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Recent progress on chemical modification of Cellulose Nanocrystal (CNC) and its application in nanocomposite films and membranes- A comprehensive review

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Abstract

Cellulose nanocrystal (CNC) has recently gained much attention due to its unique properties such as abundancy, biodegradability, high strength, large surface area, functional ability, template structure, and sustainability. To broaden its application and enhance its compatibility with other materials, CNC can be modified via different methods. The modification is based on introducing new functions, including esterification, silylation, carbamation, polymerization, and so on. The application can concern many fields, such as polymer reinforcement, packaging, water treatment, textiles, biosensors, etc. Herein, we summarize the main approaches employed for the chemical modification and the use of the modified CNC material in the preparation of nanocomposite films and membranes, along with some emerging applications.

Keywords

Cellulose nanocrystal (CNC); self-assembly; chemical modification; membrane; film; nanocomposite.

Content

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1. Introduction

According to the 2019 UN report, the world population is growing at an annual rate of 1.1%, which predicts a global population of 8.5 billion in 2030, instead of the 7.7 billion recorded in mid-2019 (ONU, 2019). Admittedly, the growth rate has been decreasing since 1950. However, it is still accompanied by strong demand for food and increased exploitation of natural resources, which contribute to sizeable environmental stress and pollution (Okada, 2002)(Sudhakar et al., 2018).

Thus, synthetic polymers are used extensively to meet humanity's needs and ensure a more convenient way of life. These polymers often present many risks; they are persistent, hardly degradable, and their degradation by-products are often toxic. Hence the use of degradable polymers, especially biodegradable ones, is encouraged. Biodegradable polymers are defined as polymers that, in the presence of microorganisms in a natural environment, degrade into carbon dioxide and water without generating toxic by-products (Okada, 2002).

Biodegradable polymers are classified into three main categories (1) polyesters produced by microorganisms, (2) natural polysaccharides and other biopolymers, and (3) synthetic polymers, in particular aliphatic polyesters. Polysaccharide materials get a growing interest due to their abundance, non-toxicity, and biodegradability, which make them a good replacement for petroleum-based polymers(Garcia-Valdez et al., 2018); not only this, but they present physicochemical properties that favor their use in several other fields (Fang et al., 2019a).

Cellulose belongs to this family of polysaccharides; it is the most abundant biopolymer on earth, with an annual production estimated between 10^{11}-10^{12} tons (Nechyporchuk et al., 2016). It is used in several fields with the following distribution: 28% in materials sciences, 17% in engineering, 16% in chemistry, 11% in chemical engineering, 8% in physics and astronomy, 5% in biochemistry, genetics, and molecular biology, 4% in environmental science, 3% in agriculture and biological sciences, 3% in medicine, 3% in energy, 1% in immunology and microbiology and 1% in pharmacology, toxicology, and pharmaceuticals (Mohamed et al., 2017). Cellulose can originate from wood, flax, cotton, and algae in the form of microfibrils. Mechanical and chemical treatment of these microfibrils allows for obtaining cellulose nanofibrils (CNF) and cellulose nanocrystal (CNC) (Hamad, 2002). Cellulose can also originate from bacteria and has a more crystalline structure than cellulose extracted from plants.

This review is dedicated to cellulose nanocrystal (CNC) specifically. The first part concerns the origin, structure of cellulose, and its ability to self-assemble and form films. The second part emphasizes the main chemical modification of CNC surfaces applied during the last decade. In contrast, the last part gathers the techniques applied to develop composite membrane and film based on CNC and their possible applications.

2. Cellulose origin, structure, and its property to form films

Natural cellulose is originated from plants through the disintegration of the microfibers that form the cell wall (Figure 1) (Mohamed et al., 2017) (Gopakumar et al., 2018) (Dong et al., 2021); extraction can be made by chemical or mechanical treatment [14][13] and lead to two types of cellulose, cellulose nanofibrils (CNF) and cellulose nanocrystals (CNC). This approach is known as top-down biosynthesis. CNF consists of two regions, an ordered region, in other words, a crystalline region that confers high resistance to cellulose, and an amorphous region which contributes to the flexibility of the material (Phanthong et al., 2018). CNF is characterized by a diameter between 1-100 nm and a length between 500-2000 nm. When subjected to acid hydrolysis, cellulose nanofibrils undergo transverse cleavage along amorphous regions because they have a lower density due to their random orientation, resulting in the formation of cellulose nanocrystals (CNC) (Gopakumar et al., 2018) (Mohamed et al., 2017). Their dimensions depend on the starting material, their diameter varies between 2-20 nm (Sharma et al., 2020), and their length is between 100-500 nm (Gopakumar et al., 2018).

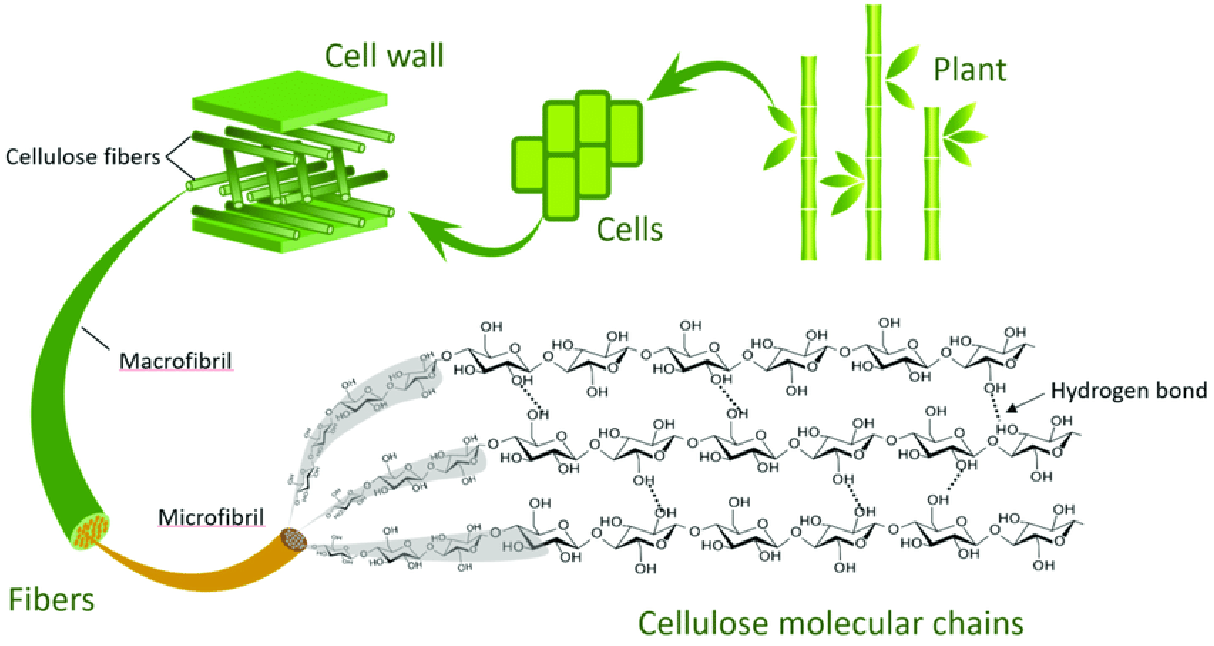

Figure 1. Illustration of the origin of natural cellulose (Han, 2019)**.**

Nanocellulose can also be obtained from bottom-up biosynthesis using bacteria (Bwatanglang et al., 2020). It is produced through the pores of bacteria membranes, so Gluconacetobacter is the species with the highest production ability (Belaustegui et al., 2020). There are other species such as Acinetobacter xylinumthrough (Sharma et al., 2020), Rhizobium, Agrobacterium, Sarcina and Alcaligenes (Belaustegui et al., 2020). Bacterial cellulose has the form of twisting ribbons with a diameter between 20-100 nm and length in micron order (Phanthong et al., 2018). It has the same structure as the cellulose extracted from the plant wall but presents higher purity and crystallinity (Revin et al., 2018).

The formula of cellulose is $(C_6H_{10}O_5)_n$, with n being the degree of polymerization that depends on the source of the cellulose and the method of isolation and purification [6]. It is composed of β-D-glucopyranose units linked together by β- (1,4) -glycosidic bonds (Arfin, 2020); each unit has 3 hydroxyl groups, a primary hydroxyl group on the C6, and two hydroxyl groups secondary on C2 and C3, presenting reactive sites that allow modification of cellulose (Fleet et al., 2008) (figure 2). The reactivity of these sites is governed by factors depending on the steric effects related to the supramolecular structure of cellulose and its isomerization. The C6 primary alcohol is ten times more reactive than the C2 and C3 secondary alcohols, thanks to the free rotation around the C5 and C6 bond. (Garcia-Valdez et al., 2018). These hydroxyl groups allow the formation of inter and intramolecular hydrogen bonds (Chu et al., 2020)(Kausar, 2020). These bonds allow the formation of a solid network giving cellulose a fibrillated structure, high resistance, and insolubility in water and most organic solvents (Phanthong et al., 2018).

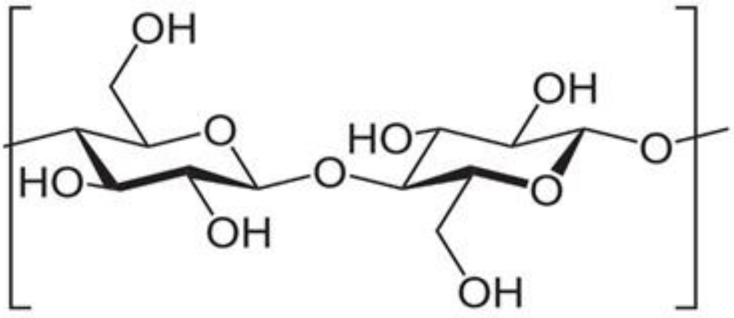

Figure 2. Cellobiose unit composed of two β-D-glucopyranose units.

CNC suspension behaves as a cholesteric crystalline liquid; this phase can be preserved after evaporation of the solvent, which leads to a well-structured iridescent film (Frka-Petesic et al., 2017). Factors such as the technic of extraction and concentration of the suspension have a direct impact on the self-assembly. CNC extracted using sulfuric acid exhibits a stable suspension due to sulfate groups negatively charged attached to the surface (Tran et al., 2020); this stability is a prerequisite to having self-assembly for cases where CNC is isolated by using phosphoric acid or hydrochloric acid, CNC will not be enough charged and will tend to flocculate which impacts the self-assembly negatively (Parker et al., 2018).

Above a particular concentration, CNC whiskers aggregate to form tactoids. While drying, they stack into layers. Each layer has a direction orthogonal to the nematic axis, and the layers are modulated to a helicoidal form (Dumanli et al., 2014) (Frka-Petesic et al., 2017), as shown in figure 3. The origin of the helicoidal arrangement is the chirality of CNC obtained due to D-glucose units (Tran et al., 2020). This specific structure displays CNC film with optical functionalities that favor its use in biophotonic material (Xiong et al., 2019).

Besides the optical properties, films based on nanocellulose show good mechanical properties compared to films made from other materials (tensile strength of 100–300 MPa and a modulus of 5–30 GPa) (Fang et al., 2019b). Thanks to their high surface area, they can be used as templates with other materials such as TiO_2, carbon, and organosilica (Lagerwall et al., 2014). Therefore, integrating novel functionalities in the CNC structure can extend their application as films in many different fields.

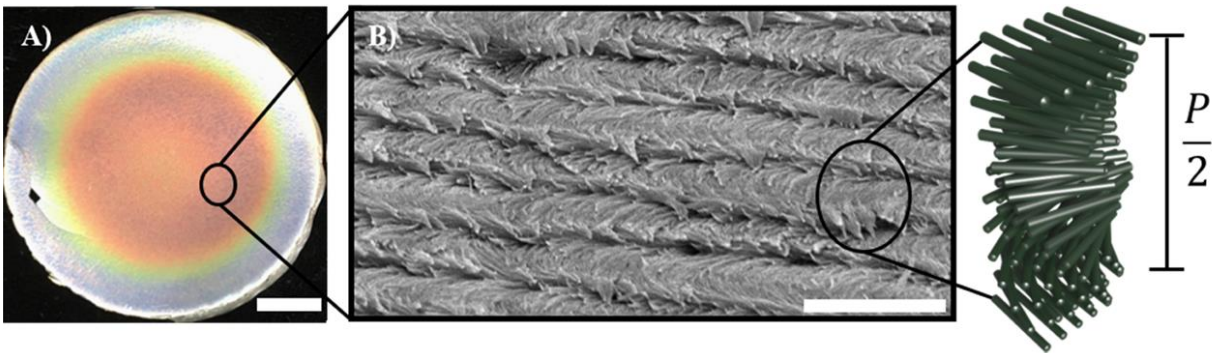

Figure 3. (A) Photograph and (B) scanning electron microscopy (SEM) image of CNC film (Tran et al., 2018)**.** John Wiley and Sons Copyright (2020).

3. Chemical modification of cellulose nanocrystal

Cellulose can be chemically modified via its hydroxyl groups, mainly the primary alcohol group. This modification can broaden its application and improve its compatibility with other materials. Modification could be done following different strategies depending on the species inserted.

3.1. Graft polymerization

Graft polymerization is considered a good approach to modifying the surface and endowing it with new physical and chemical properties (Wohlhauser et al., 2018). It consists of attaching a sequence of monomers to the cellulose backbone. The inserted polymer will give new properties to cellulose depending on its functional group (Roy et al., 2009). Two main approaches are used for graft polymerization, the “grafting to” and the “grafting from” approach (figure 4). The “grafting to“ approach involves attaching a pre-formed polymer to the cellulose's functional site via the polymer's reactive end group (Oberlintner et al., 2021). This approach can be limited because of the steric hindrance; larger polymer chains can intertwine and prevent the functional group from reaching the cellulose surface (Kedzior et al., 2019). While the “grafting from “consists of the immobilization of the initiator on the cellulose surface to allow the polymer chain's growth. This approach is widely used because it provides a high grafting density with a good control length (Wohlhauser et al., 2018) (Kedzior et al., 2019). The two approaches can be applied by using different techniques such as atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer (RAFT), nitroxide-mediated radical polymerization (NMP), ring-opening polymerization (ROP), and free radical polymerization.

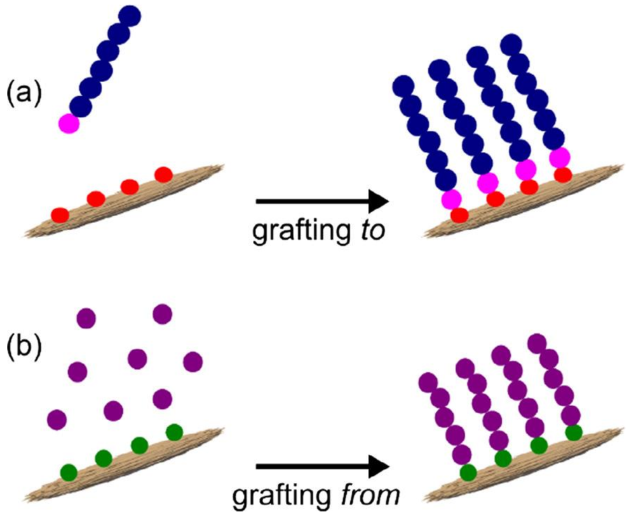

Figure 4. Schematic representation of (a) grafting to the CNC surface and (b) grafting from where polymerization is initiated from the CNC surface. (Kedzior et al., 2019)**.** Elsevier Copyright (2019).

3.1.1. Atom transfer radical polymerization (ATRP)

As its name implies, ATRP relies on the transfer of halogen atoms between a dormant species (R-X) and a transition metal catalyst M_t^n-X/ligand (Mishra & Kumar, 2012). The active radical is generated due to the transfer of the halogen atoms from the dormant species to a transition metal complex by oxidative addition. The radical created will then react with the monomer to further form a polymer chain (Roy et al., 2009).

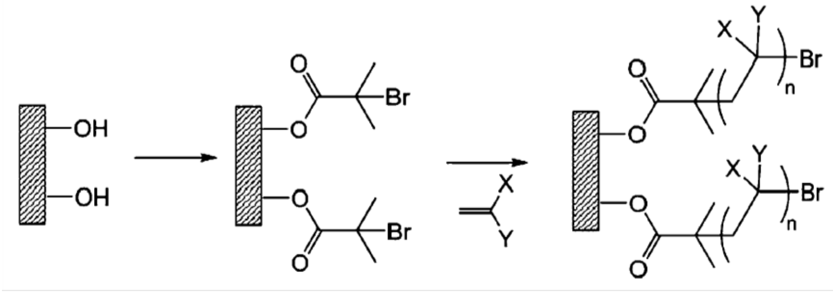

Figure 5. Modification of cellulose by grafting polymer via ATRP polymerization (Roy et al., 2009) The Royal Society of Chemistry, Copyright (2009).

ATRP has been largely used to graft polymers to substrates due to its ability to form a well-controlled polymer chain with a high grafting density. A large panel of monomers was attached to cellulose nanocrystals, as summarized in table 1. The main way used to start the surface-initiated ATRP (SI-ATRP) is to first graft the initiator to the surface of CNC by esterification; the initiator usually applied are 2-Bromoisobutyryl bromide "BIBB" and α-Bromoisobutyric acid "BIBA", then the polymer chain grows from the surface. The main negative point of using ATRP is the use of toxic transition metal complexes and the need to separate them from the final product. So, to overcome these drawbacks and decrease the amount of metal, Sèbe et al. used Activator Re-Generated by Electron Transfer ATRP (ARGET-ATRP) to graft polystyrene and poly(4-vinyl pyridine). This approach uses a reducing agent in excess to regenerate the catalyst regularly from the deactivated form. By comparing ATRP and ARGET-ATRP, it has been observed that ARGET promotes the formation of a longer chain with a low grafting density; this is because the propagation step is fast, and the amount of the catalyst is of the order of ppm (Z. Zhang et al., 2019). Another approach was applied by Cunningham et al. to reduce the amount of catalyst, based on the use of Cu(0) as a reducing agent. The Cu(0) was added in the form of wire and was easily removed at the end. (Arredondo et al., 2017)

3.1.2. Reversible addition-fragmentation chain-transfer (RAFT)

RAFT is an effective process for controlling living radical polymerization; it enables the synthesis of macromolecular with complex architecture (Semsarilar & Perrier, 2010). It involves thiocarbonylthio compounds that serve as chain transfer agents. The effectiveness of this agent relies on the radical leaving group "R", the activating group "Z" and its compatibility with monomers (Moad et al., 2013). Table 2 regroups polymers with the corresponding RAFT agent used. The R group needs to be a good homolytic leaving group and be able to reinitiate new polymer chains. In contrast, the Z group must provide the RAFT agent with good resonance stabilization and polar effects to be more active (Tsang & Holdcroft, 2012). Grafting polymers to CNC by RAFT polymerization surface can be applied by immobilizing the RAFT agent to the surface via either the Z approach or the R approach. In the Z approach, the di(tri)thio group is permanently grafted to the cellulose surface while the chain grows aside. In the R approach, the polymer chain grows from the surface (Boujemaoui et al., 2016). Li et al. used another method to graft “PDMAEMA-*b*-PGMA-*b*-PHFBA “to the CNC surface. The polymer was first synthesized by RAFT, and then it was grafted onto cellulose via the reaction between the epoxy ring of PGMA and the hydroxyl group of the cellulose. The hydrophobicity increased, confirming successful grafting (J. Zhou et al., 2021).

3.1.3. Ring-opening polymerization (ROP)

ROP is a polymerization technique that involves monomers such as epoxides, cyclic esters (ex. lactones, lactides), and cyclic carbonates (Sarazin & Carpentier, 2015). ROP occurs following mechanisms such as radical, cationic, anionic, and ring-opening metathesis polymerization (Nuyken & Pask, 2013). It mainly depends on the monomer, catalytic system, and the initiator used (Carlmark et al., 2012). The hydroxyl group can be used as an initiator for ROP. Thus modification of cellulose using ROP seems interesting (Carlsson et al., 2015) since no prior chemical treatment will be needed (Carlmark et al., 2012). Grafting PLA from CNC surface was extensively studied using Tin (II) octoate as a catalyzer (Table 3); this grafting aims to enhance CNC’s ability to adhesion with another polymer matrix to improve its properties.

Modified CNC	Polymer	Grafting Method	Reference
CNC-g-PMMAZO	Poly{6-[4-(4-methoxyphenylazo) phenoxy] hexyl methacrylate} (PMMAZO)	Grafting from	(Q. Xu et al., 2008)
CNC-g-PDMAEMA	Poly (N, N-dimethylamino ethyl methacrylate) (PDMAEMA)	Grafting from	(Yi et al., 2009) (Morits et al., 2018) (Rosilo et al., 2014) (Hu et al., 2016) (Arredondo et al., 2017)
CNC-g-PS	Polystyrene (PS)	Grafting from	(Z. Zhang, Tam, et al., 2018)(Morandi et al., 2009)
CNC-g-PEGEEMA	Poly (poly (ethylene glycol) ethyl ether methacrylate) (PEGEEMA)	Grafting from	(Hu et al., 2016)
CNC-g- P(PEGMA)	Poly (poly (ethylene glycol) methylacrylate) (P(PEGMA)	Grafting from	(X. Zhang et al., 2017)
CNC-g- PDEAEMA	Poly (diethyl aminoethyl methacrylate) (DEAEMA)	Grafting from	(Arredondo et al., 2017)
CNC-g-PNIPAAm	Poly(N-isopropyl acrylamide) (PNIPAAM)	Grafting from	(Zoppe et al., 2017)
CNC-g-PMETAC	Poly [2-(methacryloyloxy)ethyl]- trimethylammonium chloride (PMETAC)	Grafting from	(Zoppe et al., 2017)
CNC-g-PSS	Poly (sodium 4-vinylbenzenesulfonate) (PSS)	Grafting from	(Zoppe et al., 2017)
CNC-g-P(AzoC6MA-co-DMAEMA)	AzoC6MA PDMAEMA	Grafting from	(Yuan et al., 2018)
CNC-g-PBA	Poly (butyl acrylate)	Grafting from	(Kedzior et al., 2018)
CNC-g-P4VP	Poly(4-vinyl pyridine) (P4VP)	Grafting from	(Liangjiu Bai et al., 2019)(Z. Zhang, Sèbe, et al., 2018a)
CNC-g-P(NIPAAm–co-HDPAP)	PNIPAM 6,6'-(hydrazine-1,2 diylidene bis (phenyl methanylylidene))- bis(3-(allyloxy) phenol) (PHDPAP)	Grafting from	(Junyu Chen et al., 2020)
CNC-g-PFAZO	Poly(9-[4-[2-[4-(trifluorometh) phenyl] diazenyl] phenoxy] nonayl acrylate) (PFAZO)	Grafting from	(Z. Xu et al., 2020)
CNC-g-PBA	Poly (butyl acrylate) (PBA)	Grafting from	(Kiriakou et al., 2021)
CNC-g-POEGMA	Poly (Hydroxyl oligo ethylene glycol methacrylate) (POEGMA)	Grafting from	(Dupont et al., 2021)(Grishkewich et al., 2016)
CNC-g-PCEM	Poly (cinnamoyl ethyl methacrylate) (PCEM)	Grafting from	(Z. Zhang, Sèbe, et al., 2018b)
CNC-g-PBMA	Poly(butyl methacrylate) (PBMA)	Grafting from	(Boujemaoui et al., 2017)

Table 1. Summary of polymers grafted to CNC via ATRP.

Modified CNC	Agent RAFT	Polymer	Grafting Method	Reference
CNC-g-PVPy	4-cyano-4-(isopropoxycarbonothioylthio) pentanoic chloride	Poly(N-vinylpyrrolidone) (PVPy)	Grafting from	(X. Qin et al., 2021)(Ge et al., 2
CNC-g-(PDMAEMA-b-PGMA-b-PHFBA))	S-1- Dodecyl-S′-(α, α′-dimethyl-α″ -acetic acid) trithiocarbonate	Poly(2-(dimethylamino) ethyl methacrylate)-b-poly (glycidyl methacrylate)-b-poly (2,2,3,4,4,4-hexafluorobutyl acrylate) PDMAEMA-b-PGMA-b-PHFBA)	Grafting to	(J. Zhou et al., 2021) (J. Zhou et al., 2019) (Hong Li et al., 2020)
CNC-g-PDMAEMA	4-cyano-4-((phenylcarbonothioyl)-thio)pentanoic acid	Poly (dimethylaminoethyl methacrylate) (PDMAEMA)	Grafting from/ Grafting to	(Arredondo et al., 2020)
CNC-g-PDEAEMA	4-cyano-4-((phenylcarbonothioyl)-thio)pentanoic acid	Poly (diethyl aminoethyl methacrylate) (PDEAEMA)	Grafting from/ Grafting to	(Arredondo et al., 2020)
CNC-g-PDPAEMA	4-cyano-4-((phenylcarbonothioyl)-thio)pentanoic acid	Poly (diisopropylaminoethyl methacrylate) (PDPAEMA)	Grafting from/ Grafting to	(Arredondo et al., 2020)
CNC-g-(PDMAEMA-b-NIPAAm)	S-(thiobenzoyl)thioglycolic acid	Poly (N-isopropylacrylamide) (PNIPAAM) Poly (2-dimethylaminoethyl) methacrylate (PDMAEMA)	Grafting from/Grafting to	(Eskandari et al., 2020)
CNC-g-(BA-co-VI)	Macro CTA	Poly(n-butyl acrylate-co-1-vinyl imidazole)	Grafting from	(Wentao Wang et al., 2020)
CNC-g-P(DMAEMA-co-C)	S-(thiobenzoylthioglycolic) acid	Poly (2-dimethylaminoethyl) methacrylate (PDMAEMA) Pcoumarin	Grafting from	(Abousalman-Rezvani et al., 2019)
CNC-g-(PAA-b-PHFBA)	S-Benzyl-S’-trimethoxysilylpropyltrithiocarbonate	Polyhexafluorobutyl acrylate (PHFBA) Polyacrylic Acid (PAA)	Grafting to	(Yao et al., 2019)
CNC-g-PVAc	2-((Ethoxycarbonothioyl)thio) propanoic acid	Poly (vinyl acetate) (PVA)	Grafting from	(Boujemaoui et al., 2016)
CNC-g-PMMA	4-cyano-4-(phenylcarbonothioylthio) pentanoic acid	Poly (methyl methacrylate) (PMMA)	Grafting from	(Anžlovar et al., 2016)
CNC-g-P(NIMAAm-co-AA)	2-(dodecylthiocarbonothioylthio)-2-methyl propionic acid	Poly (acrylic acid) (PAA) Poly(N-isopropyl acrylamide) (PNIPAAm)	Grafting from	(Zeinali et al., 2014) (Zeinali et al., 2018)
CNC-g-(PNIPAAm-b-PAA	S-(thiobenzoylthioglycolic) acid	Poly (acrylic acid) (PAA) Poly(N-isopropyl acrylamide) (PNIPAAm)	Grafting from	(Haqani et al., 2017)
CNC-g-PAM	Macro CTA	Polyacrylamide	Grafting from	(T. Liu et al., 2017)(T. Liu et al., 2016)
CNC-g-PDMA	Macro CTA	Poly(N,N-dimethyl acrylamide)	Grafting from	(T. Liu et al., 2017) (T. Liu et al., 2018)

Table 2. Summary of polymers grafted to CNC via RAFT.

Modified CNC	Polymer	Grafting Method	Reference
CNC-g-POx	*Poly(2-oxazoline)*	Grafting to	(Gauche & Felisberti, 2019)
CNC-g-PEEP	*Poly (ethyl ethylene phosphate)*	Grafting to	(H. Wang et al., 2015)
CNC-g-PLA	*Poly (Lactide)*	Grafting from	(Jianxiang Chen et al., 2017) (Goffin et al., 2011)(Miao & Hamad, 2016)(Lizundia et al., 2016)(Habibi et al., 2013) (H. Wu et al., 2016)
CNC-g-P(CL-co-LA)	*Poly(D-lactide-co-ε,caprolactone)*	Grafting from	(Muiruri et al., 2017)
CNC-g-PLA6	*Poly(caprolactam) (Polyamide 6)*	Grafting form	(Rahimi & Otaibge, 2016)(Kashani Rahimi & Otaigbe, 2016)
CNC-g-PCL	*Poly(e-caprolactone)*	Grafting from	(Carlsson et al., 2015)

Table 3. Summary of polymers grafted to CNC via ROP.

3.1.4. Nitroxide-mediated polymerization (NMP)

NMP is based on the use of nitroxide to initiate the polymerization without the implication of another radical source or the need for a metal catalyst. The main characteristic of the alkoxyamine that could be used for NMP is its ability to provide reactive radical to initiate polymerization and form a stable mediating nitroxide radical. NMP can be used to graft polymer on a natural surface such as cellulose. For the" grafting from" approach, CNC can be functionalized with nitroxide forming, thus an alkoxyamine able to induce polymerization. Roeder and co-workers first graft BlocBuilder® (BB) on CNC via a covalent bond to the vinyl group of 4-chloromethyl styrene (CMS) that was already inserted into CNC. The polymerization was generated after adding the monomer (Roeder et al., 2016). The "Grafting to" approach was applied by Glasing et al., where they first modified CNC with glycidyl methacrylate (GMA). The polymerization was generated in the presence of macroalkoxyamines based on N-hydroxysuccinimidyl BlocBuilder® and polymers such as Styrene, N, N-(diethylamino)ethyl methacrylate(DEAEMA), and N-3-(dimethylamino)ethyl methacrylamide (DMAPMAm) (Glasing et al., 2017).

3.1.5. Free-radical polymerization (FRP)

FRP is an uncontrolled polymerization technique, and the synthesized polymers usually have a high dispersity. Several methods initiate FRP, such as chemical, thermal, and radiation. Jeun and co-workers successfully grafted 1H,1H,2H,2H-perfluorodecyl acrylate (PFDA) using electron beam (e-beam) irradiation as a technique to initiate the polymerization. The advantage of e-beam is that it avoids the application of harmful compounds (Jeun et al., 2019). Plasma was also applicated to graft polymers on CNC surfaces. Here, we can cite the research done by Alanis et al. where they graft different monomers (caprolactone, styrene, α-farnesene) (Alanis et al., 2019). The main advantage of this technique is the possibility of polymerizing a wide range of monomers.

3.2. Grafting small molecule

Grafting small molecules on the CNC surface is advantageous. Diverse functions can be grafted using reactions with suitable conditions and high yield. Many strategies are applied; we discussed below click chemistry, sylilation and esterification.

3.2.1. Click chemistry

Click chemistry was first introduced by Sharpless et al. in 2001, describing reactions that satisfy the following criteria: stereospecific, giving high yields, modular, wide in scope, implies simple experimental conditions, the product should be easily isolated and involve only benign solvent if it is necessary (Kolb et al., 2001). The commonly used click chemistry reactions are Diels-Alder, thiol-ene, the azide-alkyne Huisgen, and the Cu^1-catalyzed azide-alkyne cycloadditions (Filpponen, 2014). Click chemistry was used to modify CNC by either bringing two CNC chains together (Filpponen, 2014) or grafting new functionalities to its surface. CNC can be functionalized with an Azide or an alkyne functional group for the Azide-alkyne cycloaddition, and Thiol-ene click chemistry CNC should be modified with thiol function or a methacrylate (Table 4).

Modified CNC	Inserted species	Click-reaction	Ref
CNC-Azide	CNC-alkyne	Cu(I)-catalyzed Huisgen 1,3-dipolar	(Filpponen, 2014)
CNC-Azide	Propargyl-terminated poly(ethyl ethylene phosphate) (propargyl-PEEP)	Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC)	(H. Wang et al., 2015)
CNC-Azide	Polycaprolactone diol-C≡CH	(CuAAC)	(L. Zhou et al., 2018)
Fe_3O_4/CNC-Azide	Propargyl alcohol	(CuAAC)	(Movagharnegad et al., 2018)
CNC-methacrylate	1H,1H,2H,2H-perfluorodecanethiol	Thiol-ene	(Aalbers et al., 2019)
CNC-SH	N-phenyl maleimide	Thiol-ene	(J. L. Huang et al., 2014)
CNC-alkyne	Azide-polycaprolactone diol	(CuAAC)	(L. Zhou et al., 2019)

Table 4. Summary of species grafted to CNC via Click reactions

3.2.2. Silylation

CNC can be modified by inserting a Siloxane group to enhance the hydrophobicity of cellulose (Anpilova et al., 2020) and increase the thermal stability of the modified CNC (Khanjanzadeh et al., 2018). Zanata et al. developed crosslinked aerogels based on cellulose nanocrystals using 3-isocyanotopropyltriethoxysilane (IPTS), the developed material exhibit an amphiphilic character (De Morais Zanata et al., 2018). Silylation of CNC can have another purpose: endowing nanocellulose with flame retardancy. In this sense, Kim and co-workers modified CNC with Tris(2-chloroethyl) phosphate (TCEP) to incorporate it into a polyurethane matrix, and the result showed an increase in the limiting oxygen index up to 28% (Kim et al., 2020). To enhance CNC adsorption capacity toward CO_2, Zhu et al. modified it with 3-(2-aminoethylamino)-propyl methyl dimethoxy silane (APS); the results revealed that even after ten cycles of adsorption and desorption the adsorption capacity remained above 85% which emphasize the APS-CNC aerogel potential to adsorb CO_2 (W. Zhu et al., 2020). Incorporating organosilane-modified cellulose nanocrystal into natural rubber matrix proves its efficiency in improving mechanical properties of the latter; as Singh and co-workers showed in their research (Singh et al., 2020).

3.2.3. Esterification

The modification of cellulose nanocrystals by esterification is an interesting method to modify CNC, as summarized in table 5. Esterification can be applied using a variety of catalysts such as sulphuric acid, hydrochloric acid, iodine, potassium carbonate, and triethylamine, to name a few (Ávila Ramírez et al., 2017). The degree of substitution (DS), defined as the average number of substituent groups graft per base unit (anhydroglucose unit) for cellulose the DS may range from zero to three since it has three reactive hydroxyls (Wiley & Sons, 2011), depending on the concentration of the reagents, the concentration of catalyst and the removal of water (Abraham et al., 2016).

Grafted species	Degree of substitution	Usage	References
Canola oil fatty acid methyl ester	0.5	Hydrophobic coating agent	(Wei et al., 2017)
Acetic anhydride	2.18	Reinforcing nanocomposite	(Abraham et al., 2016)
Lauroyl chloride	0.2-2.4	Reinforcing nanocomposite	(Trinh & Mekonnen, 2018)
Succinic anhydride	1.6-2.2	Dye removal	(Emam & Shaheen, 2019)
Acetic anhydride	0.18-0.34	Reinforcing nanocomposite	(Ávila Ramírez et al., 2017)
Vinyl acetate- Vinyl cinnamate	-	Emulsifying agents	(Seìbe et al., 2013)
Palmitoyl chloride	0.3-0.8	Improve dispersibility	(Fumagalli et al., 2013)
Long-chain aliphatic acid chlorides	-	Reinforcing nanocomposite	(Bendahou et al., 2015)
Phenylacetic acid	0.5	Composite manufacturing	(Espino-Pérez et al., 2014)
Benzylacetic acid	0.3		
Rosin	-	Anti-microbial activity	(De Castro et al., 2016)
Malonate	0.16	Reinforcing nanocomposite	(Spinella et al., 2016)
Malate	0.22		
Citrate	0.18		
Lactic acid	87.7%	Reinforcing nanocomposite	(H. Wu et al., 2018)
Malic acid	0.035-0.20	Reinforcing nanocomposite	(Wei Wang et al., 2018)
Valeric acid	0.35	Reinforcing nanocomposite	(Shojaeiarani et al., 2019)
Succinic anhydride	0.12-0.32	Reinforcing nanocomposite	(Leszczyńska et al., 2019)
Octenyl Succinic Anhydride	0.539-0.768	Adsorption of Cu(II) ions	(Gupta et al., 2019)
3-thiophenetic acid	1.1	Increase planarity of the conjugated polymer chains	(Silva et al., 2021)

Table 5. Summary of species grafted to CNC via esterification, with the degree of substitution obtained and their different usage.

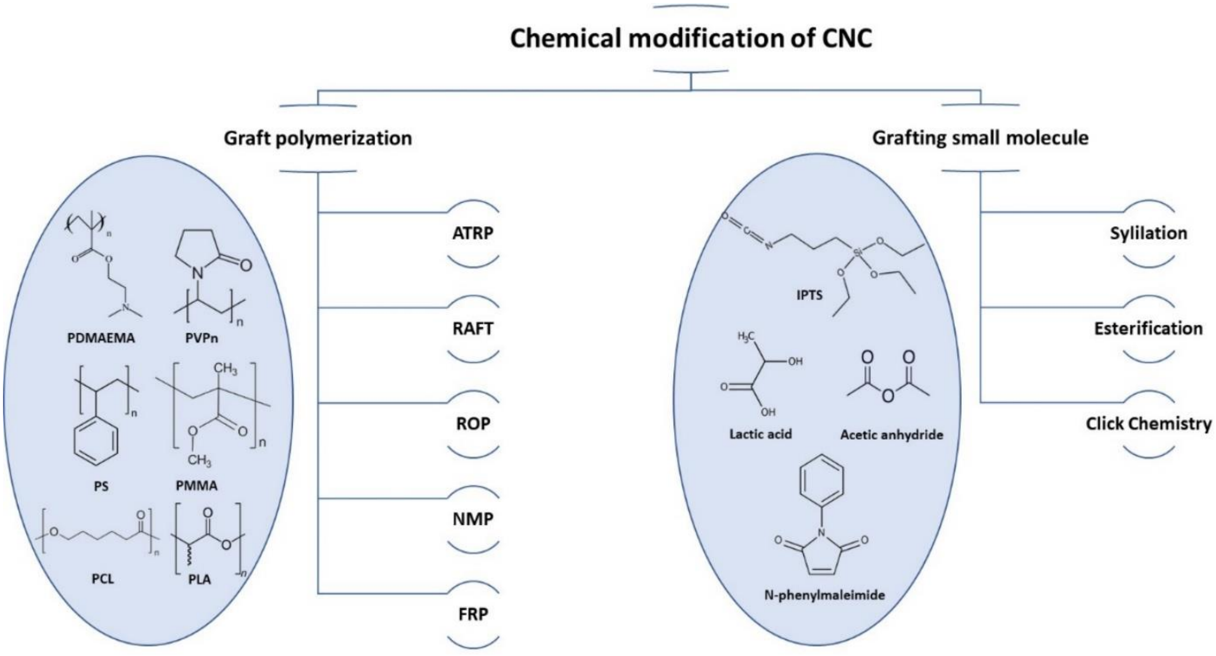

Figure 6: Schematic representation resuming strategies of chemical modification of CNC with some grafted species

4. Nanocomposite film and membrane-based on cellulose nanocrystal

4.1. Preparation of cellulose nanocrystal composite film and membrane

Cellulose nanocrystals can be used as templates with the ability to form mesoporous films (Y. Huang et al., 2020). The significant problems CNC films face are their brittleness and poor water resistance that prevent their applications. Huang et al. developed a flexible composite film using poly (ethylene glycol) diacrylate (PEGDA) to overcome this issue. PEGDA encapsulates CNC by forming a three-dimensional crosslinking network.

PEGDA was mixed with a photoinitiator, then added to a CNC suspension and cast in a plastic Petri dish. The film was obtained by evaporation-induced self-assembly (**EISA**); by the end of this step, CNC and PEGDA interacts via hydrogen bonding. To stimulate the encapsulation of PEGDA to CNC, the film was exposed to UV. It was observed that the tensile strength decreased with the increasing amount of PEGDA, while the flexibility of the composite film has been improved compared to the pristine CNC film. After soaking the prepared film for 24 h, its structure was preserved, which shows its good water-resistant property. The three-dimensional structure of the developed film allows its applications as a water-content detector, anti-counterfeiting label, and photonic paper (Y. Huang et al., 2020).

To avoid the coffee-ring phenomenon obtained due to the heterogeneity structure while the drying process, Zhang et al. used vacuum-assisted self-assembly (**VASA**) to help obtain a well-oriented and structurally homogeneous CNC film. CNC suspension was filtered using poly(tetrafluoroethene) (PTFE) as a support membrane under vacuum. After filtration and completely drying, CNC film was peeled off from PTFE. The effect of prior sonication and the volume of suspension was evaluated to emphasize their impact on the iridescent of the obtained film. It was reported that the sonication duration does not impact CNC crystallinity, but it is responsible for the coloration variation of the films obtained. A long sonication time is needed to obtain an iridescent CNC film via VASA. Beck et al. reported that sonication leads to the rejection of ions from the bound-water layer, which leads to a large pitch because of the weak chiral interaction between CNC particles (Beck et al., 2011). The amount of CNC also impacted the chiral nematic structure of the film. While changing the suspension volume, films with different colors were obtained, suggesting that the chiral nematic structure's helical pitch varies with the CNC film's thickness. The formation kinetics of CNC film also impact the iridescent of the latter so that variating the vacuum degree induces a color change (Q. Chen et al., 2014).

Vacuum filtration was used by Sulaiman et al. to prepare a nanocomposite film using a **layer-by-layer** approach. The group developed a bi-layer electrode using as layers polypyrrole/ graphene oxide (GO) and polypyrrole/CNC. The bilayer was prepared by first deposing PPy/ GO layer on a membrane filter via vacuum filtering and then adding the second layer PPy/CNC by applying vacuum filtration. After each deposition, the layers were washed with deionized water (Kulandaivalu & Sulaiman, 2020). Wagberg et al. reported that skipping the rinsing step will gender a rougher and less-defined layer (Wågberg & Erlandsson, 2021). After drying, the free-standing film was peeled off from the membrane. Multilayer film can be assembled via electrostatic interaction, hydrogen bonding, hydrophobic, and covalent bonding (Kulandaivalu & Yusran, 2019). Herein the interaction between the two layers was insured by hydrogen bonding between the oxygen in GO and the hydroxyl group of CNC. The assembly of the two layers PPy/GO|PPy/CNC induced active sites, which attributed to the generated film's high surface area (Kulandaivalu & Sulaiman, 2020). In the same context, Xia et al. developed a tri-layer membrane using mid-layer polydimethylsiloxane (PDMS), surrounded by two layers of nanocrystals cellulose modified with methyltrimethoxysilane. The silylation was intended to render the CNC surface hydrophobic and increase its dispersion in PDMS. The modification did not impact the crystallinity of CNC, which endowed the PDMS matrix with rigidity, one of the fundamental properties of CNC that favored its use as a reinforcing agent. The three layers were covalently bonded due to the crosslinking curing reaction applied during the preparation of the layers that provide strong adhesion between the layers. Barrier performance of the multilayer membrane improved compared with neat PDMS material; it was noted that oxygen permeability decreased due to the presence of Si-CNC, which was explained by the fact that Si-CNC nanoparticles block O_2 from diffusing while crossing the composite layers (Xia et al., 2018).

Shojaeiarani et al. developed a nanocomposite film based on poly (lactic acid) and CNC using EISA and **spin coating**. A mixture of PLA-CNC was prepared in chloroform, injected into a spin coater plate, and kept for 180s under a constant spin speed of 150 rpm; the film was obtained after the evaporation of solvent at room temperature (figure 7). It was concluded that spin coating allows good dispersion of CNC due to the high drying rate, compared to EISA, which improves the degree of crystallinity and decreases the hydrophilicity (Shojaeiarani et al., 2020).

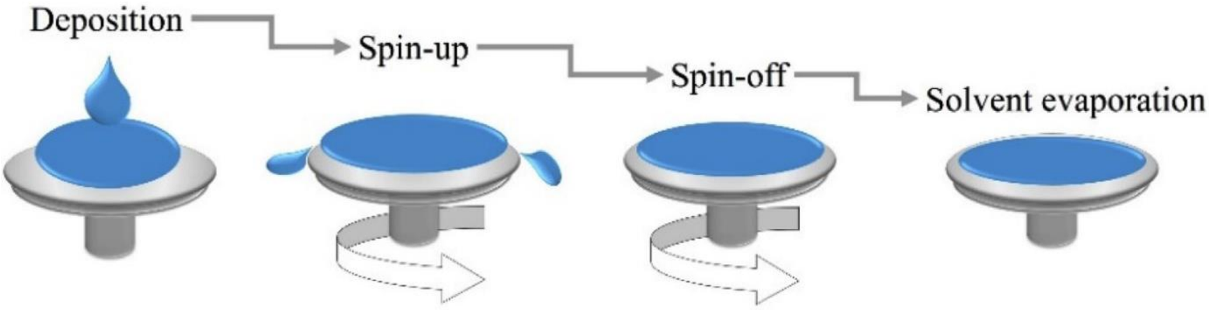

Figure 7. Formation of the film via the spin-coating method (Shojaeiarani et al., 2020)**.** Elsevier Copyright (2019).

Electrospun nanocomposite mats-based chitosan/Polyethyleneoxide /CNC was prepared by Nasri et al. using CNC isolated by hydrochloric acid or sulphuric acid to investigate the effect of surface functionalities of CNC. During the electrospinning process, it was observed that the jet was stable for the solution prepared with CNC (HCl), which led to the formation of fibers of good quality. In contrast, the fiber obtained by using CNC (H_2SO_4) was non-uniform. The mechanical properties increased with the reinforcement of the matrix fiber with both types of cellulose nanocrystals (Naseri et al., 2015). In another study by Nair et al., they reported a decrease in both tensile strength and Young's modulus for nanocomposite fiber mats based on CNC and Cellulose acetate (CA), and it was explained by the fact that CNC acted more defects due to the aggregation during the loading (Naseri et al., 2015).

4.2. Application of cellulose nanocrystal composite membrane and film

Film and membrane have promising use in electronics, sensors, solar cells, water treatment, and so on. Several studies have been carried out in this direction. They have shown the possibility of integrating cellulose into different matrices to develop films with good performance depending on their field of application.

4.2.1. Conductive materials

To endow cellulose with electrical properties, a conductive material such as conductive polymers (Polyaniline, Polypyrrole, etc.), metallic particles, and conductive carbon material was combined with cellulose, so the developed nanocomposite material exhibits properties of both materials (Du et al., 2017). Polyaniline (PANI), one of the conductive polymers, has drawn much attention due to its high electrical conductivity. However, PANI tends to aggregate, limiting its application (S. Wang et al., 2016)(Nepomuceno et al., 2021). PANI was synthesized in the presence of other materials such as CNC to overcome this issue. Nepomuceno et al. synthesized PANI via in situ polymerization in the presence of CNC; the latter played the role of a backbone to PANI deposition. The group reported that while adding aniline to CNC, the amino group of aniline interacted with the hydrogen bond between the hydroxide group of CNC, which promoted the in-situ polymerization. The negative charge on the CNC surface interacted with positively charged amine groups of polyanilines which slowed the polymerization time. In other words, increasing the amount of aniline monomer enhanced the probability of polymerization occurring, thus decreasing the polymerization time. Increasing PANI concentration led to CNC coating, facilitating electrons' mobility. For a PANI/CNC ratio of 0.4, the conductivity obtained was $8.9x10^{-1}$S cm^{-1}; this value matches the requirement for using sensors and electromagnetic interference shielding (Nepomuceno et al., 2021). To increase the stability of CNC/PANI, Wang et al. used cellulose nanofibers as a dispersant. The obtained film exhibits a conductivity of 104.7 S cm^{-1}. The group reported that the presence of CNF avoids the agglomeration of CNC and PANI (S. Wang et al., 2016). Wu et al. have also used polypyrrole with CNC to develop a nanocomposite material for supercapacitor application. To obtain a well-controlled and uniform coating of PPy, poly(N-vinyl-pyrrolidone) PVP was first adsorbed on the CNC surface to modify the hydrophilicity of CNC and favored the coating of PPy. PPy also acts as a stabilizer that inhibits the formation of aggregates. Due to hydrogen bonds between the carbonyl groups of PVP and the N-H group of pyrroles, the PPY growth uniformly on PVP-coated CNC. The core-shell PPy/PVP/CNC material exhibit a conductivity of 36.9 S cm^{-1} (X. Wu et al., 2014). Incorporating nanoparticles into CNC matrices enhances conductivity, as reported by El-Nahrawy et al. The group developed a nanocomposite material consisting of CNC coated with PPy and Ag Nanoparticles and (Ni_2O_3) nanoparticles. The formed material had unique electroconductive properties due to the support of PPy with the presence of an excess of charge carries (El-nahrawy et al., 2020).

4.2.2. Water treatment

Nanocomposite membranes are promising materials for mitigating fouling and compromise between selectivity and permeability. Cellulose nanocrystal presents an excellent material to be part of this nanocomposite membrane, so the last can exhibit all the properties mentioned. The choice of cellulose nanocrystal is because they can be easily functionalized with other moieties to enhance their efficiency in retaining pollutants. Moreover, their hydrophilic nature due to the presence of hydrophilic groups can help mitigate fouling (C. Xu et al., 2020). The presence of CNC contributes to the membrane's good mechanical properties by increasing the tensile strength (Cruz-Tato et al., 2017), and it is favored over other nanoparticles because it is considered a renewable, non-toxic, and biodegradable material (Asempour et al., 2018) solving thereby leaching problem related to toxic nanoparticles.

Composite material	%CNC	Pollutants	Removal rate	Reference
PES	*2 % (wt%)*	*Humic acids (HAs)* *Bovine serum albumin (BSA)*	*71.9% (HA)* *82.7% (BSA)*	(Langming Bai et al., 2020)
PES	*5.5 µg/cm*^{2}	*Heavy metal ions*	*98 % (*$CuSO_4$*)* *96.5% (*$CuCl_2$*)* *90.8% (*$PbCl_2$*)*	(Hoang et al., 2020)
PA/PES	*0.01 wt% CNC/Ag*	*Salt* *Bacteria*	*99.1% (*Na_2SO_4*)* *99.4% (Escherichia Coli)*	(C. Xu et al., 2020)
PA	-	*Bacteria*	*~ 89% (Escherichia Coli)*	(Jackson et al., 2021)
PA	*0.1% (w/v)*	*Salt*	*97.8%*	(Asempour et al., 2018)
PES	*1 wt%*	*Color* *Chemical oxygen demand (COD)*	*94 % (color)* *88 % (COD)*	(Jonoobi et al., 2019)
PA/PLS	*0.05 wt%*	*Salt*	*98.3% (*Na_2SO_4*)* *96.1% (*$MgSO_4$*)*	(S. Huang et al., 2019)
PVDF	*4 wt%*	*Oil/water*	*97% of separation*	(X. Wang et al., 2019)
Cellulose ester	*26.7 mg.ml*$^{-1}$	*Antibiotic*	*89% Tetracycline hydrochloride*	(J. Liu et al., 2020)
Chitosan	*90 wt%*	*Dyes*	*98% (Victoria Blue 2B)* *84% (Methyl Violet 2B)* *70% (Rhodamine)*	(Karim et al., 2014)
Cellulose Sludge/ CNF	-	*Heavy metal ions*	*0.87 mg g*$^{-1}$ *(*Ag^+*)* *374 mg g*$^{-1}$ *(*Cu^{2+}*)* *456 mg g*$^{-1}$ *(*Fe^{2+}/Fe^{3+}*)*	(Karim et al., 2017)
Cu mesh	-	*Aqueous crude oil mixture*	-	(M. B. Wu et al., 2019)
PES	-	*Aqueous crude oil emulsion*	-	(M. B. Wu et al., 2019)
PA	-	Na_2SO_4	*96.7%*	(J. J. Wang et al., 2017)
GO/PA	-	Na_2SO_4	*94.2%–97.2%*	(C. Y. Zhu et al., 2021)

Table 6.Summary of composite membranes based on CNC for water treatment with the targeted pollutants and the removal rate

CNC was incorporated with different materials such as polyethersulfone (PES), polyamide as an active layer (PA), polysulfone (PSF), and polyvinylidene fluoride (PVDF), among others to remove diverse pollutants (Table 6). Several researchers used PES to develop nanocomposite membranes due to its high thermal stability and chemical resistance in organic solvents (Langming Bai et al., 2020). Janoobi et al. developed a nanocomposite membrane based on PES and CNC to remove color and reduce chemical oxygen demand from industrial wastewater. The group first modified CNC with (3-aminopropyl) triethoxysilane (APTES), then mixed it with polyethersulfone polymer. The membrane was then prepared based on this blend solution. Adsorption tests showed that the presence of CNC enhanced the removal of color and contributed to the reduction of chemical oxygen demand. The adsorption was ensured by hydrogen interaction between hydroxyl groups of CNC and the different groups of the colored compounds. The presence of amino group from APTES help increase the removal of color due to its interaction with anionic groups of color, so they play the role of new adsorption sites (Jonoobi et al., 2019). Another reason to prepare composite membranes using CNC is to prevent fouling. Bai et al. used CNC due to its hydrophilic property. Comparing composite membrane based on CNC and PES to neat PES membrane, they note that the composite membrane is more hydrophilic, has a higher porosity than the neat one, and exhibits good performance in terms of antifouling ability. However, the excess of CNC renders the membrane surface rough due to the poor dispersibility of high concentrated solution of CNC, which impact the porosity and the permeability of the nanocomposite membrane too (Langming Bai et al., 2020). To endow a nanofiltration membrane with antifouling and antibacterial properties, Xu et al. prepared a composite membrane by incorporating CNC and Ag nanoparticles into an active polyamide layer, and PES was applied as the support material for this active layer. The developed membrane exhibits good antifouling and antibacterial performance and helps reduce energy consumption known for the nanofiltration process due to the enhancement in water flux and salt rejection (C. Xu et al., 2020). In the study by Jackson et al., CNC was used only as an anti-microbial agent and incorporated into the membrane; the result showed the inactivation of up to 89% of *Escherichia Coli*. The group relates the anti-microbial activity of CNC to its rod-like morphology that damage the cell membrane of the bacteria after contact (figure 8) (Jackson et al., 2021).

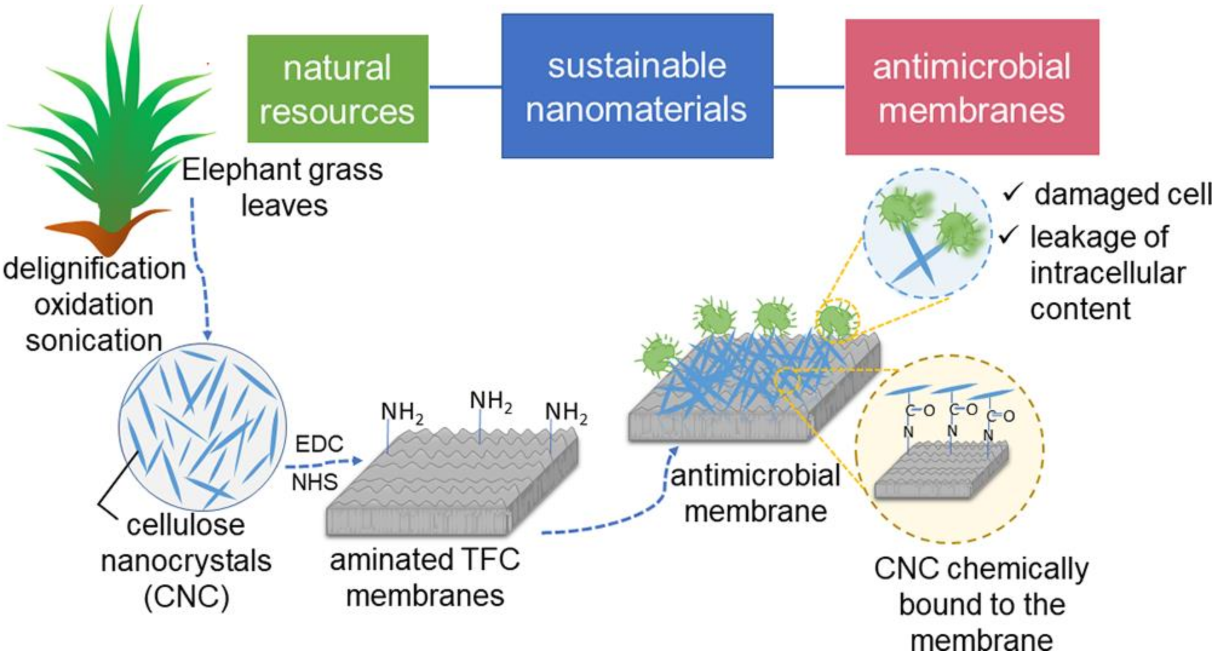

Figure 8. Representative scheme of membrane-based on CNC with antibacterial activity (Jackson et al., 2021)**.** American Chemical Society Copyright (2021).

4.2.3. Packaging

CNC has been widely used in packaging as a reinforcing material. Due to the CNC network, the mechanical properties of the reinforced material improve significantly (S. Liu et al., 2019). Furthermore, this network plays the role of a barrier to water vapor and oxygen, one of the crucial criteria for selecting the packaging material. Packaging films based on CNC blending with PLA and PVA were extensively studied and showed promising results in thermal stability, stiffness, and anti-microbial activity. (Pal et al., 2019) reinforced PLA with CNC and reduced graphene oxide (rGO). The developed film exhibited a higher crystallinity due to the strong physical interaction between CNC and PLA. Thus, the crystallinity increase reduces the water vapor permeability value. (Salmieri et al., 2014) developed a bioactive packaging film based on CNC-PLA coated by nisin, the results showed a promising inhibiting capacity against *Listeria monocytogenes.* On the other hand, (Dey et al., 2021) emphasize the antifungal property of CNC, incorporated into PVA film, against postharvest pathogens. The study showed the potential application of CNC for the packaging of fresh fruits. CNC was incorporated into other natural polysaccharides, such as alginate, chitosan, and carrageenan (Yadav et al., 2019). In general, polysaccharides are a promising material for packaging due to the considerable advantages they present as the preservation of aromas, inhibition of oxygen penetration, and water absorption, not to mention their abundance and price (Hui Li et al., 2020).

4.2.4. Biomedical

CNC has been known to be biocompatible and non-toxic for biomedical applications. It can be used for artificial blood vessels, tissue engineering (Dugan et al., 2010), drug delivery(Lin et al., 2016), etc. (Zeimaran et al., 2019) reinforced urethane with CNC to develop a self-healing nanocomposite film. The developed material showed an excellent cytocompatibility toward human dermal fibroblasts, making it promising for application in material engineering. In a more concrete study, (L. Qin et al., 2020) introduced CNC into a collagen-based film for corneal repair. The film was tested in vitro on rabbit corneal epithelial cells and keratocytes. The film showed its effectiveness in promoting epithelial wound healing and inhibiting keratocyte-myofibroblast transformation, which emphasizes CNC's potential to be applied as reinforcing agent material for corneal regeneration and reconstruction. A film based only on CNC can also be applied for medical purposes. As the study by (Prathapan et al., 2018) affirmed, the researchers prove the ability to use CNC film for blood typing. Despite all these advantages, the nanotoxicity of CNC needs to be more investigated since some studies reported some possible CNC toxic outcomes (Seabra et al., 2018).

5. Summary

Cellulose is the most abundant biopolymer that can replace petroleum-based materials that harm health and the environment. CNC can be extracted from native cellulose and is known for its important mechanical properties (similar to Kevlar), surface reactivity, and its ability to self-assemble. Chemical modification of CNC broadens its application in different domains of material science and enhances its compatibility with other materials. Developing film and membrane based on CNC or modified CNC is a good solution to minimize the use of non-biodegradable material. These films and membranes could be used in various applications such as biosensors, electrodes, and membranes for water treatment, to name a few. Developing composite material from CNC could provide solutions to a broad range of technological bottlenecks in the industry and replace toxic materials currently being banned from use due to their impact on human health and environmental issues.

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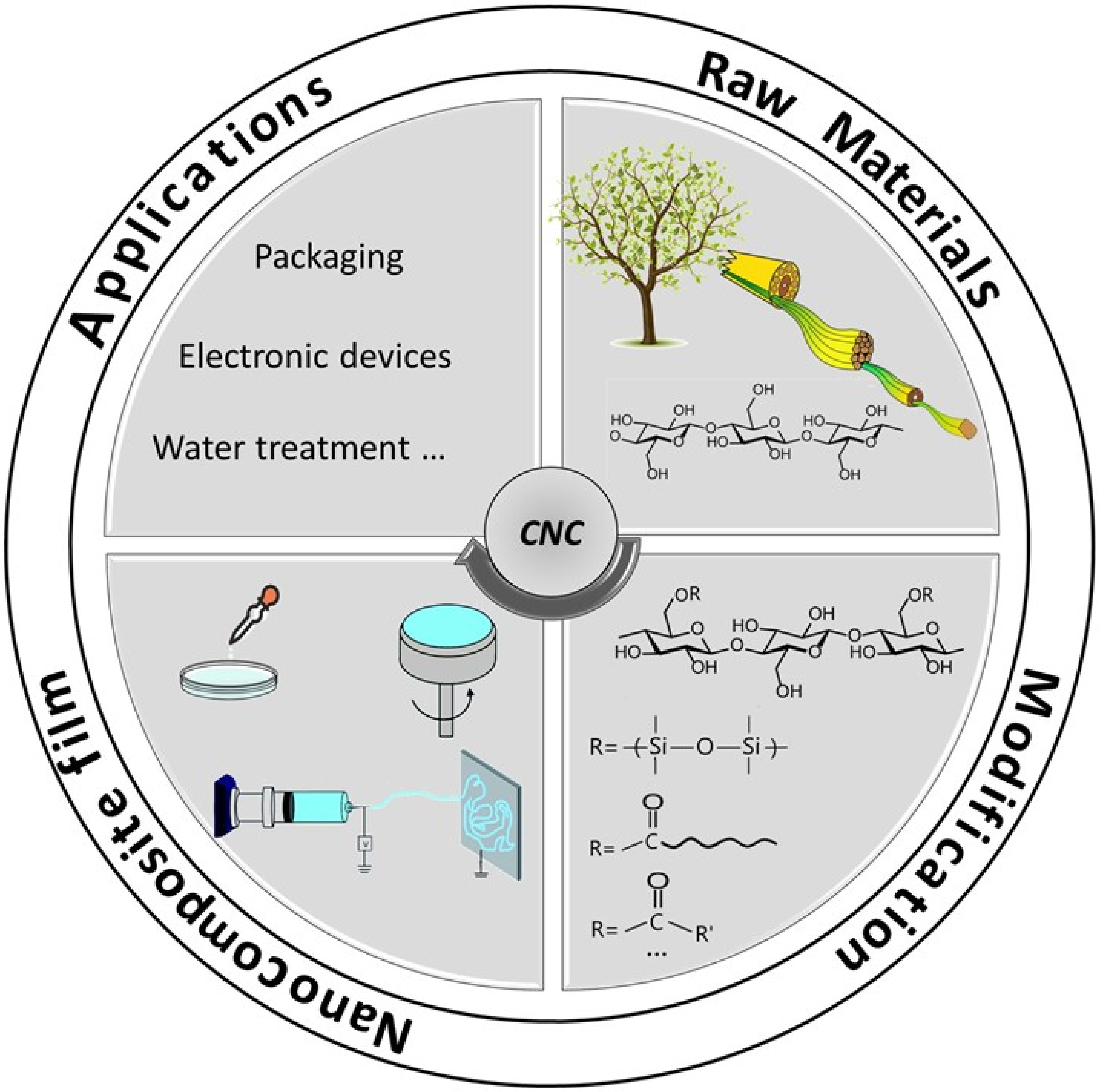
Applications
Raw Materials
Modification
Nanocomposite film
Packaging
Electronic devices
Water treatment …
CNC
R= Si—O—Si
R= C=O
R= C(=O)—R'
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