properties of nanocellulose-based hydrogels are different from those of other hydrogels as nanocelluloses form a colloidal suspension in water, while others form a solution. Nanocellulose-based hydrogels can generally be produced by electrostatic or covalent crosslinking as well as hydrophobic interactions. Nanocellulose-based hydrogels can be formed by physical or chemical crosslinking of aqueous solutions of specific concentrations, because of the abundant hydroxyl groups on the surface of nanocellulose which can be used to form hydrogen bond network for gel formation. The structures of hydrogels formed through reversible interactions, such as electrostatic hydrogen bond, Van der Waals, chain entanglements, and ionic and hydrophobic interactions, can

be disrupted easily. For instance, the sodium citrate can be used as electrostatic cross-linker to network cellulose nanofibers to produce hydrogels in acetic acid suspensions. Shefa *et al.*^[62] used TEMPO-oxidized cellulose nanofiber (TOCNF) and polyvinyl alcohol (PVA) to prepare a Cur incorporated physically crosslinked TOCNF-PVA-Cur hydrogel by a freeze-thaw process, which the hydrogel can release Cur to accelerate wound healing. Millon *et al.*^[63,64] obtained PVA/BNC hydrogel by using freeze-thaw cycles, which the PVA component are formed to be a solid hydrogel by physical crosslinking and the bacterial cellulose nanofibers exhibit good hydrophilicity. Chemical cross-linkers like epichlorohydrin, aldehyde, citric acid, metal ions, succinic anhydride and so on can be covalently crosslinked, which is an irreversible process. Zhu *et al.*^[65] fabricated a highly temperature resistant CNF/PVA hydrogel using aldehyde cellulose nanofiber as crosslinker. The hydrogel exhibits good thermal and dimensional stability for high-temperature sterilization treatment and a water content (82.7%) close to that of the biological tissue. Naseri *et al.*^[66] prepared a novel

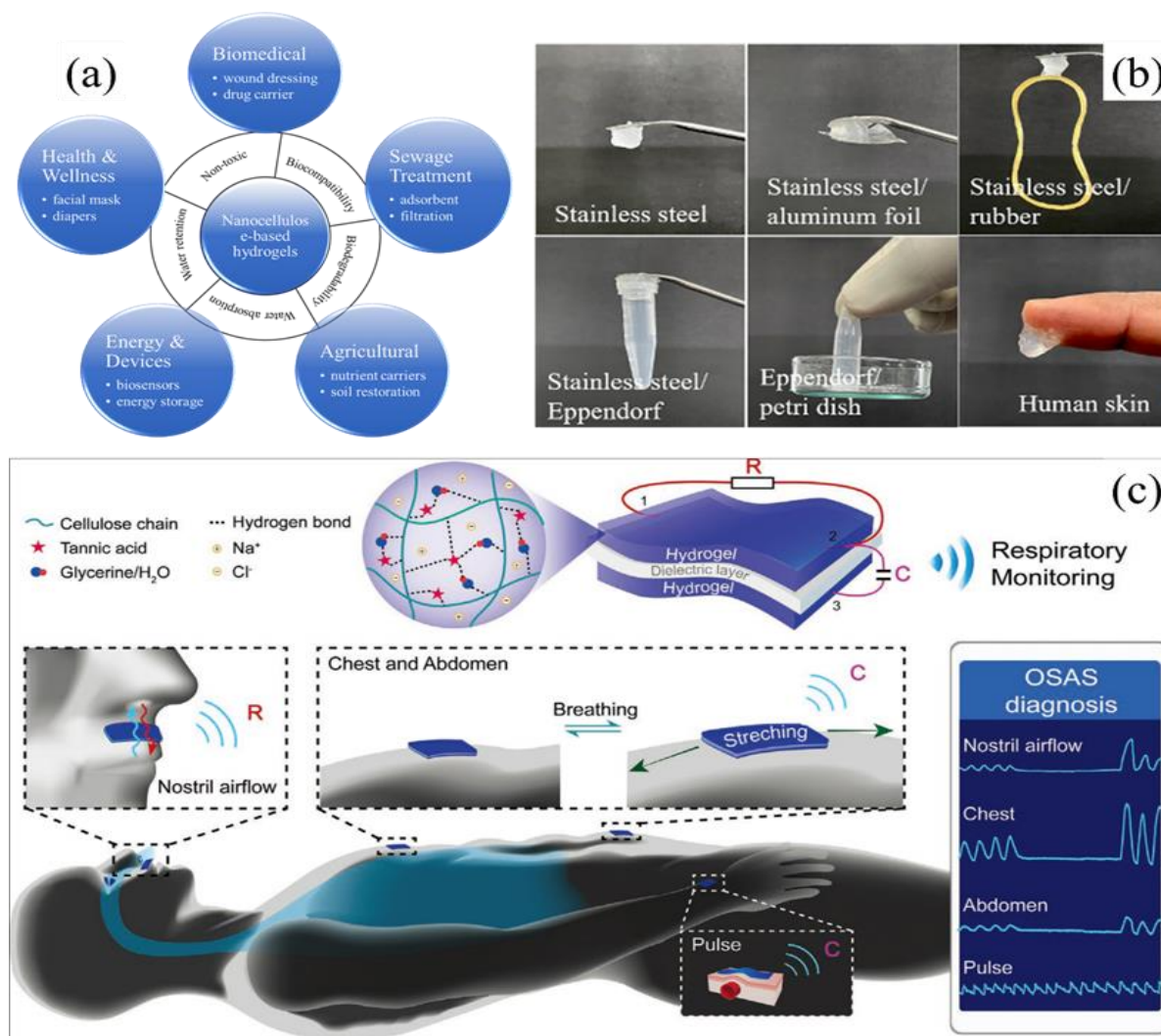


Fig. 7 (a) Applications of nanocellulose-based hydrogels, (b) Nanocellulose-based hydrogel with superior antibacterial efficiency for wound healing, Reproduced with the permission from [73], Copyright 2022 Elsevier Ltd. (c) Schematic illustration of cellulose-based hydrogel sensor with multimodal sensing capability for monitoring respiration. Reproduced with the permission from [75], Copyright 2022 Wiley-VCH GmbH.

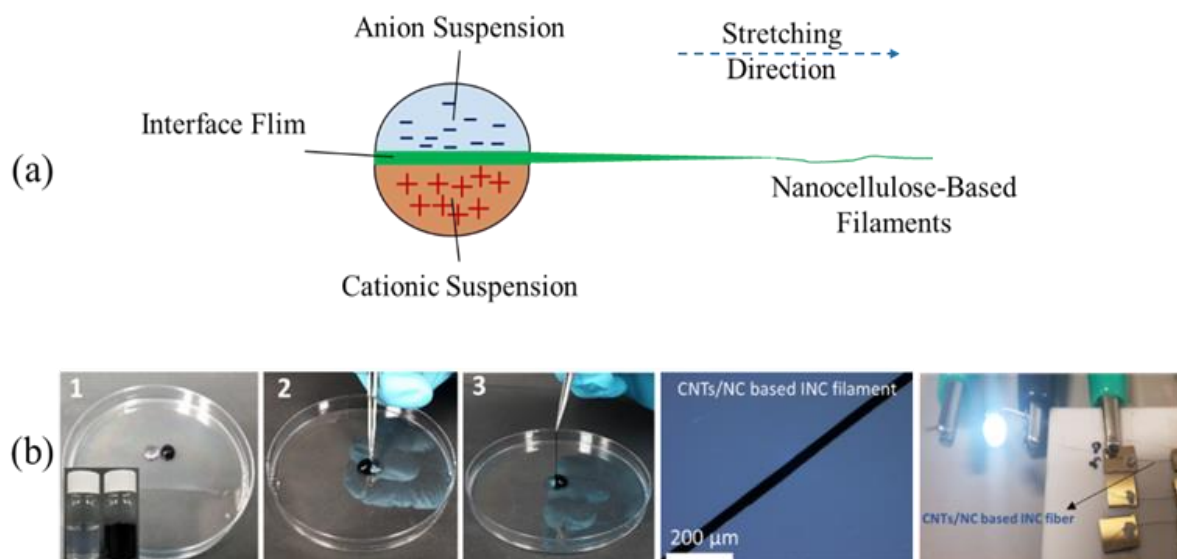


Fig. 8 (a) Schematic diagram of interfacial complexation spinning with oppositely charged nanocellulose suspensions. (b) Stretching process for preparing CNTs/NC based INC conductive filament. Reproduced with the permission from [81], Copyright 2019 American Chemical Society.

double crosslinked interpenetrating polymer network (IPN) hydrogels based on gelatin (G), sodium alginate (SA), and cellulose nanocrystals (CNC) were prepared through ionic crosslinking process. The IPNs were designed to incorporate CNC with carboxyl surface groups as a part of the network, which can contribute to the structural integrity and mechanical stability of the hydrogel. The IPN hydrogels exhibit a three-dimensional network of interconnected pores with hierarchical pore structure, which has potential benefits for cell adhesion. In addition, bacterial nanocellulose-based hydrogels are developed using many techniques. The BNC/poly (2-hydroxyethyl methacrylate) (PHEMA) hydrogels can be synthesized in situ by UV radical polymerization with HEMA as monomer.^[67,68] BNC-chitosan hydrogel composites were prepared in 1-ethyl-3-methylimidazolium acetate (EMIN-Ac) ionic liquid.^[69] Recently, a new type of high-performance CNF-based hydrogel has been developed by novel physical cross-linking and assembly technologies, without using toxic chemical crosslinking agents.^[70,71]

As shown in Fig. 7, nanocellulose-based hydrogels have widely used in packaging, biomedicine, biomedical materials, sewage treatment and energy electronics, due to their excellent water absorption, water retention, mechanical properties, eco-friendly, biocompatibility, and biodegradability.^[72-75]

4.3 Nanocellulose-based filaments

Nanocellulose-based cellulosic filaments is a new type of macroscopic fiber based on nanocellulose, that is, nanocellulose assembled along the axial direction to form a continuous thread and its diameter is usually to several micrometers or tens of micrometers. It has attracted growing interest in recent years and been used in composite reinforcement, textiles, biomedical product, sensor, and so on. Previously, many techniques have been explored to prepare

continuous nanocellulose-based filaments, such as electrospinning, wet-spinning, microfluidics, and flow focusing.^[12,76,77] Recently, a simple approach known as interfacial polyelectrolyte complexation (IPC) spinning has been used to fabricate the continuous nanocellulose-based filaments, which is a process based on the spontaneous self-assembly of filament upon stretching of the insoluble polyelectrolyte complex formed at interface of two oppositely charged polyelectrolytes.^[78-80] The schematic diagram of the formation mechanism of nanocellulose-based filaments is shown in Fig. 8a and the actual experimental procedure of filaments is exhibited in Fig. 8b. As discussed previously, nanofibers can alter their surface electronegativity and charge density through surface modification. Thus, the combination of IPC spinning and nanocellulose is a technological platform to develop multifunctional long fibers, by introducing other nanoparticles with specific functionalities, such as carbon nanotubes (CNTs),^[81,82] graphene,^[83] and boron nitride nanosheets (BNNS).^[84] For example, as combined with polyethylene glycol (PEG) and BNNS, a novel fibrous form-stable phase change materials with high thermal conductivity can successfully be fabricated by IPC spinning. Based on similar combinations, many types nanocellulose based functional fibers, such as conductive filaments, antibacterial filaments, and even hydrogel threads, have also been obtained successfully.^[78,80,81]

5. Conclusions

Nanocellulose is one of the most abundant renewable bio-nanofillers obtained from various lignocellulosic fibers, recyclable cellulosic-based material. Nanocellulose exhibits excellent mechanical properties, biodegradability, biocompatibility, and extensive chemical modification and has been widely used in biomedical, filtration, pharmaceutical,

reinforcing material, and so on. Currently, the extraction of nanocellulose is mainly achieved through two pathways, namely a top-down crushing and exfoliation method by removing all non-cellulosic components and a bottom-up biosynthesis route by microorganisms. The former is suitable for commercial production (generally obtaining CNCs and CNFs), while the latter is more suitable for the production of medical nanocellulose-based products (generally obtaining BNCs). However, the extraction of nanocellulose from cellulosic biomass is still a main challenge, due to the strong aggregation of lignin, hemicelluloses, and other components in plant cell wall. The morphologies and performances of nanocelluloses depend on the source of the cellulosic materials and their processing parameters. Due to the abundant active groups on the surface of nanocellulose (including CNCs, CNFs and BNCs), it has many modification possibilities to obtain various functionalized nanocellulose, resulting in the formation of multifunctional composites with specific functions such as excellent electrical or thermal conductivity, antibacterial properties, and outstanding mechanical properties. Although nanocellulose is derived from seemingly fragile plants or organisms, it can be used as a matrix or reinforcement material to fabricate high value-added cutting-edge materials or devices. In conclusion, nanocellulose is an environmentally friendly bio-nanomaterial with promising applications and should receive widespread attention in future research.

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Conflict of interest

There are no conflicts to declare.

Supporting information

Not applicable

References

- [1] J. Pennells, I. D. Godwin, N. Amiralian, D. J. Martin, Trends in the production of cellulose nanofibers from non-wood sources, *Cellulose*, 2020, **27**, 575-593.
- [2] J. Huang, J. Su, M. Weng, L. Xiong, P. Wang, Y. Liu, X. Lin, Y. Min, An innovative phase change composite with high thermal conductivity and sensitive light response rate for thermal energy storage, *Solar Energy Materials and Solar Cells*, 2022, **245**, 111872.
- [3] B. Wu, S. Lyu, H. Han, T. Li, H. Sun, J.-K. Wang, D. Li, F. Lei, J. Huang, D. Sun, Biomass-based shape-stabilized phase change materials from artificially cultured ship-shaped diatom frustules with high enthalpy for thermal energy storage, *Composites Part B-Engineering*, 2021, **205**, 108500.
- [4] J. T. McNamara, J. L. Morgan, J. Zimmer, A molecular description of cellulose biosynthesis, *Annual Review of Biochemistry*, 2015, **84**, 895.
- [5] M. Ghasemlou, F. Daver, E. P. Ivanova, Y. Habibi, B. Adhikari, Surface modifications of nanocellulose: From synthesis to high-performance nanocomposites, *Progress in Polymer Science*, 2021, **119**, 101418.
- [6] K. Heise, E. Kontturi, Y. Allahverdiyeva, T. Tammelin, M.B. Linder, Nonappa, O. Ikkala, Nanocellulose: recent fundamental advances and emerging biological and biomimicking applications, *Advanced Materials*, 2021, **33**, 2004349.
- [7] A. Sharma, M. Thakur, M. Bhattacharya, T. Mandal, S. Goswami, Commercial application of cellulose nano-composites – a review, *Biotechnology Reports*, 2019, **21**, e00316.
- [8] J. Xing, P. Tao, Z. Wu, C. Xing, X. Liao, S. Nie, Nanocellulose-graphene composites: a promising nanomaterial for flexible supercapacitors, *Carbohydrate Polymers*, 2019, **207**, 447-459.
- [9] M. B. Noremylia, M. Z. Hassan, Z. Ismail, Recent advancement in isolation, processing, characterization and applications of emerging nanocellulose: A review, *International Journal of Biological Macromolecules*, 2022, **206**, 954-976.
- [10] H. Kargarzadeh, M. Ioelovich, I. Ahmad, S. Thomas, A. Dufresne, Handbook of nanocellulose and cellulose nanocomposites. John Wiley & Sons, 2017.
- [11] A. Isogai, Emerging nanocellulose technologies: recent developments, *Advanced Materials*, 2021, **33**, 2000630.
- [12] M.M. Hamed, A. Hajian, A.B. Fall, K. Håkansson, M. Salajkova, F. Lundell, L. Wågberg, L.A. Berglund, Highly conducting, strong nanocomposites based on nanocellulose-assisted aqueous dispersions of single-wall carbon nanotubes, *ACS Nano*, 2014, **8**, 2467-2476.
- [13] Y. Chen, L. Zhang, Y. Yang, B. Pang, W. Xu, G. Duan, S. Jiang, K. Zhang, Recent progress on nanocellulose aerogels: preparation, modification, composite fabrication, applications, *Advanced Materials*, 2021, **33**, 2005569.
- [14] T. Xu, H. Du, H. Liu, W. Liu, X. Zhang, C. Si, P. Liu, K. Zhang, Advanced nanocellulose-based composites for flexible functional energy storage devices, *Advanced Materials*, 2021, **33**, 2101368.
- [15] S. Xie, X. Zhang, M.P. Walcott, H. Lin, Applications of cellulose nanocrystals: a review, *Engineered Science*, 2018, **2**, 4-16.
- [16] S. Ahankari, P. Paliwal, A. Subhedar, H. Kargarzadeh, Recent developments in nanocellulose-based aerogels in thermal applications: a review *ACS Nano*, 2021, **15**, 3849-3874.
- [17] B. Yuan, L. Li, V. Murugadoss, S. Vupputuri, J. Wang, N. Alikhani, Z. Guo, Nanocellulose-based composite materials for wastewater treatment and waste-oil remediation, *ES Food &*

Agroforestry, 2020, **1**, 41-52.

- [18] A. Subhedar, S. Bhadauria, S. Ahankari, H. Kargarzadeh, Nanocellulose in biomedical and biosensing applications: a review, *International Journal of Biological Macromolecules*, 2021, **166**, 587-600.
- [19] F. Jiang, Y.-L. Hsieh, Super water absorbing and shape memory nanocellulose aerogels from TEMPO-oxidized cellulose nanofibrils via cyclic freezing–thawing, *Journal of Materials Chemistry A*, 2014, **2**, 350-359.
- [20] Q. Huang, Y. Yang, R. Chen, X. Wang, High performance fully paper-based all-solid-state supercapacitor fabricated by a papermaking process with silver nanoparticles and reduced graphene oxide-modified pulp fibers, *EcoMat*, 2021, **3**, e12076.
- [21] P. Phanthong, P. Reubroycharoen, X. Hao, G. Xu, A. Abudula, G. Guan, Nanocellulose: extraction and application, *Carbon Resources Conversion*, 2018, **1**, 32-43.
- [22] T. Saito, S. Kimura, Y. Nishiyama, A. Isogai, Cellulose nanofibers prepared by TEMPO-mediated oxidation of native cellulose, *Biomacromolecules*, 2007, **8**, 2485-2491.
- [23] T. Saito, Y. Nishiyama, J.-L. Putaux, M. Vignon, A. Isogai, Homogeneous suspensions of individualized microfibrils from TEMPO-catalyzed oxidation of native cellulose, *Biomacromolecules*, 2006, **7**, 1687-1691.
- [24] D. Abol-Fotouh, M.A. Hassan, H. Shokry, A. Roig, M.S. Azab, A.E.-H.B. Kashyout, Bacterial nanocellulose from agro-industrial wastes: low-cost and enhanced production by *Komagataeibacter saccharivorans* MD1, *Scientific Reports*, 2020, **10**, 3491.
- [25] T. Xu, Q. Jiang, D. Ghim, K.-K. Liu, H. Sun, H.G. Derami, Z. Wang, S. Tadepalli, Y.-S. Jun, Q. Zhang, S. Singamaneni, Catalytically active bacterial nanocellulose-based ultrafiltration membrane, *Small*, 2018, **14**, 1704006.
- [26] B. Deepa, E. Abraham, N. Cordeiro, M. Mozetic, A. P. Mathew, K. Oksman, M. Faria, S. Thomas, L. A. Pothan, Utilization of various lignocellulosic biomass for the production of nanocellulose: a comparative study, *Cellulose*, 2015, **22**, 1075-1090.
- [27] Y. Habibi, A.-L. Goffin, N. Schiltz, E. Duquesne, P. Dubois, A. Dufresne, Bionanocomposites based on poly(ϵ -caprolactone)-grafted cellulose nanocrystals by ring-opening polymerization, *Journal of Materials Chemistry*, 2008, **18**, 5002-5010.
- [28] E. K. Sijabat, A. Nuruddin, P. Aditiawati, B. Sunendar Purwasmita, Optimization on the synthesis of bacterial nanocellulose (BNC) from banana peel waste for water filter membrane applications, *Materials Research Express*, 2020, **7**, 055010.
- [29] C. Gousset, H. Chanzy, M. L. Cerrada, E. Fleury, Surface silylation of cellulose microfibrils: preparation and rheological properties, *Polymer*, 2004, **45**, 1569-1575.
- [30] A. Dadkhah Tehrani, E. Neysi, Surface modification of cellulose nanowhisker throughout graft polymerization of 2-ethyl-2-oxazoline, *Carbohydrate Polymers*, 2013, **97**, 98-104.
- [31] K.-M. Chin, S. Sung Ting, H. L. Ong, M. Omar, Surface functionalized nanocellulose as a veritable inclusionary material in contemporary bioinspired applications: a review, *Journal of Applied Polymer Science*, 2018, **135**, 46065.
- [32] W. Zhang, L. Zhong, T. Wang, Z. Jiang, X. Gao, L. Zhang, Surface modification of cellulose nanofibers and their effects on the morphology and properties of polysulfone membranes, *IOP Conference Series: Materials Science and Engineering*, IOP Publishing, 2018, **397**, 012016.
- [33] N. Jamaluddin, T. Kanno, T.-A. Asoh, H. Uyama, Surface modification of cellulose nanofiber using acid anhydride for poly(lactic acid) reinforcement, *Materials Today Communications*, 2019, **21**, 100587.
- [34] Y. He, J. Zhu, W. Wang, H. Ni, Surface modification of cellulose nanocrystals with different acid anhydrides for improved dispersion in poly (butylene succinate), *RSC Advances*, 2018, **8**, 38305-38314.
- [35] Y. Chu, Y. Sun, W. Wu, H. Xiao, Dispersion properties of nanocellulose: a review, *Carbohydrate Polymers*, 2020, **250**, 116892.
- [36] C. Goussé, H. Chanzy, G. Excoffier, L. Soubeyrand, E. Fleury, Stable suspensions of partially silylated cellulose whiskers dispersed in organic solvents, *Polymer*, 2002, **43**, 2645-2651.
- [37] K. Sahlin, L. Forsgren, T. Moberg, D. Bernin, M. Rigdahl, G. Westman, Surface treatment of cellulose nanocrystals (CNC): effects on dispersion rheology, *Cellulose*, 2018, **25**, 331-345.
- [38] M.B. Agustin, F. Nakatsubo, H. Yano, Improving the thermal stability of wood-based cellulose by esterification, *Carbohydrate Polymers*, 2018, **192**, 28-36.
- [39] M. S. Peresin, K. Kammiovirta, H. Heikkinen, L.-S. Johansson, J. Vartiainen, H. Setälä, M. Österberg, T. Tammelin, Understanding the mechanisms of oxygen diffusion through surface functionalized nanocellulose films, *Carbohydrate Polymers*, 2017, **174**, 309-317.
- [40] X. Tian, M. Wu, Z. Wang, J. Zhang, P. Lu, A high-stable soybean-oil-based epoxy acrylate emulsion stabilized by silanized nanocrystalline cellulose as a sustainable paper coating for enhanced water vapor barrier, *Journal of Colloid and Interface Science*, 2022, **610**, 1043-1056.
- [41] A. G. Cunha, M. Lundahl, M. F. Ansari, L. -S. Johansson, J. M. Campbell, O. J. Rojas, Surface structuring and water interactions of nanocellulose filaments modified with organosilanes toward wearable materials, *ACS Applied Nano Materials*, 2018, **1**, 5279-5288.
- [42] Y. Shen, D. Li, L. Wang, Y. Zhou, F. Liu, H. Wu, B. Deng, Q. Liu, Superelastic polyimide nanofiber-based aerogels modified with silicone nanofilaments for ultrafast oil/water separation, *ACS Applied Materials & Interfaces*, 2021, **13**, 20489-20500.
- [43] K. Pacaphol, D. Aht-Ong, The influences of silanes on interfacial adhesion and surface properties of nanocellulose film coating on glass and aluminum substrates, *Surface and Coatings Technology*, 2017, **320**, 70-81.
- [44] Y. Ma, S. Qian, L. Hu, J. Qian, C. A. Fontanillo Lopez, L. Xu, Mechanical, thermal, and morphological properties of PLA biocomposites toughened with silylated bamboo cellulose nanowhiskers, *Polymer Composites*, 2019, **40**, 3012-3019.
- [45] J. Wang, C. Wang, W. Wang, W. Li, J. Lou,

- Carboxymethylated nanocellulose-based gel polymer electrolyte with a high lithium-ion transfer number for flexible lithium-ion batteries application, *Chemical Engineering Journal*, 2022, **428**, 132604.
- [46] L. G. Germiniani, L. C. da Silva, T. S. Plivelic, M. C. Gonçalves, Poly(ϵ -caprolactone)/cellulose nanocrystal nanocomposite mechanical reinforcement and morphology: the role of nanocrystal pre-dispersion, *Journal of Materials Science*, 2019, **54**, 414-426.
- [47] M. J. Dunlop, B. Acharya, R. Bissessur, Study of plant and tunicate based nanocrystalline cellulose in hybrid polymeric nanocomposites, *Cellulose*, 2020, **27**, 249-261.
- [48] J.-G. Gwon, H.-J. Cho, S.-J. Chun, S. Lee, Q. Wu, S.-Y. Lee, Physicochemical, optical and mechanical properties of poly(lactic acid) nanocomposites filled with toluene diisocyanate grafted cellulose nanocrystals, *RSC Advances*, 2016, **6**, 9438-9445.
- [49] Z. Shi, H. Xu, Q. Yang, C. Xiong, M. Zhao, K. Kobayashi, T. Saito, A. Isogai, Carboxylated nanocellulose/poly(ethylene oxide) composite films as solid-solid phase-change materials for thermal energy storage, *Carbohydrate Polymers*, 2019, **225**, 115215.
- [50] W. Wang, Z. Yu, F. K. Alsammarraie, F. Kong, M. Lin, A. Mustapha, Properties and antimicrobial activity of polyvinyl alcohol-modified bacterial nanocellulose packaging films incorporated with silver nanoparticles, *Food Hydrocolloids*, 2020, **100**, 105411.
- [51] Z. Song, H. Xiao, Y. Zhao, Hydrophobic-modified nanocellulose fiber/PLA biodegradable composites for lowering water vapor transmission rate (WVTR) of paper, *Carbohydrate Polymers*, 2014, **111**, 442-448.
- [52] K. D. Hendren, T. W. Baughman, P. A. Deck, E. J. Foster, In situ dispersion and polymerization of polyethylene cellulose nanocrystal-based nanocomposites, *Journal of Applied Polymer Science*, 2020, **137**, 48500.
- [53] A. Junior de Menezes, G. Siqueira, A. A. Curvelo, A. Dufresne, Extrusion and characterization of functionalized cellulose whiskers reinforced polyethylene nanocomposites, *Polymer*, 2009, **50**, 4552-4563.
- [54] A. Nazrin, S. M. Sapuan, M. Y. M. Zuhri, I. S. M. A. Tawakkal, R. A. Ilyas, Flammability and physical stability of sugar palm crystalline nanocellulose reinforced thermoplastic sugar palm starch/poly(lactic acid) blend bionanocomposites, *Nanotechnology Reviews*, 2022, **11**, 86-95.
- [55] B. Chihaoui, Q. Tarrés, M. Delgado-Aguilar, P. Mutjé, S. Boufi, Lignin-containing cellulose fibrils as reinforcement of plasticized PLA biocomposites produced by melt processing using PEG as a carrier, *Industrial Crops and Products*, 2022, **175**, 114287.
- [56] T. C. Mokhena, A. S. Luyt, Investigation of polyethylene/sisal whiskers nanocomposites prepared under different conditions, *Polymer Composites*, 2014, **35**, 2221-2233.
- [57] H. Zhang, J. Huang, L. Yang, R. Chen, W. Zou, X. Lin, J. Qu, Preparation, characterization and properties of PLA/TiO₂ nanocomposites based on a novel vane extruder, *RSC Advances*, 2015, **5**, 4639-4647.
- [58] C.-N. Yu, H.-C. Zhang, S.-X. Su, Y. Liang, Dynamic rheological behavior, crystallization and friction performance of ultrahigh molecular weight polyethylene/polypropylene blends by multi-step melt processing strategy, *Journal of Materials Research and Technology*, 2021, **15**, 6747-6757.
- [59] W. Zou, J. Huang, J. Su, W. Zeng, Y. Liang, R. Chen, H. Zhang, Y. Min, Z. Guo, Review on modification of poly (lactic acid) in physical and mechanical properties, *ES Food & Agroforestry*, 2021, **6**, 3-11.
- [60] K. Sakakibara, Y. Moriki, H. Yano, Y. Tsujii, Strategy for the improvement of the mechanical properties of cellulose nanofiber-reinforced high-density polyethylene nanocomposites using diblock copolymer dispersants, *ACS Applied Materials & Interfaces*, 2017, **9**, 44079-44087.
- [61] J.-K. Kim, Y.-W. Mai, Engineered interfaces in fiber reinforced composites. Elsevier, 1998
- [62] A. A. Shefa, T. Sultana, M. K. Park, S. Y. Lee, J.-G. Gwon, B.-T. Lee, Curcumin incorporation into an oxidized cellulose nanofiber-polyvinyl alcohol hydrogel system promotes wound healing, *Materials & Design*, 2020, **186**, 108313.
- [63] L. E. Millon, G. Guhados, W. Wan, Anisotropic polyvinyl alcohol-bacterial cellulose nanocomposite for biomedical applications, *Journal of Biomedical Materials Research Part B-Applied Biomaterials*, 2008, **86**, 444-452.
- [64] L. E. Millon, W. K. Wan, The polyvinyl alcohol-bacterial cellulose system as a new nanocomposite for biomedical applications, *Journal of Biomedical Materials Research Part B-Applied Biomaterials*, 2006, **79**, 245-253.
- [65] L. Zhu, Y. Liu, Z. Jiang, E. Sakai, J. Qiu, P. Zhu, Highly temperature resistant cellulose nanofiber/polyvinyl alcohol hydrogel using aldehyde cellulose nanofiber as cross-linker, *Cellulose*, 2019, **26**, 5291-5303.
- [66] N. Naseri, B. Deepa, A. P. Mathew, K. Oksman, L. Girandon, Nanocellulose-based interpenetrating polymer network (IPN) hydrogels for cartilage applications, *Biomacromolecules*, 2016, **17**, 3714-3723.
- [67] R. Hobzova, J. Hrib, J. Sirc, E. Karpushkin, J. Michalek, O. Janouskova, P. Gatenholm, Embedding of bacterial cellulose nanofibers within PHEMA hydrogel matrices: tunable stiffness composites with potential for biomedical applications, *Journal of Nanomaterials*, 2018, **2018**, 5217095.
- [68] R. Curvello, V.S. Raghuwanshi, G. Garnier, Engineering nanocellulose hydrogels for biomedical applications, *Advances in Colloid and Interface Science*, 2019, **267**, 47-61.
- [69] P. Chen, F. Xie, F. Tang, T. McNally, Ionic liquid (1-ethyl-3-methylimidazolium acetate) plasticization of chitosan-based bionanocomposites, *ACS Omega*, 2020, **5**, 19070-19081.
- [70] Y. Liu, Y. Sui, C. Liu, C. Liu, M. Wu, B. Li, Y. Li, A physically crosslinked polydopamine/nanocellulose hydrogel as potential versatile vehicles for drug delivery and wound healing, *Carbohydrate Polymers*, 2018, **188**, 27-36.
- [71] Q.-F. Guan, H.-B. Yang, Z.-M. Han, Z.-C. Ling, C.-H. Yin, K.-P. Yang, Y.-X. Zhao, S.-H. Yu, Sustainable cellulose-nanofiber-based hydrogels, *ACS Nano*, 2021, **15**, 7889-7898.
- [72] H. Takeno, H. Inoguchi, W.-C. Hsieh, Mechanical and

structural properties of cellulose nanofiber/poly(vinyl alcohol) hydrogels cross-linked by a freezing/thawing method and borax, *Cellulose*, 2020, **27**, 4373-4387.

[73] D. K. Patel, K. Ganguly, J. Hexiu, S. D. Dutta, T. V. Patil, K.-T. Lim, Functionalized chitosan/spherical nanocellulose-based hydrogel with superior antibacterial efficiency for wound healing, *Carbohydrate Polymers*, 2022, **284**, 119202.

[74] B. Wang, L. Dai, L.A. Hunter, L. Zhang, G. Yang, J. Chen, X. Zhang, Z. He, Y. Ni, A multifunctional nanocellulose-based hydrogel for strain sensing and self-powering applications, *Carbohydrate Polymers*, 2021, **268**, 118210.

[75] J. Liu, H. Wang, T. Liu, Q. Wu, Y. Ding, R. Ou, C. Guo, Z. Liu, Q. Wang, Multimodal hydrogel-based respiratory monitoring system for diagnosing obstructive sleep apnea syndrome, *Advanced Functional Materials*, 2022, 2204686.

[76] N. Ardila, N. Medina, M. Arkoun, M.-C. Heuzey, A. Ajji, C. J. Panchal, Chitosan-bacterial nanocellulose nanofibrous structures for potential wound dressing applications, *Cellulose*, 2016, **23**, 3089-3104.

[77] K. De France, Z. Zeng, T. Wu, G. Nyström, Functional materials from nanocellulose: utilizing structure-property relationships in bottom-up fabrication, *Advanced Materials*, 2021, **33**, 2000657.

[78] M. Do, B.G. Im, J. P. Park, J.-H. Jang, H. Lee, Functional polysaccharide sutures prepared by wet fusion of interfacial polyelectrolyte complexation fibers, *Advanced Functional Materials*, 2017, **27**, 1702017.

[79] M. Amaike, Y. Senoo, H. Yamamoto, Sphere, honeycomb, regularly spaced droplet and fiber structures of polyion complexes of chitosan and gellan, *Macromolecular Rapid Communications*, 1998, **19**, 287-289.

[80] J. Zou, F. Kim, Self-assembly of two-dimensional nanosheets induced by interfacial polyionic complexation, *ACS Nano*, 2012, **6**, 10606-10613.

[81] K. Zhang, S.D. Hujaya, T. Järvinen, P. Li, T. Kauhanen, M.V. Tejesvi, K. Kordas, H. Liimatainen, Interfacial nanoparticle complexation of oppositely charged nanocelluloses into functional filaments with conductive, drug release, or antimicrobial property, *ACS Applied Materials & Interfaces*, 2020, **12**, 1765-1774.

[82] K. Zhang, L. Ketterle, T. Järvinen, S. Hong, H. Liimatainen, Conductive hybrid filaments of carbon nanotubes, chitin nanocrystals and cellulose nanofibers formed by interfacial nanoparticle complexation, *Materials & Design*, 2020, **191**, 108594.

[83] L. Geng, Y. Lin, S. Chen, S. Shi, Y. Cai, L. Li, X. Peng, Superior strength and toughness of graphene/chitosan fibers reinforced by interfacial complexation, *Composites Science and Technology*, 2020, **194**, 108174.

[84] H. Fang, J. Lin, L. Zhang, A. Chen, F. Wu, L. Geng, X. Peng, Fibrous form-stable phase change materials with high thermal conductivity fabricated by interfacial polyelectrolyte complex spinning, *Carbohydrate Polymers*, 2020, **249**, 116836.

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