Nanocellulose for Paper and Textile Coating: The Importance of Surface Chemistry
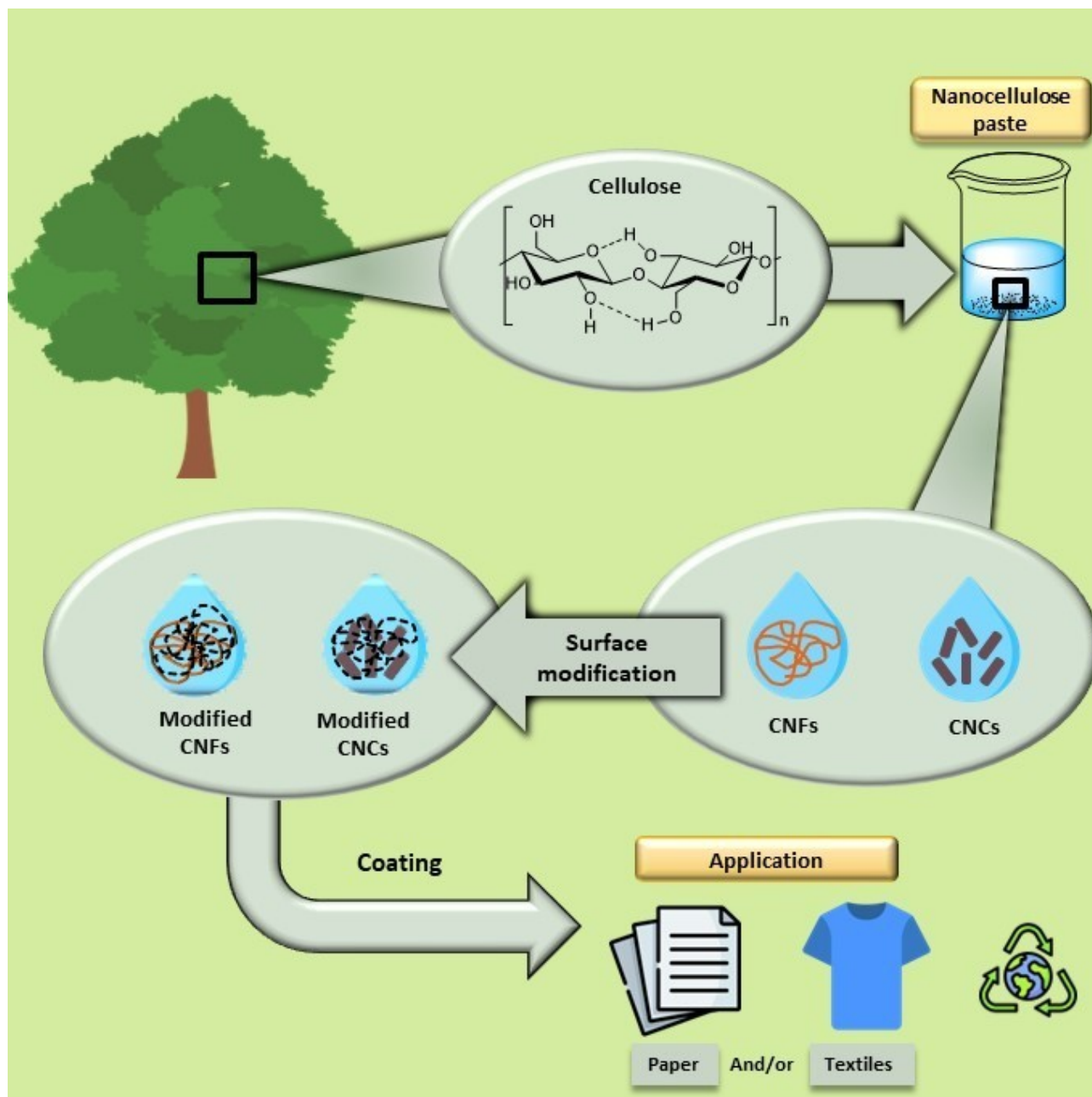
Laura Spagnuolo+,[a, b] Rosarita D'Orsi+,[a, b] and Alessandra Operamolla*[a, b]

Nanocellulose has received enormous scientific interest for its abundance, easy manufacturing, biodegradability, and low cost. Cellulose nanocrystals (CNCs) and cellulose nanofibers (CNFs) are ideal candidates to replace plastic coating in the textile and paper industry. Thanks to their capacity to form an interconnected network kept together by hydrogen bonds, nanocelluloses perform an unprecedented strengthening action towards cellulose- and other fiber-based materials. Furthermore, nanocellulose use implies greener application procedures, such as deposition from water. The surface chemistry of nanocellulose plays a pivotal role in influencing the performance of the coating: tailored surface functionalization can introduce several properties, such as gas or grease barrier, hydrophobicity, antibacterial and anti-UV behavior. This review summarizes recent achievements in the use of nanocellulose for paper and textile coating, evidencing critical aspects of coating performances related to deposition technique, nanocellulose morphology, and surface functionalization. Furthermore, beyond focusing on the aspects strictly related to large-scale coating applications for paper and textile industries, this review includes recent achievements in the use of nanocellulose coating for the safeguarding of Cultural Heritage, an extremely noble and interesting emerging application of nanocellulose, focusing on consolidation of historical paper and archaeological textile. Finally, nanocellulose use in electronic devices as an electrode modifier is highlighted.

1. Introduction

Coatings are used in industry on various materials such as glass, concrete, metal and furniture, paper, and textile. Worldwide demand for low-cost coating materials is expanding because they provide greater value to end manufacturers, increasing their profit margins. At the same time, the requirements that must be met by coatings are increasing in terms of performance and quality needs and the emerging demand to replace plastic coatings with sustainable alternatives is very powerful.[1] In this review, we discuss the usefulness and requirements of coatings applied to paper and textiles, highlighting how coating materials could be replaced by more sustainable nanocellulose. The recent research has brought about meaningful advancements in the field of paper and textile coatings based on nanocellulose,[2] pointing at the use of water as a greener solvent and at the preserved biodegradability of the coated material. At the same time, recent research is dealing with how to ensure the same or superior coating properties. We focus on the potentialities of nanocellulose use as a coating material for paper and textiles, highlighting the advantages of the proposed technologies. Nanocellulose, a renewable and biodegradable material with abundant surface groups that can be further chemically functionalized to finely tailor its properties, entails precious opportunities for the coating technology even if some critical aspects still prevent this technology from large-scale application.

1.1. Paper coating

Paper is used for information transmission and storage, packaging, and sanitary uses. The paper industry represents a market that produces more than ~400 million tons of paper and paperboard per year worldwide, with over half of the raw material coming from recovered sources.[3] In Europe, around 178,000 employees are involved in paper and pulp production, while 3 million people work along the forest and paper value chains.[4] The annual revenue of the European pulp and paper industry accounts for 83 billion €.[5] 253.9 million € of this market in 2019 was occupied by barrier coatings for flexible paper packaging.[6] To date, the consumption of paper has remained high. The demand for the same functional and barrier coatings in paper packaging is expected to increase at a rapid pace and any forecast published before 2020 is likely underestimated since the crisis resulting from the pandemic due to COVID-19 has increased the need for safe products in the packaging industry. Paper is an affordable product. The prices range between 0.3 and 3 €/m^2 depending on its grammage and quality; it is flexible and low weight, recyclable, and harmless to the environment.[6,7] In addition, it is compatible with printing technologies and biocompatible. For this reason, there is increased interest in the application of paper in mass and niche consumer products. Emerging applications of paper in electronics, sensors, and photonics, are gaining tremendous interest.[8-12]

The paper coating is a process of surface smoothening achieved by covering the cellulosic fibers and filling the space between them with agents that generally include pigments, binders, thickeners, dispersants, crosslinkers, optical brightening agents (OBA), and lubricants.[13,14] Most of these agents result in non-biodegradable contaminants. In general, paper coating materials, applied particularly to binding covers and corrugated boxes, include components of fossil origin: certain polymers, such as waxes, polyethylene or polypropylene, polyethylene terephthalate (PET), or other polyesters are commonly adopted as coating materials, also in combination to kaolin clay or talc, widely used as coating fillers.[15,16] Furthermore, deposition processes of these polymers often require the use of organic solvents, which may imply the manipulation of hazardous chemicals.

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The paper for food packaging use needs to achieve both hydrophobic and oleophobic properties as it will progressively replace plastics in food packaging; however, the best performing amphiphobic coating materials are perfluoroalkyl substances (PFAS).[17] Fluorinated compounds, in the form of polymers, surfactants, or lubricants, display very low surface energy.[18,19] Perfluorinated compounds exhibit very high stability, imparted by the high energy of the C−F covalent bond.[20] Furthermore, their polarizability is low, thanks to the high electron-withdrawing tendency of fluorine, who dominates the periodic table of elements in terms of electronegativity. For their low polarizability and lack of net permanent dipole, perfluorinated compounds result in the repellence of hydrophobic liquids as well as hydrophilic ones. As a result of their chemical stability, these compounds are also very persistent. The most unstable ones degrade forming PFOA (perfluorooctanoic acid), PFOS (perfluorooctanesulfonic acid), and smaller perfluorinated substances, which are stable.[21] The environmental mobility and persistency of PFAS[22] cause their accumulation in water bodies, plants, soil, and air. For this reason, PFAS are the object of great concern for the environment and for human health. Several PFAS can bioaccumulate[23] in humans, animals, and plants with toxic effects. The main effects of PFAS on human health include thyroid disease, increased cholesterol levels, effects on reproduction and fertility, immunotoxicity and endocrine effects, liver or kidney damage, and testicular cancer. They may even cause reduced antibody response to vaccination or reduced resistance to infections. For this reason, some perfluorinated substances, such as PFOA and PFOS, have been listed under the Stockholm Convention on Persistent Organic Pollutants (POPs). The use of these substances is now progressively restricted at the international level. Therefore, replacing PFAS and petrol-based components of coating formulation with more sustainable alternatives

is an interesting point of research to provide paper surfaces with new properties and to obtain truly biodegradable paper.

The optimal paper coating will give a uniform deposition, good adhesion to the substrate, and excellent resistance, increasing the stability of paper against chemicals and altered physical conditions. As "green materials", some biopolymers such as polysaccharides, proteins, and polyhydroxyalkanoates (PHA) have been used as coating agents but were limited in hydrophilicity, crystalline behavior, melt instability, or brittleness.[24] Sustainable methyltrimethoxisilane (MTMS) was applied to paper from acid water suspensions (HCl 0.1 M). By controlling the hydrolysis degree of its methoxy groups, Tang et al. achieved oleophobic paper.[25] MSOHO (maleated high oleic sunflower oil) is among the water processable paper coatings.[26] MSOHO, synthesized by ene-reaction of maleic anhydride with sunflower oil, is a green sizing agent alternative to alkenyl succinimidyl anhydrides (ASA) and alkyl ketene (AKD).

The development of nanotechnology has accelerated research efforts on functional paper, giving access to more sophisticated products. Worldwide, research is focusing on conventional and unconventional nanostructured materials and nanocomposites. In this context, nanostructured cellulose materials can provide special properties, including transparency and a relevant mechanical resistance. Nanocelluloses can be applied as additives to paper pulp,[27] causing strengthening and flocculation in the wet end, and can be also used for surface applications (by lamination methods or coating technologies).[28] The use of nanocellulose as a coating material is of interest to improve the strength and durability of paper. Fibrillated celluloses have been shown to impart high strength to composites, are lightweight, highly absorbent, modify viscosity, and improve barrier properties against grease, oil, and
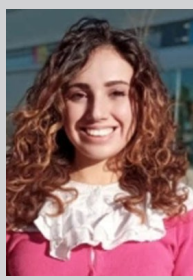
Laura Spagnuolo received her Bachelor's degree in 2018 from the University of Salerno and her Master's in Chemistry (Laurea) in 2021 from the University of Pisa. Laura is a Ph.D. student at the Doctoral School in Chemistry and Materials Science at the University of Pisa. The aim of her project is to extract cellulose nanocrystals and nanofibres from waste lignocellulosic biomass and apply them as a coating for textiles.

Rosarita D'Orsi received her Ph.D. in Chemistry in 2020 from the University of Salerno. In 2018 she was visiting fellow at the Department of Pharmaceutical Chemistry of the University of Wien. In 2020/2021 she was a post-doc researcher at the Department of Sciences of the University of Basilicata. Since July 2021 Rosarita is a post-doc researcher in Organic Chemistry at the Department of Chemistry and Industrial Chemistry of the University of Pisa. She works on the delignification of biomass and on the chemical and structural characterization of lignin residues and their chemical functionalization toward novel applications in the field of advanced materials.

Alessandra Operamolla received her Ph.D. in Chemistry of Innovative Materials in 2009 from the University of Bari and was a postdoctoral fellow between 2009 and 2015 at the Chemistry Department of the same University. In 2010 she received an exchange grant from the European Science Foundation for a postdoc stay at the Linz Institute for Organic Solar Cells (LIOS), Austria. In 2016 she was appointed Assistant Professor of Organic Chemistry at the University of Bari, where she started independent research on cellulose nanomaterials. In 2019 she moved to the Chemistry and Industrial Chemistry Department of the University of Pisa, where she holds a position as Associate Professor of Organic Chemistry. Alessandra leads the NanoLeaves group, focusing on the functionalization of nanocrystalline cellulose for several technological applications, and is interested in the application of Nature-derived biopolymers as innovative materials.

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oxygen. Cellulose nano- and micro-fibers are also considered compatible with food packaging[29,30] and are biodegradable.[31]

1.2. Textile coating

The global demand for textile coating materials from various industries, including automotive, construction, footwear and apparel, and medical and protective garments, is increasing. In this field, Europe is the third-largest economy after Asia-Pacific and North America. In Europe, the textile market represents a business volume of ~162 billion € and involves 160,000 enterprises.[32] A wide part of this market belongs to the construction industry, with applications in architectural membranes, canopies, and scaffolding netting. Manufacturers must adhere to guidelines, regulations, and procedures set forth by organizations such as ISO (International Organization for Standardization) and OSHA (Occupational Safety and Health Administration). The properties of textile, as well as the properties of paper, are standardized by the EN-ISO standards, a combination of quality management information used to define the performances of a given product or material agreed upon by an international community of experts. For example, it is mandatory to manufacture fabrics with fire retardant properties for the automotive industry. Breathability and water resistance are additional performances required for fabrics. Moreover, a protective coating against the profiling of bacteria and microbes on fabric surfaces is necessary for preserving hygiene and public health. These requirements need to be met to produce advanced apparel that can provide enough competitiveness in the textile market.

The most cost-effective coatings for textiles are thermoplastic polymers, like polyurethane, polyvinyl chloride (PVC), acrylics, nylon, polyolefins, etc. Thermoplastic polymers are often preferred to thermosetting materials, like rubber, either natural or synthetic, and silicones.[33] However, polyurethane coatings are often manufactured using N,N-dimethylformamide (DMF), a water-soluble solvent. DMF has been identified by the European Chemicals Agency (ECHA) as a substance of high environmental concern.[34] Some of the fossil-based compounds mentioned above pose potential human health risks and are environmentally unsustainable, representing an important source of microplastic dispersed in the environment. This risk sums up the risk posed by the ubiquitous presence of PFAS as coating materials. PFAS are especially present in water-repellent textiles used to manufacture outdoor apparel.[35] PFAS adhesion to textile is persistent, therefore these substances are gradually released into the environment through washing. This makes their use for fabric manufacture of great environmental concern. To limit the use of hazardous and environmentally harmful materials, there is growing space for the development of innovative materials with minimized cost and environmental impact. This would be optimal not only for reducing the accidental release of microplastic and for minimizing health risks, but also for achieving CO_2 neutrality of the coating industry. For this reason, manufacturers are introducing bio-based or recycled alternatives into coating formulations, replacing fossil-based compounds. Some of the materials used comprise polyamides or polyurethanes deriving from bio-based monomers.[36] The challenge will be to ensure that the performance of the bio-based coating is at least identical to the less sustainable traditional material while materials production is coherent with the principles of the green economy.

2. Nanocellulose

2.1. Cellulose origin and uses

Cellulose is an affordable biomaterial derived from plants. It is a renewable and green biopolymer, abundant, and environmentally friendly. Cellulose existence is known to us since 1838.[37] Cellulose is composed of linear repetitions of D-glucopyranose units bonded together through the β-(1,4)-glycosidic bond (Figure 1). Morphologically, natural cellulose is usually fibrous with alternated crystalline and amorphous sections. Natural cellulose is synthesized in plant cells by an enzymatic transmembrane complex, called cellulose synthase (CESA), according to a bottom-up approach.[38] The enzymatic complex extrudes cellulose chains from the cell wall. The chains are extruded parallelly, enabling the simultaneous formation of interchain hydrogen bonds. The fibrous domains of native cellulose are crystalline and classified as allomorphs I_α and I_β.[39]

Its regenerated forms have been used as a coating for packaging, construction and transportation materials, electrical insulation, and water or air filtration among others. Cellulose technological importance is mainly linked to the industry of papermaking and other cellulose products and derivatives. Due to the insolubility of the native cellulose structure, its derivatives are industrially obtained by cellulose regeneration, which is followed by extrusion processes to yield rayon and cellophane.[40] At the same time, industrial and academic research has started to focus on the conversion of cellulose into biofuels or into other high-value products to respond to new material challenges.[41]

Soluble forms of cellulose,[42] produced by chemical derivatization, are commonly employed in paper coating. Among them, carboxymethylcellulose (CMC) and hydroxyethylcellulose (HEC) are products of the etherification of cellulose. CMC, used as sodic salt, has negative charges that cause stable electrostatic repulsion. The whiteness and printing performance of paper are usually improved with the increase of CMC in the coating. HEC has been used to avoid the formation of intramolecular crosslinks by CMC.[43] Hydroxyethylcellulose is widely used in the field of binders and thickeners in many
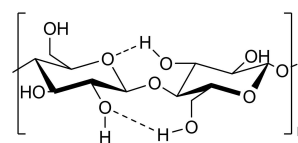

Figure 1. Cellulose structure represented as a repetition of cellobiose disaccharide units.
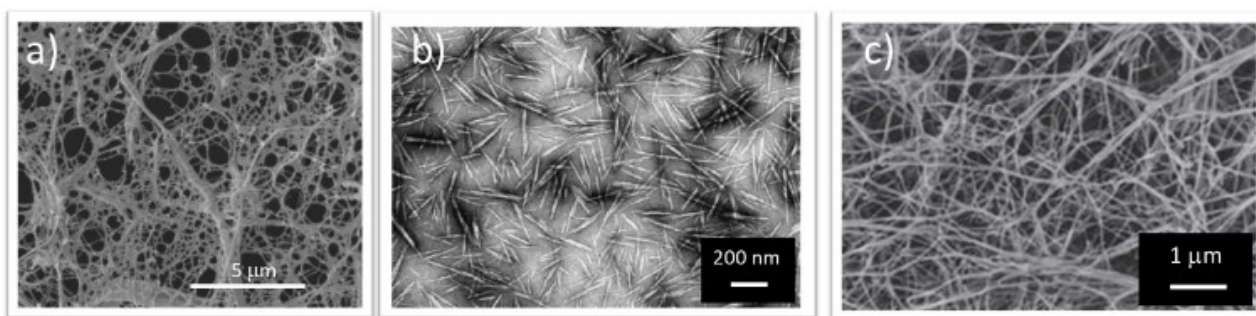
Figure 2. (a) FE-SEM micrograph of cellulose nanofibers (CNFs) obtained by a mechanical disintegration process with a high-pressure homogenizer from oat straw. Scale bar: 5 µm. Reproduced from ref. [56] with permission from Springer. (b) TEM micrograph of cellulose nanocrystals (CNCs) with 6–8 nm diameter and 150–250 nm length, obtained from purified ramie fibers by H_2SO_4 hydrolysis. Scale bar: 200 nm; reproduced from ref. [54] with permission from the Royal Society of Chemistry. (c) FE-SEM micrograph of a purified bacterial cellulose pellicle (fiber content of 1% vol/vol) produced by the bacterial strain *Acetobacter xylinum* using a culture of coconut milk and sucrose. Reproduced from ref. [57] with permission from NPG.
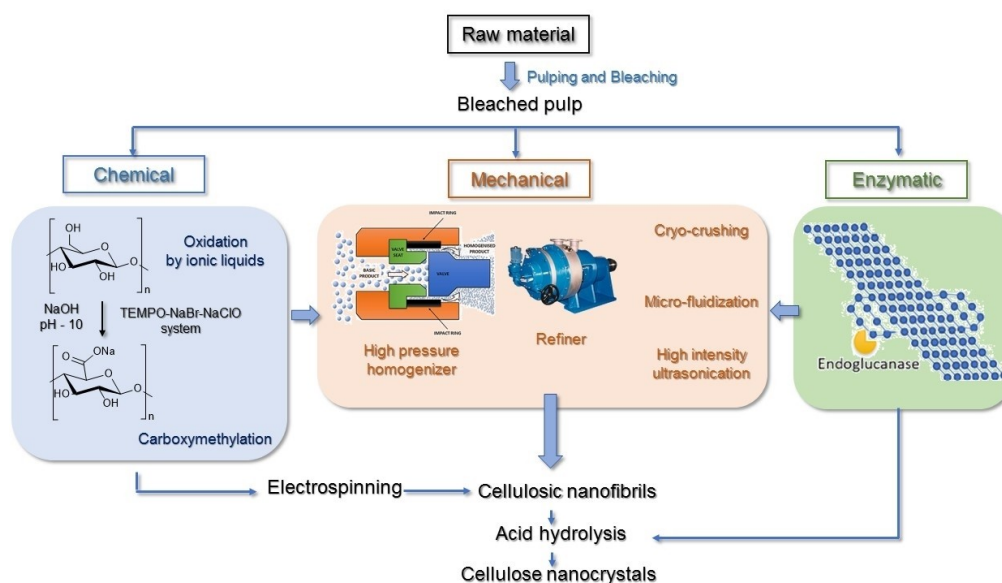

Figure 3. CNFs and CMFs top-down production. Reproduced from ref. [60] with permission from Elsevier.
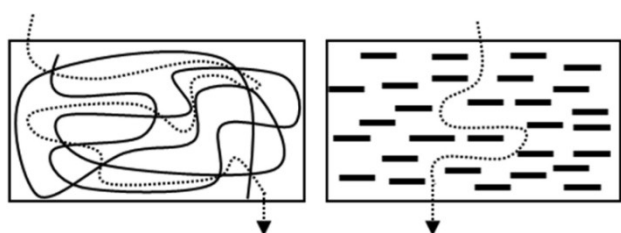

Figure 4. Model representing the passage of a gas through a CNF (left) and CNC (right) film cross-section. Reproduced from ref. [168] with permission from Elsevier.

industrial applications. It can be present in personal care products, pharmaceutical formulations, building materials, adhesives, etc. and as a stabilizer for liquid soaps.[44]

2.2. Typologies of nanocellulose

Nanocellulose[45] is the nanometric fibrillar version of natural cellulose and an important candidate to replace petroleum-based polymers, which are difficult to degrade, in paper and textile coatings. Nanocellulose, in the form of rods or fibers, has attracted the interest of different industries, the scientific community, and policymakers. This recent interest is justified by its appealing features such as high tensile modulus, high specific surface area, and sustainability.[46] Furthermore, nanocellulose is commonly considered nontoxic,[47] biocompatible,[48] and biodegradable.[31]

Nanocellulose exhibits unique potentialities in paper coating.[49] Thanks to the presence of several surface hydroxyl groups it can bind strongly to paper fibers by hydrogen bonding, enhancing the mechanical, barrier, and hydrophobic properties of paper. Similar relevant effects are also expected in the textile coating.
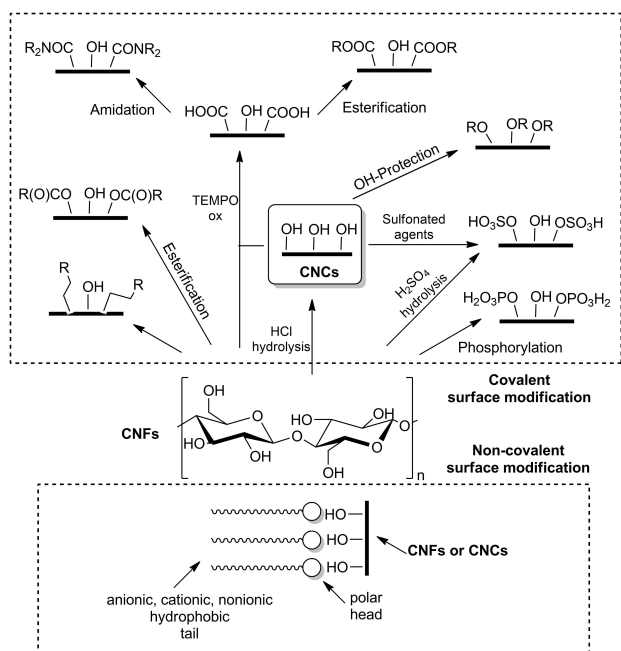
Scheme 1. Covalent and noncovalent surface modifications of the nano-cellulose side-face, containing hydroxyl groups.
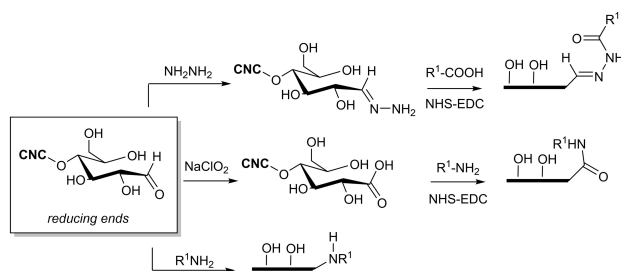
Scheme 2. Chemical modifications of the CNCs reducing ends.

Nanofiber extraction from native cellulose can be achieved by mechanical, chemical, or combined mechanochemical top-down approaches.

Nanocellulose can be classified as:[50]

1) Microcrystalline cellulose (MCC): particles with diameters between 10 and 200 μm.
2) Cellulose nanofibrils (CNFs): particles with a diameter between 20 and 50 nm and length between 500 and 2000 nm.
3) Cellulose microfibrils (CMF): particles with a width between 20 and 100 nm and length between 500 and 10000 nm.
4) Cellulose nanocrystals (CNCs): short stick-shaped crystalline nanoparticles with a diameter ranging from 5 to 50 nm and a length between 100 and 500 nm.
5) Cellulose nanoyarn or electrospun nanofibers: particles with 500-800 nm diameter, low crystallinity and thermal stability.[51-53]
6) Amorphous nanocellulose (ANC): spherical particles with an average diameter of 50 to 200 nm.
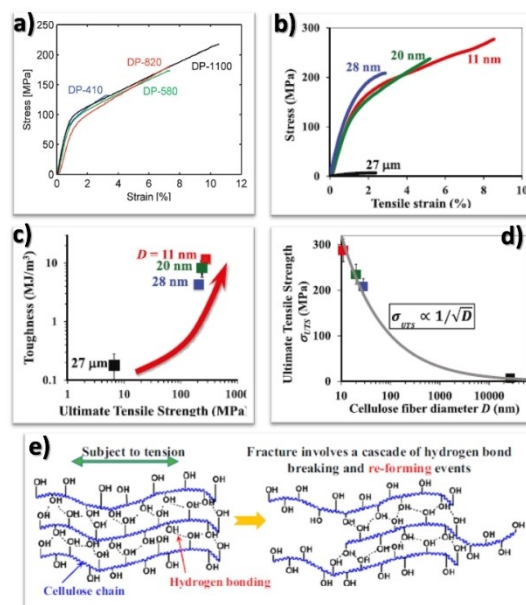

Figure 5. (a) Typical stress-strain curves in uniaxial tension for cellulose nanofibril networks prepared from cellulose nanofiber (CNF) with different degrees of polymerization. (b) Stress-strain curves of paper prepared from CNFs of various mean diameters. Reproduced from ref. [172] with permission from the American Chemical Society. (c) Plot of paper toughness vs. the ultimate tensile strength. (d) Dependence of the ultimate tensile strength from the square root of CNF diameter. (e) A model describing at the molecular level the failure of nanopaper. Reproduced from [106] with permission from the National Academy of Sciences of the United States of America.
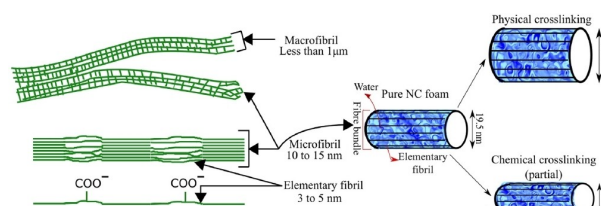
Figure 6. Effect of PEI (physical crosslinking) or HMDA (partial chemical crosslinking) on the CNF bundle swelling. Reproduced from ref. [116] with permission from Elsevier.

Though a major difference is given by their dimension, CNFs and CNCs present other differences due to their origin, which influences, among other properties, the crystallinity index.[54,55] An example of both types of nanostructures is shown in Figure 2, where microscopies of (a) CNFs from oat straw[56] and (b) CNCs from ramie[54] are presented.

Bacterial nanocellulose (BNC) represents the purest form of cellulose (Fig. 2c).[57] BNC is produced by various microorganisms, such as the bacterium *Acetobacter xylinum*.[51] BNC is obtained directly from sugars by a bottom-up approach and is extremely useful in pharmaceutical technology. Its crystallinity and degree of polymerization are somewhat inferior to the crystallinity of cellulose polymer produced by plants, since bacterial nanocellulose contains I_α allomorph to a higher extent than cellulose synthesized by plants. BNC, isolated in the form of a hydrogel, is often considered less performing for some

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Table 1. Characteristics of paper coatings.

Coating objective	Cellulose type	Property achieved	Additive, kind of action	Applications	Refs
Mechanical reinforcement	CNFs, CNCs, BNCs	higher stress-strain resistance	via empowering the hydrogen bonding network	generic reduced ink penetration	[121] [120,122]
Conservation	BNCs			Cultural Heritage	[123-126]
	CNCs	antibacterial	AgNPs		[127]
	CNCs	hydrophobicity and pH stability	$CaCO_3$ NPs		[128]
	oleyl CNCs				[129]
	TO-CNFs	pH-responsiveness		packaging	[130]
	TO-CNF	reduced water absorption	polyethyleneimine (PEI) hexamethylenediamine (HMDA) or epichlorohydrin (ECH) and Ca^{2+}		[116] [116,118]
	CNCs	anti-reflection	via layer-by-layer techniques		[131,132]
Barrier	MFCs	antibacterial	via bismuth complex	packaging	[133]
	CNF		ZnO/starch		[134]
			Ag nanoparticles		[135,136]
			Polypyrrole		[137,138]
	MFCs or CNFs	oxygen barrier (reduced air permeance)	via Bar-coating- via PVA coating via co-deposition with shellac		[139] [140] [141]
	MFCs		via spray coating	generic	[142]
		oleophobic paper		ink printing	[143]
	CNCs and CNFs	gas, oil, grease barrier	via Spray coating	surface gloss	[144,145]
	CNCs	amphiphobic paper	fluorosylane	self cleaning	[146]
	CNCs, CNFs	UV screen	lignin additive	reinforce general-purpose	[147,148]
	CNCs	hydrophobic paper	CO2 or SiO2 Nanoparticles	polymers	[149]
	MFC		via esterification with oleic acid	packaging	[150]
			blend with polyhydroxybutyrate		[151]
			acrylated epolxidized soybean oil		[152]
			PLA coating		[153]
	BNCs	anticounterfeiting	via ZnO quantum dot	security marking	[154,155]
Electrodes	CNCs	surface conductivity	with polypyrrole or polyaniline with carbon fiber with graphene with fulleropyrrolidines	electronic devices photoresponsive films	[156,157] [158] [159-161] [162]

material science applications, but very interesting for biomedical and pharmaceutical applications.

Nanocellulose exhibits distinctive morphological, physical-chemical, mechanical, and biological characteristics, such as a three-dimensional fibrous network-like structure, high crystallinity, good mechanical resistance, biocompatibility, biodegradability, optical transparency, a high specific surface area (SSA), polyfunctionality, hydrophilicity, and moldability into 3D structures.[58] Thanks to these intriguing properties, nanocellulose displays unique potentialities in various fields such as wound dressing, textiles and clothing, food, cosmetics, regenerative medicines, tissue engineering, energy, optoelectronics, bioprinting, environmental remediation, etc.[59] Chemical modifications applied to nanocellulose can also induce additional characteristics such as adhesion, preservation, and antimicrobial properties. Based on this, this review aims to analyze how nanocellulose infuses into paper and textile coatings.

2.3. Production of nanocellulose

The strategies used to produce nanocellulose are various and depend on their source. Top-down strategies involve mechanical treatments, such as high-pressure homogenization or grinding. A present research challenge concerns the definition of new manufacturing methods, for both CNCs and CNFs, that will improve efficiency, yield, and reduce production costs (presently esteemed in ~6.6 €/g of nanocellulose). At present, the main production methods reckon on mechanical means applied for a prolonged time. These treatments are usually combined with chemical or enzymatic treatments, as sketched in Figure 3.[60] The chemical treatments have the objective to allow fibers preliminary swelling, which facilitates the action of the mechanical treatment. Enzymatic pretreatment can assist the mechanical one in facilitating the formation of nanocellulose in shorter times. Furthermore, cellulose deriving from plants usually requires a careful purification from lignin and hemi-celluloses prior to the mechanical, chemo-mechanical, or mechanical-enzymatic treatment. Delignification is a process requiring the complete solubilization of lignin, which is usually removed and represents a waste of the pulping process.[61,62]

Other approaches, like mechanical treatments using a refiner and a high-pressure homogenizer; microfluidization, high-intensity ultrasonication (HIU) or cryo-crushing, and swelling of cellulosic fibers with water,[63-65] are also used to scale down the cellulosic materials. Presently, these techniques are not efficient and cost-effective enough to be used in the paper and paperboard industries. Additionally, a popular research
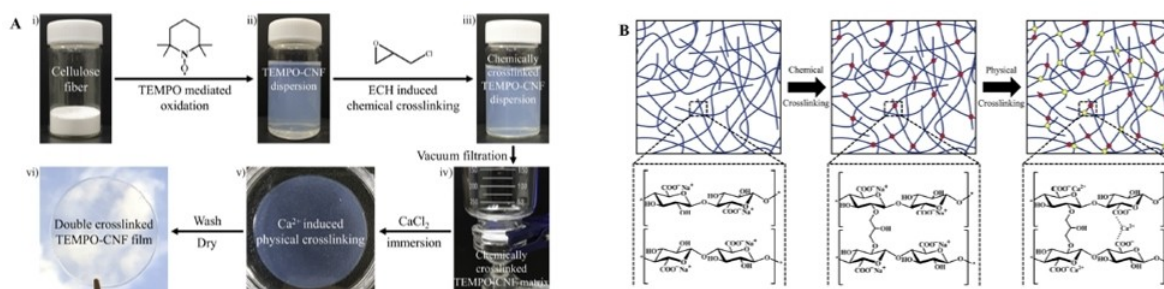
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Figure 7. Double-crosslinking process of the TEMPO-CNF film (A) (i) starting cellulose material; (ii) TEMPO – oxidized cellulose; (ii) (iii) epichloridrine crosslinked TEMPO-CNF dispersion; (iv) preparation of the chemically-crosslinked TEMPO-CNF matrix by vacuum filtration; (v) immersion of the chemically-crosslinked TEMPO-CNF matrix into the CaCl$_2$ solution for the physical crosslinking reaction; (vi) the resultant double cross-linked film. (B) Schematic illustration and chemical structure of TEMPO-CNFs during the chemical and physical crosslinking reactions, respectively. Reproduced from ref. [118] with permission from Elsevier.

topic is an increase in solid content of the cellulose slurry which is normally very low (e.g., 1-2 w/w %).

Enzymatic or chemical pretreatments can reduce the energy demand to mechanically produce nanocellulose. The enzymatic treatment is a potentially cost-efficient method for industries, but it is a challenging point of research, since to date yields of the process and reaction times have not been completely optimized.[66] The enzymatic hydrolysis is performed with cellulases, a group of enzymes that traditionally are divided into endoglucanases, exoglucanases, and cellobiohydrolases.[67–69] Whilst a combination of the three typologies of enzymes is commonly used to decompose cellulose into glucose,[70] endoglucanases (EG, endo-1,4-β-D-glucanase, EC 3.2.1.4) are the
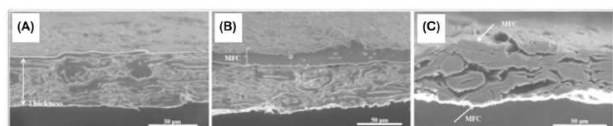

Figure 8. SEM of the cross-section of: (A) calendered paper from the unbleached pulp (pure paper); (B) paper in (A) with 10 layers bar-coated with microfibrillated cellulose rods (MFC); (C) paper in (A) with 10 layers size pressed of MFC. Reproduced from ref. [139] with permission by Springer-Nature.

Figure 10. (a) Schematic representation of the proposed continuous coating line for multi-layered nanocellulose/PLA coating; (b) reverse gravure coating of cationic starch; (c) extrusion coating of PLA/LDPE; (d) slot-die coating of nanocellulose; and (e) illustration of final coating structure. Reproduced from ref. [153] with permission from the American Chemical Society.

Figure 9. Scheme of the experimental procedure used for spray coating on paper with cellulose nanofibrils (CNFs) suspension. Reproduced from ref. [179] with permission from Taylor & Francis Group.
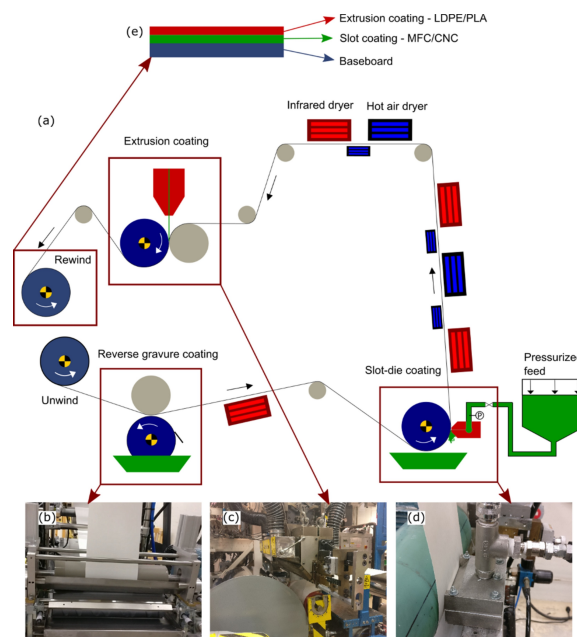
enzymes with the highest interest for nanocellulose production. This is justified by their capacity to break cellulose polymer chains, especially in the amorphous regions.[68] Cellulases usually require an operational temperature of ~50°C and an operative pH of ~5. These reaction conditions are milder than those entailed by acid hydrolysis and result in a lower energy requirement for the production process. Enzymatic treatment will produce less toxic and corrosive waste, making the production process compatible with the cosmetic and pharmaceutical industries. Furthermore, CNCs produced via cellulase action usually display a higher crystallinity index than CNCs obtained by other methods. Counterbalancing these advantages, the long reaction times requested for the enzymatic hydrolysis limit the large-scale application of this process.
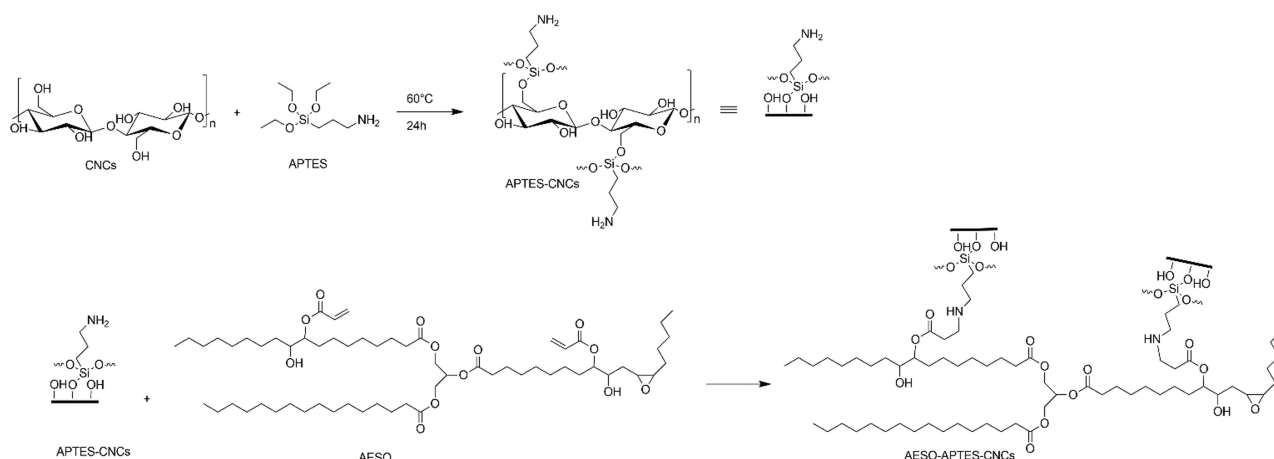
Scheme 3. Chemical modification of CNCs with APTES, followed by covalent anchorage onto acrylated epoxidized soybean oil (AESO) microparticles surface.

Therefore, at the moment the chemical approach is usually preferred for the production of CNCs. In the chemical approach, CNCs are obtained by acid hydrolysis with sulfuric or hydrochloric acid, to cut the non-crystalline portions of the cellulose fibers, followed by intense mechanical or ultrasonic treatment.[71–73]

Common chemical pre-treatment involves the oxidation by TEMPO radical (2,2,6,6, -tetramethylpiperidine-1-oxyl)-NaClO with NaBr as co-catalyst; in this way, all accessible primary hydroxyl groups become carboxylic groups to convert cellulose into the water-soluble sodium salt of polyglucuronic acid. This reaction is used to promote cellulose swelling and facilitate the following fiber disintegration to produce the nanocellulose, isolated as TEMPO-oxidised cellulose nanofibers (TO-CNF).[74] Another oxidant used is $NaClO_2$ in aqueous media with pH ranging from 3.5 to 6.8. This oxidant is less efficient in inducing cellulose chain depolymerization.[75]

2.4. Industrial applications of nanocellulose

Nanocellulose-based materials and composites represent ideal and sustainable candidates for materials enhancement. The applications that have been identified for these materials imply either "high or low volumes" (mass and medium-size applications). Some of the proposed applications are new and have no current market benchmarks. The applications with the largest potential volume of cellulose nanomaterials are related to paper and paper packaging, including coating technology and pulp fillers. Further applications include textiles, hygiene and absorbent products, cement, bio-based plastic, and automotive parts. In contrast, smaller volume applications embrace sensors, construction (body panels and interiors), aerospace materials, cosmetics, pharmaceuticals, and paint additives.[76] Some specialty applications use relatively small amounts of cellulosic nanomaterials such as those involving the field of pharmaceutical excipients. 3D printing may represent a manufacturing method for large-volume applications of cellulose nanomaterials in toys, architectural models, and more, but further work is

needed before bringing 3D-printed nanocellulose to the global market.

Niche applications of nanocellulose comprise innovations without current markets and may employ the dielectric and photonic properties of cellulose nanomaterials.[77,78] A new field on the rise, which presently represents a niche application, involves the use of nanocellulose as a substrate in flexible electronics. Recent studies have shown progress in the development of photovoltaic and energy storage devices on cellulosic substrates: in these devices, one or more active layers are deposited by solution processing or printing.[79] Paper can be used simply as a substrate or, by exploiting its porous fiber-like nature, as an active film for infiltration or co-packing with electronic materials. Several approaches are reported in the literature to process commercial paper or to prepare novel cellulose products and composites producing an electronic paper ideal for use as a substrate in thin-film optoelectronic devices or energy storage devices. Another interesting area of application of nanocellulose is pertinent to the preparation of filtration systems and membranes for water purification.[80]

The plethora of applications envisioned for nanocellulose materials could have a great impact on the demand for wood fibers and, consequently, on forest land management. For this reason, it was necessary to estimate the volume of nanocellulose needed for such applications. This necessity was estimated in a projection based on the U.S. market, as 5.9 million tons/year for the high-volume category.[81] Even if CNCs and CNFs will likely face competing technologies in many potential applications, there will certainly be some applications where both economic, environmental, and performance revenues favour the use of nanocellulose.

2.5. Nanocellulose surface chemistry

Nanocellulose structure presents numerous hydroxyl groups that confer a hydrophilic nature to the cellulose polymer. Surface modification via alcohol chemistry is widely practiced to tailor nanocellulose surface properties and to extend applica-

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tion potentialities as advanced functional nanomaterial. Furthermore, this biopolymer is a good candidate for the construction of biologically active nanomaterials, such as drug carriers. With this respect, the modification of the cellulose surface properties is an interesting research point.[82] According to a model proposed so far,[83] the crystals have the side face decorated by hydroxyl pendant groups and one of the termini exposing the reducing ends consisting of hemiacetal functionalities.

All the chemical functionalities may be exploited to carry out a surface functionalization of nanocrystals or nanofibers. This functionalization would involve only the surface of the nanocellulose and is called topochemical functionalization. This is opposed to bulk functionalization, which entails the complete dissolution of the cellulose crystalline structure due to stoichiometric derivatization of all alcoholic functionalities.[84] For this reason, mild reaction protocols, with controlled reaction times, are preferred over harsh reaction conditions, which can induce crystalline phase transitions or dissolution of the cellulose polymer.[85] Topochemical reactions on nanocellulose imply reactivity at the solid-liquid interface. This introduces difficulties to control surface functionalities, their number, and homogeneity. The difficulty may also be connected to finding characterization techniques with enough sensitivity to reveal the presence of new functionalities, even in samples with a very low degree of substitution (DS). Surface modifications of hydroxyl pendant groups can be divided into two categories: covalent, which consists of a chemical modification of surface functionalities, or noncovalent, which is ensured through nonspecific interactions, such as hydrophilic affinity, electrostatic attractions, hydrogen bonds, or van der Walls forces (Scheme 1). A preliminary covalent surface modification can be carried out during the synthesis and the isolation of CNCs from cellulose fibers by strong acid hydrolysis: indeed, CNCs surface groups are determined by the hydrolyzing agent used for their preparation.[86,87] Hydrolysis with hydrochloric acid[88] (or other halogenidric acids) preserves the hydroxyl groups of native cellulose, while sulfuric acid hydrolysis[89] produces sulfation of the primary hydroxyl groups.[90] The extent of esterification can be varied depending on the treatment conditions.[91] Sulfation can also be achieved via a chemical reaction of hydroxylic groups with sulfonated agents.[92] Phosphorylation of nanocellulose can be achieved by the reaction of cellulosic pulp and inorganic phosphoric acid.[93] Oxidation with TEMPO radical converts hydroxylmethyl groups of CNCs or CNFs into carboxyl groups,[94,95] that are good starting compounds for amidation, esterification, or carbamation reactions.[96] Esterification of hydroxylic groups, such as acetylation, is another chemical modification widely used and studied. For example, acetylated CNCs were produced by a one-pot reaction of esterification of hydroxyl groups and hydrolysis of amorphous cellulose chains by acetic acid.[97] Furthermore, simultaneous esterification and defibrillating of cellulose fibers by ball miller were proved.[98] Acylation was also achieved from acyl chlorides in the liquid or vapour phase.[99,100] However, the control of the esterification degree is quite tough. In general, all reactions of OH protection or modification, such as silylation, isocyanation, epoxidation,

could be applied to nanocellulose surface to change its properties or to introduce other small molecules.[101,102] Another technique of surface modification is called "grafting onto", a method that involves the attachment of pre-synthesized polymer chains, carrying reactive end groups, onto (modified) hydroxyl groups of the cellulose surface. Poly (ethylene glycol) (PEG) or polyoxyethylene (PEO) grafted onto the surface of CNCs was widely studied.[103] Alternatively, polymer brushes were grown on the surface hydroxyl groups of nanocellulose, used as initiating sites for ring-opening polymerization.[104] In another work, polymer brushes were grown on a nanocellulose surface modified with initiator sites by atom-transfer radical polymerization (ATRP) and other radical polymerization techniques.[105] Covalent bonds were used also for introducing fluorophores[106,107] or metal complexes[108] on the surface of CNCs, for several purposes.
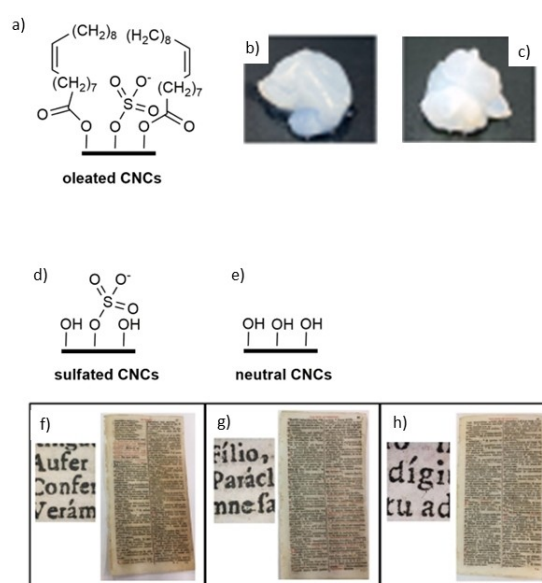
Figure 11. a) Schematic representation of oleyl CNCs and photography of oleyl CNCs gel (b) and oleyl CNCs/carbonate nanoparticles gel (c). Reproduced from ref. [129] with permission from Elsevier. Schematic representation of sulfated (d) and neutral (e) CNCs. Images of pages and details from "*Breviarium romanum ad usum fratrum minorum*" treated with (f) water (pristine); (g) S CNC; and (h) N CNC. Reproduced from ref. [127] with permission from the American Chemical Society.
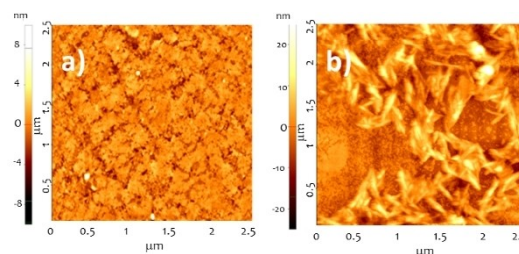
Figure 12. AFM topographies of a) cationic fulleropyrrolydine and b) cationic fulleropyrrolydine/sulfated cellulose nanocrystals 2D films deposited by the Langmuir-Shaefer technique on ITO surfaces. The right panel refers to a single horizontal transfer and clearly shows the 2D organization of sulfated CNCs by the layer-by-layer technique. Reproduced from ref. [162] with permission from Elsevier.

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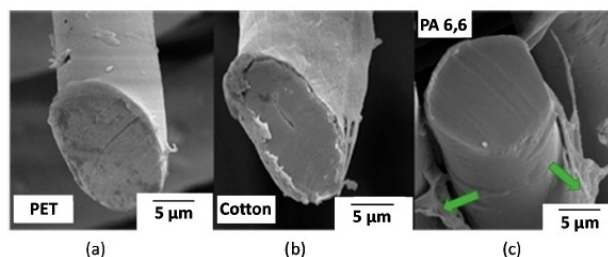doi.org/10.1002/cplu.202200204

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Figure 13. SEM images of (a) poly (ethylene terephthalate) (PET), (b) cotton, and (c) nylon 6,6 (PA 6,6) single fibers coated with cellulose nanofibers. Reproduced from [202] under Creative Commons agreement.
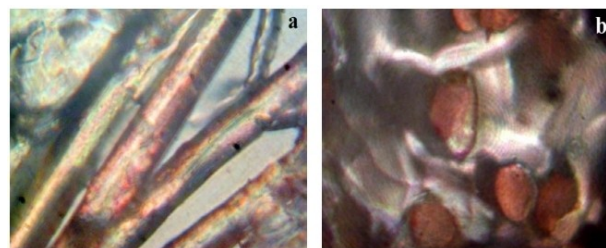

Figure 14. Images (100X) of a polyester substrate treated with red nano-cellulose: (a) longitudinal and (b) cross-sectional view. Reproduced from [203] with permission from Hilaris Publishing SRL.

To enable nanocellulose dispersion in nonpolar solvents a noncovalent surface modification was applied. The surface of nanocrystals was covered by cationic, anionic, or nonionic surfactants bearing polar heads and long hydrophobic tails. Cationic surfactants, such as dimethyldioctadecylammonium bromide, are able to absorb on the surface of sulfated CNCs: the driving force, in this case, is the strong electrostatic interactions between the negatively charged sulfate groups of nanocrystals and the cationic charge of the ammonium polar head.[109] Whilst an anionic surfactant, such as polyoxyethylene nonylphenyl ether, facilitates the dispersion of the nanocrystals in a polymeric matrix and improves the nucleation effect of the matrix for the ensuing materials.[110] Non-ionic surfactants, such as sorbitan monostearate, are used to prevent CNCs self-aggregation.[111,112]
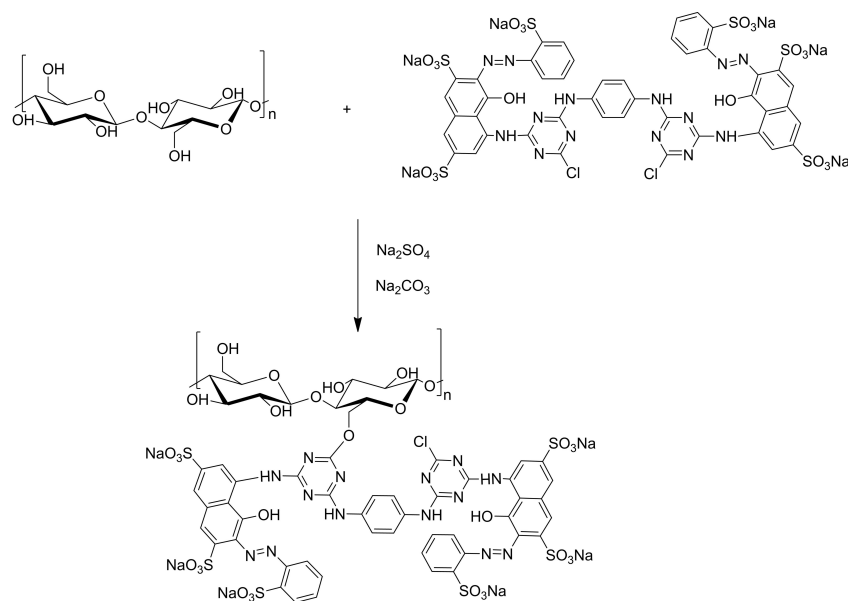
Surface modifications of the reducing ends of CNCs chains are usually covalent modifications that occur via chemical reaction on hemiacetal groups to graft molecules as sketched in Scheme 2.[86] Hemiacetal groups could be activated via hydra-zone linkages or carboxylation and then coupling reactions allow the attachment of macromolecules with reactive end

Figure 15. Cotton fabrics colored by using (a) a conventional exhaust dyeing method, (b) an exhaust dyeing method with a lower concentration of salt and alkali, and (c) the NFC-based dyeing method. Fabrics before (left column) and after (right) the accelerated laundering test (AATCC 61–2013, 2 A) are shown side by side. Reproduced from [207] with permission from the Royal Society of Chemistry.

groups to cellulose nanocrystals.[113] To explain better, EDC-NHS (1-ethyl-3-(3-dimethylaminopropyl)carbodiimide/N-hydroxysuc-

Table 2. Characteristics of textile coatings.						
Fabric type	Coating objective	Cellulose type	Property achieved	Additive (kind of action)	Applications	Refs
Polyester, polyamide, poly-ethylene	mechanical reinforce-ment	CNFs or CNCs	Coating adhesion	polyethylene imine (PEI); glycidyl methacrylate (GMA)-co-oligo(ethylene glycol) methacrylate (OEGMA) (P(GMA-OEGMA)) polycarboxylic acid	generic	[201,202] [202] [202]
Polyester	dyeing smart textile	CNCs CNFs	color fastness elasticity	reactive dye starch	Generic protective garments	[203] [204]
Cotton	sustainable dyeing	CNFs	color fastness	reactive dyes	generic den-im Manufacture	[205,206] [207]
Cotton	barrier	CNCs	anti-UV	chitosan, tannic acid	generic	[208]
Cotton	barrier	CNCs	antibacterial	lysozyme, allicin	generic	[209]
Cotton canvas	conservation	CNFs, CNCs CNFs CNCs	resistance to degradation, transparency	- polyamidoamine-epichlorohydrin (PAAE) silica nanoparticles	Cultural Heritage	[210] [211] [212]
Archaeological Silk	conservation	BNC	resistance to degradation	-	Cultural Heritage	[213]

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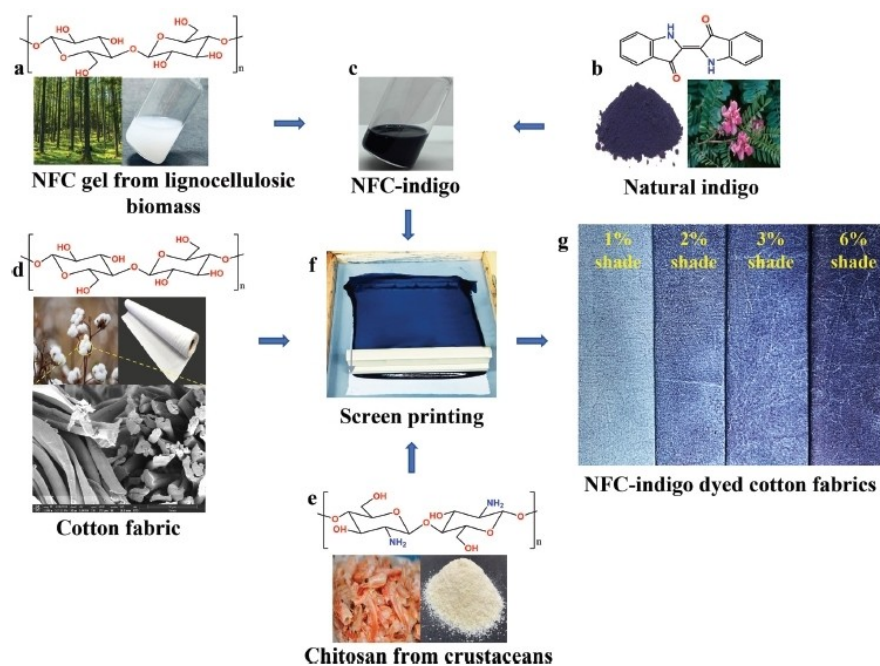**Scheme 4.** Textile dyeing mechanism with Red 120.

Figure 16. NFC-indigo dyeing scheme: (a) NFC gel obtained from wood pulp; (b) natural indigo powder produced by the plant Indigofera tinctorium; (c) NFC-indigo; (d) cotton fabric, from the natural cotton fibers; (e) chitosan, from the deacetylation of chitin (food waste); (f) screen printing/coating on cotton fabric with NFC-indigo; (g) cotton fabric dyed with NFC-indigo and post-treated with chitosan. The amount of indigo pigment is expressed as a percentage of the weight of the undyed cotton fabric. Reproduced from [206] with permission from the Royal Society of Chemistry.

cinimide) mediated activation and reaction with nucleophilic amine carrying functionalised termini produce in this way CNCs with topochemical functionalization whilst the nanocrystal surface remains available for further chemical manipulation.[114] Recently, the reductive amination reaction was reported to prepare CNCs with photophysical properties, by functionalization with organic light-emitting fluorophores.[115]

3. Nanocellulose in paper coating

Low cost, availability, and renewability expand the likelihood of using nanocellulose as a coating. It is a bio-based agent that can be chosen as a coating component among other green alternatives that are less economically feasible than their petrol-based counterparts.[16] Because of its large specific surface area, good chemical reactivity, and good rheological properties,
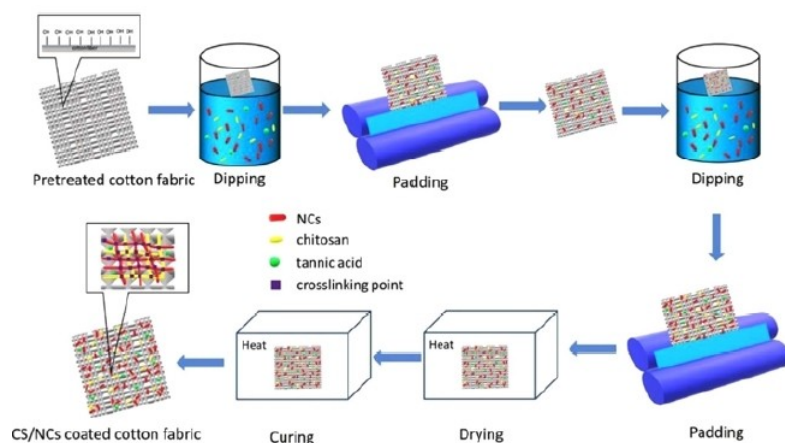
Figure 17. Diagram of CS/NCs coated cotton fabrics preparation procedure. Reproduced from [208] with permission from Springer-Nature.

nanocellulose can display unique efficiency in paper coatings.[116-119] The coating properties may be modulated by choosing the kind of action that the nanocellulose will perform on the coated paper. The basic property of improving the mechanical paper stability will be achieved by empowering the hydrogen bonding network formed on the surface of the paper. Entanglement of cellulose nanofibers or nanocrystals, and their interaction with paper, will produce mechanical improvement. Furthermore, other coating effects may influence paper appearance, by including in the coating pigments or gloss modifiers, or its barrier properties. In the last case, the barrier effect can be triggered towards oxygen, water and water vapor, or oil, or water and oil (amphiphobic coating). These features are summarized in Table 1 along with a synthetic description of the strategy used to achieve them.

Both CNFs and CNCs have the capability to adhere to paper surfaces by establishing a hydrogen-bonding network with paper fibers. Actually, coating paper with a CNFs or CNCs layer has several positive effects: smoothing the surface will improve the hindrance to ink penetration during printing processes,[120] while the intertwined hydrogen-bonded network spontaneously produced by CNFs or CNCs self-assembly on the paper surface will enhance its mechanical properties.[121] The coating formulation will have a remarkable impact on print sharpness and water fastness, benefiting also the water repellence and gas barrier properties of standard paper.[122]

Cellulose nanofibers are usually considered more effective than CNCs as a coating layer. According to Qianlong et al., their higher aspect ratio allows CNFs to organize in a more tightly entangled network with respect to CNCs.[163] Conversely, cellulose nanocrystals will form a stacked structure. The self-assembled nanostructure (e.g., film) of CNCs is very brittle due to the lack of an energy-dissipating amorphous phase and its inability to form entangled networks.[164] This conclusion is generally accepted for freestanding nanocellulose films (named "nanopaper"), but for paper coating, this is actually questionable, since literature reports quite positive results achieved from CNCs coating, too. Actually, these comparisons are very hard to carry out in a systematic way, because, based on the

available data, mechanical properties are often extrapolated from research carried out by independent laboratories.[165,166] A consistent comparison should be done specifying at least paper grammage and coating thickness. Early literature does not furnish enough material to extract the necessary conclusion. Furthermore, different base papers will give quite different results. As we will discuss, there are several factors that need to be taken into account to achieve a successful coating with either CNFs, MFC and CNCs. These include the deposition technique, the rheology of the suspension, the nanocellulose aspect ratio and the surface functionalization. The failure of a CNC coating is therefore also linked to the deposition process and to the capacity to achieve coating layers that are thick enough to be compared with films of CNF. Though results on CNCs coating are often controversial, nanocrystals are amply used with success in the field of Cultural Heritage as historical paper consolidants, as we will discuss later, for their transparency and easy water dispersibility. Data from Cultural Heritage studies are often in countertendency with data from other disciplines. Another aspect that must be taken into account is relevant to the higher specific surface area of CNCs which enables easier surface functionalization, with more probability to maintain water dispersibility with respect to CNFs. This aspect can be exploited to achieve multifunctional coatings by CNCs use with a very dense and effective anchorage of functional groups or active molecules. Finally, whether CNCs or CNFs are better in terms of gas barrier property remains an object of debate.[167] Thin films from both of them are excellent oxygen barriers, but paths available for the diffusion of gases across them are different depending on their morphological properties. The different behavior is shown in Figure 4:[168] CNFs possess a higher aspect ratio, and can form a web structure, leading to a tortuous diffusion path;[169] conversely, CNCs are monodisperse rigid nanofibers and can yield a more ordered layered structure, presenting higher density and a very limited number of voids and spaces available for the passage of gases.[170]

Several factors influence the mechanical properties of CNF coating. However, these factors are not yet comprehensively

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rationalized.[171] This is a consequence of the diverse morphological characteristics and crystallinity index of the nanocellulose used, which makes a reliable comparison hard to achieve. Indeed, a comparison of different coating solutions based on nanocellulose can be systematically done only if the aspect ratio of the fibers is maintained comparable. Using stress-to-failure tests, the mechanical properties of paper or nanocellulose coatings can be studied. The failure of these samples is supposed to occur by slippage of the cellulose chains by breaking the H-bonds, which are weaker than covalent bonds. If the fiber aspect ratio is kept constant, other parameters possessed by the nanofibers, such as the degree of polymerization (DP) (i. e., the average number of monomeric units in the cellulose chains composing the nanofibers), can be taken into consideration to evaluate their influence on the mechanical resistance. Henriksson et al. studied the stress-strain behavior of films of nanofibrils differing from the DP.[172] The stress-strain curves of the samples under investigation are reported in Figure 5a. Even if the films roughly followed the same stress-strain curve, their strain-to-failure performances were different.

The stress-strain curves for CNF networks prepared from fibers with DP 410 (blue), 580 (green), 820 (red), and 1100 (black) display a different line break. This corresponds to strain-to-failure, that is, the maximum elongation percentage sustained by the films. Since a higher number of intermolecular hydrogen bonds would result in a higher strain to failure, the highest DP corresponds to the highest resistance to failure. This effect is clearly a consequence of the increased capacity to form a high number of H-bonds possessed by the longest polymeric chains.

Zhu et al.[106] identified a relation between nanocellulose film mechanical resistance and nanofibers' diameter. They compared papers, fabricated with the same grammage, from cellulose fibers with mean diameters of 27 μm, and 28, 20, and 11 nm. The stress-to-failure curves as a function of the diameter of the fibers are shown in Figure 5b. The nanocellulose networks displayed a higher mechanical resistance with respect to standard paper. Paper toughness (i.e., work to fracture, measured from the areas under the stress-strain curves in Figure 5b) is plotted in Figure 5c. This parameter increased proportionally to ultimate tensile strength but decreased with increasing nanofibers diameter. Furthermore, the ultimate strength displayed a proportional dependence from the reversal of the square root of the diameter of CNFs (plot d of Figure 5). In conclusion, a decrease in the mean fiber diameter yielded an overall increase in the mechanical properties of paper. The authors observed a general improvement of mechanical properties of a paper comparing regular paper to CNF films (nanopaper), provided the comparison was performed on samples with the same grammage. This behavior was attributed to the decreased diameter of constituent cellulose fibers, that implied a lower number of defects. The applied tension forced the initially entangled random cellulose fiber network to deflect and twist to align parallel to the tensile direction. A progressive increase in the tensile load caused an overall failure of the paper, generated by stress-to-failure of the cellulose fibers.

Therefore, the overall tensile strength of nanopaper, according to this idea, would be determined by the stress-to-failure behavior of individual CNFs. During the fracture of the nanopaper, the individual nanofibers will slide on each other. Increasing the load, CNFs will also start to fracture: their hydrogen bonds will start to break and reform, but, depending on the amount of load, their fractured segments will remain bonded to the surrounding fibers. This theory is represented in Figure 5e. The capacity of CNFs to "absorb" or mitigate fractures is surely justified by their crystallinity. This process of hydrogen bonds breaking and reforming dissipates a significant amount of energy, preventing the occurrence of dramatic fractures. Overall, all this behavior results in a much-enhanced fracture toughness.

TEMPO-oxidized CNF fibers display an increased water absorption capacity as an effect of the presence of the highly polar carboxyl surface groups.[173] CNF cross-linking via carboxyl groups would, at the same time, benefit the mechanical properties of the coating layer and decrease its water absorption capacity, if the carboxyl moieties are made less accessible to water by the cross-linking agent. In a recent study, TO-nanocellulose was blended with polyethyleneimine (PEI) or cross-linked with hexamethylenediamine (HMDA).[116] Blending TO-CNF with PEI reduced CNF water absorption capacity. This was justified by invoking a shielding action exerted by amine groups in PEI on the carboxylate groups (COO) of CNF. However, it is much more feasible that a hydrophobic effect was obtained thanks to the presence of the aliphatic molecular skeleton possessed by PEI. A decrease in physical fiber swelling was given by the partial chemical crosslinking of the amine groups in HMDA. Indeed, when fiber bundles of CNF are soaked in water, the liquid diffuses by the capillary flow between the elementary fibrils and solvates the carboxyl groups (H bonding) resulting in a swelling of fiber bundles. This phenomenon is much less dramatic when the carboxyl groups are converted into amide bonds. (Figure 6).

Another strategy for reducing the water absorption properties of a TO-CNF film was proposed by Lee et al.[118] Transparency of TO-CNF films was preserved after dual cross-linking. This approach, combining chemical and physical interactions, was used to achieve high-performance nanocellulose -based bioplastics. The hydroxyl groups of TEMPO-CNF suspensions were firstly crosslinked with epichlorohydrin (ECH). After the formation of a cross-linked film, TEMPO-CNF matrices were crosslinked physically via the strong electrostatic interaction between carboxylate groups and Ca^{2+} ions (Figure 7). The optimized dual cross-linked TEMPO-CNF films exhibited thermal stability, water resistance and tensile strength that were superior to the neat TO-CNF film.

Tarrés et al. demonstrated that the use of enzymatic CNF as bulk additive during papermaking induced significant improvement in the mechanical properties of the paper, especially if the paper preparation was followed by surface coating with TEMPO-oxidized CNF. The overall process was more cost-effective than the sole use of TEMPO-oxidized CNF as a bulk additive.[174] This was justified since the enzymatic pretreatment is supposed to be significantly cheaper and environmentally

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friendly compared with the chemical treatment. Following, the same group converted fluted paper into pulp and applied the same combined technology to the preparation of cheap paper with enhanced strength, increased grease resistance (kit test 3), and reduced air permeability and water vapor transmission rate when TO-CNF were mixed to poly(vinyl alcohol) as co-deposition additive.[140] Further surface treatment with alkyl ketene dimer led to an increase of water contact angle to 115°, but to a decreased breaking length of the substrates.

The coating deposition technique is crucial in the determination of paper quality: a pressure applied to paper during coating, for instance, can induce the penetration of the coating solvent (i.e. water) into paper with subsequent undesired swelling. Lavoine et al. systematically demonstrated that the aqueous medium used to dispense the nanocellulose impacted differently on the mechanical properties of the paper when the deposition was performed by bar coating (rod-coating) or format printing.[139] Format printing yielded swelled paper with poor overall mechanical properties, while bar coating yielded a film-like MFC deposition on the paper surface. In bar coating,[175] a solution is deposited on the substrate and a stainless-steel rod, which is wrapped with a narrow wire spiral, is rolled through the solution onto the surface. This first produces the deposition of a series of solution strips, which coalesce into a homogeneous layer, provided that their spacing and the surface tension of the liquid are adequate. Control of the wet coating thickness is provided by the diameter of the wire used. No additional pressure or heat is required, and the coating is only applied to one face of the paper. In the format printing,[176] the paper is pressed between two laminating rods at a controlled pressure and speed and is instantly coated on both faces. In figure 8, SEM micrographs of paper cross-sections are reported. While 10 depositions of bar-coated MFC yielded a 3 μm thick MFC film (Fig. 8B), the same number of repetitions performed with the format printing technique, produced, instead, a swelled sample where the MFC layer was hardly recognizable (Fig. 8 C). This morphological effect was attributed to the size press mechanism, which forces the solution.

MFC between the cracks between the fibers, promoting swelling of the paper; in contrast, the bar coating technique promotes interaction of the aqueous solution predominantly with the surface of the paper. This is reflected also in reduced air permeance of the bar-coated sample (256 ± 155 nm Pa^{-1} s^{-1}) with respect to the pristine paper (2680 ± 140 nm Pa^{-1} s^{-1}) and the pressed samples (2706 ± 342 nm Pa^{-1} s^{-1}). Nonetheless, the mechanical strength of the coated samples was always inferior to the mechanical performance of the pristine paper. Water infiltration was always responsible for weakening the hydrogen bonding among paper fibers, although the strengthening action of the MFC partially compensated the detrimental effect of water on the paper compactness.

Many milder deposition methods for paper coating, such as solvent evaporation, spin coating or chemical vapor deposition, are inadequate to control important parameters like particle organization, density and thickness of the film. Fine control over these parameters is required to achieve an optimal performance of the coating. Conversely, spraying techniques

display more promising potentialities. These techniques present some advantages with respect to the ones formerly presented: spray coating is a contactless technique, which will not damage the paper surface. In 2009, the first literature report by Aulin et al. described the beneficial effects of spraying micro-fibrillated cellulose suspensions (MFC) on paper by an improvement of the mechanical properties.[142] Furthermore, the authors demonstrated the coating's ability to reduce paper air permeability. Spray coating was better suited than the rod coating technique to ensure a good oil resistance property and suitability to ink printing.[143] A spray coater design is shown in figure 9. Among the controllable variables to consider, the concentration of suspension, spray pressure and distance from the sample, time of spraying, nozzle type and drops size influenced the coating results. This technique has the advantage that surfaces may be sprayed with any pattern shape. If the surface is immovable, as in the case of paper, the preferred nozzle is usually a full cone nozzle since its pattern will cover a larger area than other types of nozzles.[177] The technique is time-effective and achieves low coating weights avoiding material waste and permitting the deposition of a dense film from a decreased amount of liquid. Overall, spray coating reduces costs and improves coating quality.[178] Paper properties that may be influenced by the spraying deposition parameters include the tensile strength, water-vapor transmission rate (WVTR), and oxygen transmission rate (OTR). A thicker CNF layer will enhance paper strength and barrier properties. A CNF layer with the following characteristics: 11 μm thickness and basis weight of 9.9 g/m^2, was deposited from a 1.4% w/w CNF suspension, at an air spray pressure of 5 bar, spraying distance of 15 cm and 30 s of spraying application. This resulted in an 18% increase in tensile strength of base paper and a 16% decrease in WVTR in comparison to control paper (with no coating). The CNF coating was not able to influence the OTR property. Whilst the inclusion of CNFs in the coating solution can improve gas and oxygen barrier properties, the coating itself is still sensitive to moisture.[179] These issues were observed in spite of the good adhesion of CNF film, observed by the microscopic and tensile investigations. Spray coating was also used to enable the deposition of multilayers of MFC and shellac, a hydrophobic natural resin.[141] In this way, the water vapor transmission rate of paper and paperboard reached values considered a high barrier in food packaging (6.5 g/m^2 24 h).

CNCs are less sensitive than MFC and CNF to chemicals, including atmospheric moisture, but show brittleness during coating.[180] Even so, CNCs are transparent[181] and their films display better gas barrier properties.[182] Spray-coated paper with sulfated CNCs showed an increase in surface gloss (from 2.65 to 4.09 gloss units) and print gloss (from 5.27 to 10.61 units).[144] To reap the benefits and reduce the respective problems, a multilayer coating, combining CNFs and CNCs was studied to provide barrier properties to the paper for gas, oil, and grease, proving a reduced water vapor permeability (6.5 g/m^2 24 h).[145]

This technique can densify the paper sheet, reduce shrinkage, and increase the retention of solids. To reduce the impact of water absorption during CNCs coating, a nano-
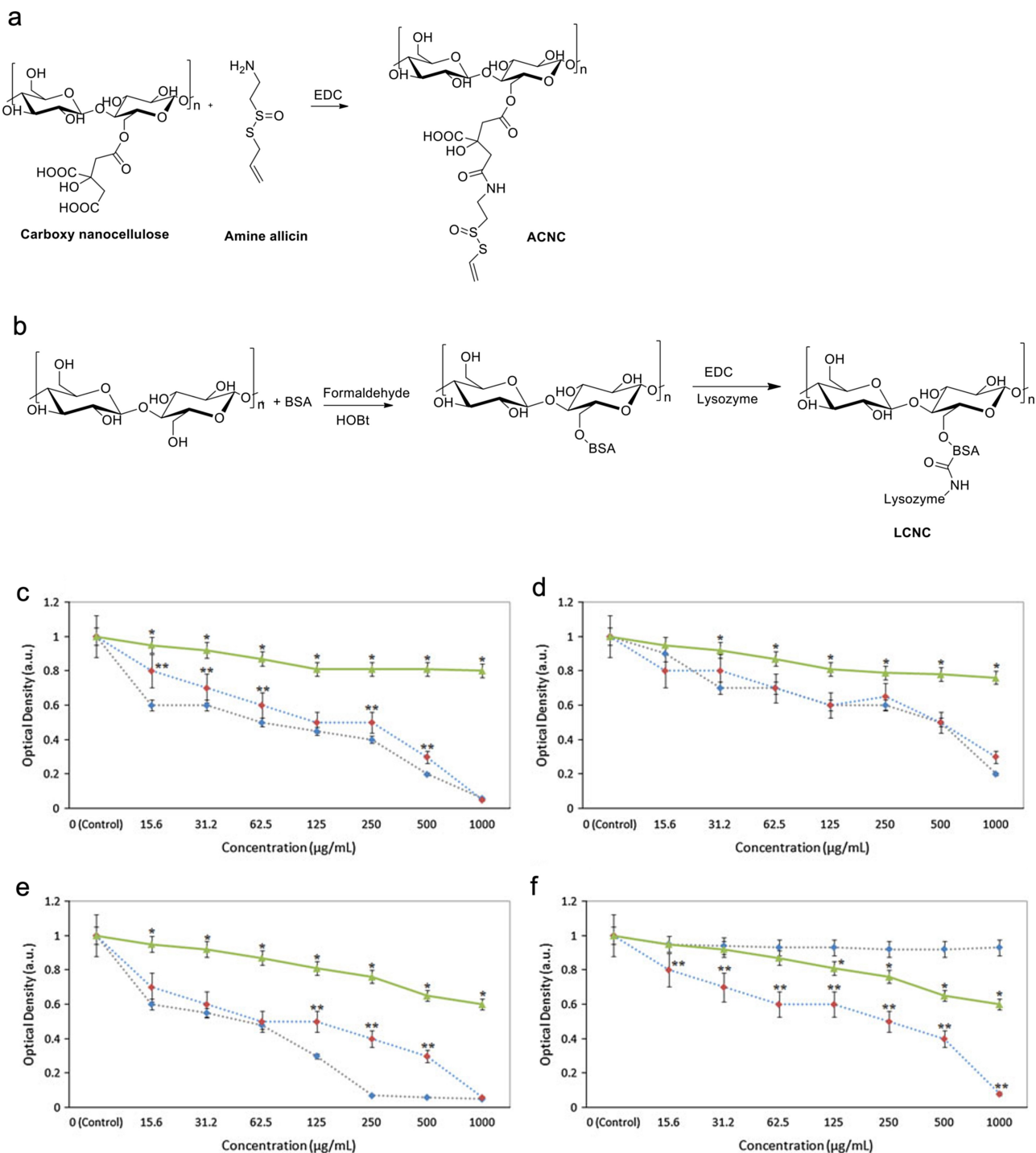
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Figure 18. Schematic representation of conjugation between carboxy-nanocellulose and amine allicin (a), and between BSA-nanocellulose and lysozyme (b) promoted by EDC as a cross-linker. Broth microdilution tests of nanocellulose, lysozyme, and LCNC samples on C. albicans (a), A. niger (b), S. aureus (c), and E. coli (d). Samples were incubated for 48 hours at 25, 35, and 35 °C. The Optical density (OD) of each well was read at 405 nm on an ELISA plate. The optical density of microorganisms suspensions measured in the presence of lysozyme alone, cellulose nanocrystals and cellulose nanocrystals/lysozyme bioconjugates (LCNC) is represented in blue, green, and red, respectively. Reproduced from [209] with permission from Springer-Nature.

cellulose containing around 5–15% lignin may be useful.[147] Indeed, lignin is hydrophobic and responsible for protecting plant cells from moisture and microbial attack. The lower hydrophilicity of the nano-lignocellulose (NCL) allowed their dispersion in water-alcohol mixtures. Furthermore, the hybrid

nanocellulose still displayed tailorable surface coverage, surface smoothness, ink compatibility and improved printability.[183] The tolerability of low lignin content (below 11%) on CNF films was also demonstrated by Rojo et al.[184] Since the uncontrolled presence of lignin can impact the coating performances in an
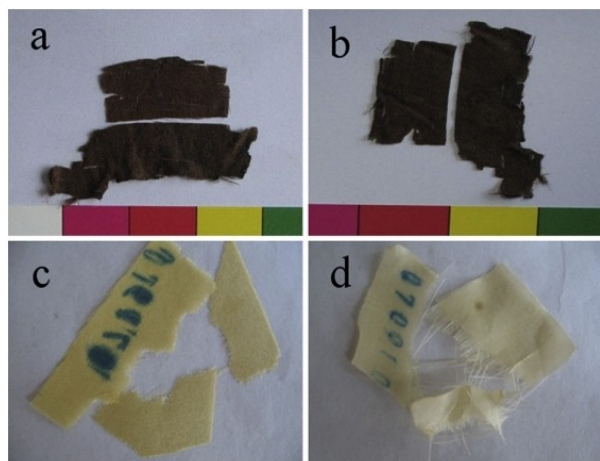
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Figure 19. Images of the fragments of (a) PHS, (b) BC/PHS, (c) AAS and (d) BC/AAS. Reproduced from [213] with permission from Elsevier.

unexpected way, Farroq et al. added homogeneously distributed colloidal lignin nanoparticles (CLPs) to CNF films. The films displayed reproducible waterproof, antioxidant and UV-shielding activities and were promising for applications in food packaging, water purification, and biomedicine.[148] Less sustainable than lignin use as additive to the coating, was the use of an alkyd resin to reduce the WVTR of CNF barriers.[185] UV-screen properties were also achieved by blending CNCs with CeO_2 and SiO_2 nanoparticles.[149]

Sulfated CNCs are excellent film formers, in spite of the necessity to use a strong mineral acid to prepare them. In a rheological study of formulations for paper coating, cellulose nanoparticles were obtained from corncob residues. Hydrolysis by sulfuric acid and TEMPO-mediated oxidation methods were used to yield sulfated CNCs and TEMPO-oxidised nanofibers. Formic nanoparticles were prepared by formic acid hydrolysis, as a less corrosive process with respect to sulfuric acid treatment. The study showed that, even if morphologies and surface chemical properties of the nanoparticles have a big impact on the behavior of their aqueous suspensions, the surface chemical properties played a much more important role in the

rheological modification of paper coating. Indeed, formic cellulose nanoparticles exhibited larger dimensions and limited negative surface charge with respect to sulfated CNCs. Therefore the former presented poor dispersion stability in water. Conversely, sulfated CNCs displayed excellent efficiency in paper coating, with superior thickening capacity and enhanced rheological function, thanks to their higher surface charge and strong interactions with pigments and immobilized water molecules present on the paper surface.[186] Sulfated CNCs were also used successfully as coating partners of thermoplastic polyhydroxybutyrate (PHB) to enhance the water resistance of paperboard for packaging.[151] Likewise, 5 % w/w CNCs were added to a polysaccharide electrolyte based on chitosan and carboxymethyl cellulose to obtain an excellent barrier coating against liquid (grease, water and oil) penetration on paperboard substrates.[187]

A continuous process for the deposition on paperboard of a multi-layered coating containing micro-fibrillated cellulose (MFC) or CNCs was devised by Koppolu et al.[153] Their approach was based on the use of poly(lactic acid) (PLA) as part of the multi-layered coating to reduce nanocellulose sensitivity to moisture in extreme relative humidity (RH) conditions. The two materials were deposited by different techniques: while a roll-to-roll slot-die coating was used to deposit nanocellulose,[188,189] an extrusion process was used for PLA. Low-density polyethylene (LDPE) was deposited alternatively to PLA as reference material, while a starch coating was used to improve the adhesion of the nanocellulose layer. The continuous process is represented in Figure 10. These completely biodegradable coatings displayed several interesting properties: the combined nanocellulose/PLA multi-layer coating presented an oxygen transmission rate (OTR) 98 % lower than the one of the sole PLA; a similar reduction was observed with heptane vapor transmission rate (HVTR); the grease barrier was improved by 5-fold compared to nanocellulose alone and 2-fold compared to PLA alone. The water vapour transmission rate (WVTR) of the multilayer coatings remained lower than the control PLA and LDPE coating even at a high RH of 90 %, confirming the usefulness of the PLA layer in protecting the nanocellulose layer from a high humidity environment. The same continuous
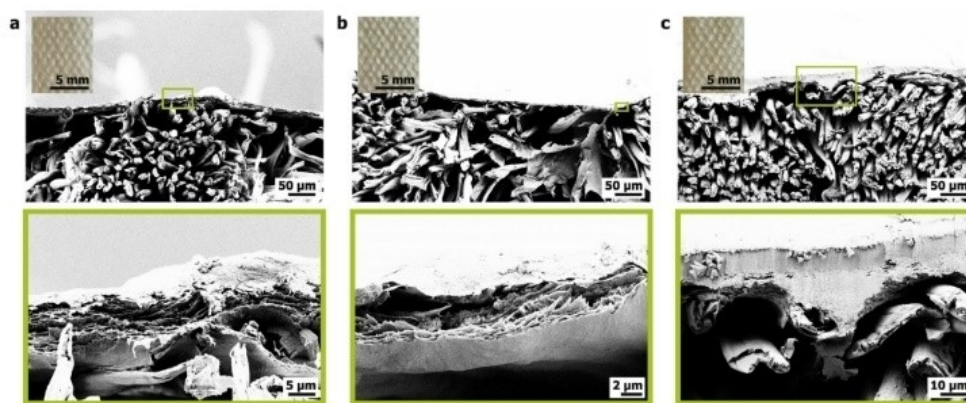

Figure 20. Scanning electron microscopy images of aged cotton canvases coated 3 times with: (a) CNF; (b) CCNF and (c) CNC, with optical microscopy images as insets (left top). Reproduced from [210] with permission from Elsevier.
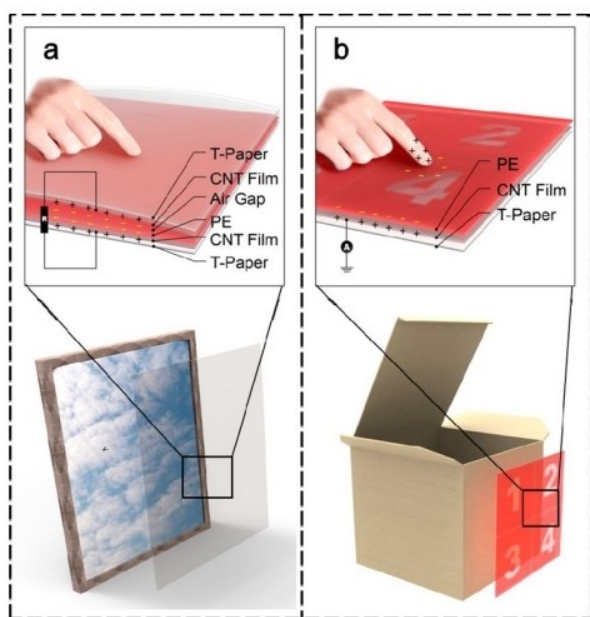
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Figure 21. Diagram of (a) transparent paper-based anti-theft system and (b) transparent paper-based anti-fake system. Reproduced from [221] with permission from the American Chemical Society.

process was used to coat conductive nanocellulose/nano-graphite composites onto untreated greaseproof paper or pigment-coated paperboard.[190]

Cellulose nanocrystals were used to enable the deposition from water of a polymer based on soybean oil: this material is very promising as a water barrier and is sustainable; however, it displays very poor water solubility. In this work, CNCs were first aminated by reaction with APTES (aminopropyltriethoxysilane). Then, functionalized cellulose nanocrystals were used to covalently bind acrylated epoxidized soybean oil (AESO) exploiting a Michael addition of the amine pendant groups introduced by APTES on the surface of CNCs with the acryl ester groups of AESO. The procedure is summarized in Scheme 3. The covalently linked CNCs acted as capping agents for big micro-particles of AESO (average diameter 2.92 μm), allowing their dispersion in water. After the application of a film of AESO-APTES-CNCs microparticles on paper, the coating was cured into a continuous barrier film. The water vapor transmission rate (WVTR) of paper was reduced from 1926.7 g/m² 24 h to 1286.3 g/m² 24 h.[152]

Recently, nanocellulose coating was involved in the consolidation of fragile biomaterials, with interesting implications for the field of Cultural Heritage safeguarding.[123] In these cases, the different aspect ratios or functionalizations of nanocellulose displayed various consolidation effects. The research initially focused on the use of bacterial nanocellulose (BNC), recognized as the purest form of nanocellulose, to preserve historical paper.[124-126] However, the use of CNCs allowed them to reach the best results. CNCs display the advantage that they can be applied directly to paper surfaces from a suitable suspension using a brush, a technique commonly used in conservation ateliers. Xu et al. used CNCs hydrophobization via esterification

with oleic acid to confer the coating, applied using ethanol as solvent, the necessary hydrophobic properties for protection against humidity. This approach was proposed to allow the consolidation of paper artworks that cannot be restored using water suspensions.[129] However, the CNCs alone were not able to stabilize paper pH. To ensure control over paper pH, they added carbonate nanoparticles to the coating. CNCs blends with silver nanoparticles were exploited by Bergamonti et al. to confer paper biocidal properties and protection from attack of *Escherichia coli* and *Bacillus subtilis*. Furthermore, the coating was useful to prevent the proliferation of *Aspergillus niger*. The Ag nanoparticles did not appreciably affect the aesthetic appearance of the paper.[128] Operamolla et al. described an innovative strategy for consolidation of degraded paper by reversible application of neutral and sulfated cellulose nano-crystals (N CNC and S CNC, respectively) as sustainable fillers to reinforce paper mechanical properties and resistance to further degradation.[127] They definitively demonstrated that surface sulfation of nanocellulose features some consolidation and protection effects but causes the decrease of the pH of paper with aging, negatively affecting the conservation. Conversely, neutral CNCs, prepared by HCl hydrolysis, are safer for paper conservation treatment because they do not compromise its pH and mechanical properties. The innovation of the conservation method based on cellulose nanocrystals consists of the facility to remove nanocrystalline cellulose by surface cleaning with a gellan hydrogel, as demonstrated by Operamolla et al. After, the authors applied the conservation treatment to a real paper artefact dated 1738, the book *"Breviarium Romanum ad usum fratrum minorum"*. An extensive study on the aesthetic impact of the nanocellulose treatment on the book pages revealed not only that the presence of transparent CNCs on coated paper did not influence the features of the written parts, but also that the application of CNCs induced a slight improvement in the optical quality of paper with respect to the untreated one due the improvement of lightness and chromaticity values. Figure 11 shows the chemical structure of sulfated, neutral, and oleyl CNCs and images of pages and details from *"Breviarium romanum ad usum fratrum minorum"* before and after treatment.

Historical paper that contains written parts of iron gall inks is notoriously affected by acidification and oxidation processes activated by the ink and represents another well-known conservation problem that needs a straightforward solution. Völker et al demonstrated the feasibility of successfully applying a CNF conservation treatment to paper with parts written by iron gall ink. The application of CNF in combination with phytate or other deacidifying agents displayed great conservation potential to stabilize severely damaged manuscripts.[191] A blend of inorganic halloysite nanotubes and cellulose nano-crystals was applied to a historical paper dated 1943. The transparent consolidation layer demonstrated also UV-protection properties.[192]

The electrostatic self-assembly approach was applied by different research groups to develop blends of nanocellulose with potential antibacterial properties, to use for paper coating with food-packaging applications. Freestanding MFC sheets,

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containing a bismuth complex (~2:4% g Bi/g dry paper), such as organophosphinate, were studied for developing packaging solutions with antimicrobial properties.[133] An antibacterial paper was prepared by size pressing a suspension of cellulose nanofibers/ZnO/starch in water.[134] The coated paper displayed bacteriostatic or bactericidal properties against Gram-positive (*Staphylococcus aureus* and *Bacillus cereus*) and Gram-negative (*Klebsiella pneumoniae*) bacteria. A similar approach was adopted to inglobate antibacterial Ag nanoparticles into a CNF/starch coating.[135] Alternatively, green Ag nanoparticles capped with starch were blended with PVA and CNCs to achieve an antibacterial coating with potential food packaging application.[193] A coating formulation compatible with food packaging was also prepared polymerizing pyrrole in the presence of TEMPO-oxidized CNFs. The coating was applied by casting on paperboard, reducing its water sensitivity and improving its mechanical properties. Furthermore, the coated paperboard demonstrated very good antibacterial and antioxidant properties, determining the delayed maturation of cherry tomatoes.[137,138] More generally, CNFs or CNCs spraying has been proposed as an effective deposition method of an edible coating for fruit and vegetable preservation against natural decay.[194–197]

Paper coating displays intriguing perspectives also for the fabrication of conductive supports for flexible and portable electronic devices, electroluminescent devices, and electrochemical sensors and biosensors.[198] The conductivity of cellulosic paper is determined by the kind of conductive fillers added and by its fabrication process. It can be manufactured either by the wet-end formation process and/or surface coating of preformed paper. Several fillers could be used like polypyrrole or polyaniline[156,157] or carbon fiber, carbon black, nanotubes CNTs, and graphene.[158,159] Carbon nanotubes, CNTs, are very promising candidates due to their unique nanostructure and excellent physical properties. Conversely, they display very poor water dispersibility, therefore several efforts are directed to enhance this property. Graphene oxide (GO), due to the hydrophilic oxygen-containing functional groups, could be used as a dispersant in an aqueous system.[160] Tang et al. described the use of green multi-walled carbon nanotube (MWCNT)/graphene oxide (GO) nanocomposites to impart conductivity to cellulosic paper. MWCNT and GO were applied to paper by surface coating, facilitated by cellulose nanocrystals deriving from cotton fibers used as enhancers of their water dispersibility. The successful dispersion in water and application of MWCNT/GO nanocomposites to cellulosic paper was able to impart a conductivity as high as 892 S m^{-1} to the cellulosic paper while improving the overall mechanical properties.[161]

The Langmuir–Blodgett (LB) method is able of making homogeneous nanomaterial coatings[199] The surface charge of sulfated cellulose nanocrystals was exploited by Sawalha et al. to prepare 2D-films of CNCs and cationic fulleropyrrolidines, exploiting their electrostatic interactions to self-assemble well-organized bilayers at the air-water interface. The chloroform solution of the cationic fulleropyrrolidine was spread over a water subphase containing dispersed cellulose nanocrystals. The amphiphilic cationic fulleropyrrolidine was able to self-

organize at the air-water interface, orienting the hydrophobic cages toward air and the cationic appendages to the water subphase. An anionic exchange in favor of the sulfated CNCs generated a floating fulleropyrrolidine/CNCs bilayer. Horizontal transfer of the bilayers onto ITO electrodes yielded photo-responsive films with enhanced performances with respect to electrodes modified by deposition of the sole fulleropyrrolidine.[162,200] Figure 12 shows AFM topographies of 2D films of the sole fulleropyrrolidine and a fulleropyrrolidine/CNCs bilayer, evidencing the 2D-organization of CNCs induced by the cationic counterpart. More generally, layer-by-layer techniques were identified as ideal methods to produce self-organized CNCs thin films from their water dispersions, possessing a 2D organization, which may be of interest for anti-reflection coatings.[131,132] Other uses of self-organized CNCs thin films may include reinforcing or anticounterfeiting coating for banknotes. Ngoensawat et al. used electrostatic blends of bacterial cellulose nanocrystals (BCNC) and UV-responsive ZnO quantum dots to obtain inks able to write encrypted messages on paper. The messages were unreadable under daylight and were revealed only under UV illumination, but could be quenched by CuCl$_2$ aqueous solutions.[154] The same authors developed an eco-friendly flexible surface-enhanced Raman scattering (SERS) substrate based on bacterial nanocellulose (BNC) for in-situ detection of pesticides by laser reading. The BNC was blended with plasmonic Ag nanoparticles, to get a direct and rapid detection of methomyl on fruit peels (oranges).[155]

4. Nanocellulose in textile coating

The application of a nanocellulose-based coating is of interest to the textile industry not only as a mechanical enhancer but also to solve some pivotal problems connected to the phases of textile production, such as the reduction of hazardous wastes, especially from phases of coating application and textile dyeing. A complex point in the textile application is due to the fact that not all fabrics are composed of cellulose. Therefore, the requirements for the nanocellulose chemical functionalization may be different depending on the kind of fiber, natural or synthetic, that needs to be coated because the surface functionalization of nanocellulose needs to provide the necessary adhesion to the substrate.

However, the literature in this direction is still very poor. Table 2 summarizes the features of nanocellulose coating applied, so far, to cotton and other textile and their field of application.

While CNF or CNC coating has been documented for cotton fabric, so far there is little information in the literature about nanocellulose coating on fabrics of different compositions or quality. For low concentrations of cellulose nanofibers (<1%, w/w), the viscosity of the hydrogel is so low that it diffuses across the fiber surface. Therefore, to achieve an appreciable and uniform coating layer of nanocellulose, suspensions with high viscosity are necessary to express all the film-forming properties of the coating. Furthermore, ozone plasma treatment

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of synthetic fibers can improve nanocellulose adhesion by empowering the formation of hydrogen linkages with the fibers.[201] Saremi et al. performed a systematic study (Figure 13) on the adhesion and resistance to swelling in water of CNF and CNC thin film coatings applied to cellulose/cellophane (CL), cotton, poly(ethylene terephthalate) (PET) and nylon 6,6 (PA 6,6).[202] The authors compared diverse adhesion methods to elucidate major mechanisms of coating stabilization. A cationic polyelectrolyte, poly(ethylene imine) (PEI), was added as a hydrogen bond former to strengthen the network of nano-cellulose particles and their interaction with the substrate (films and textiles). Strong hydrogen bond formation was expected between amino groups of PEI and hydroxyl, amide and ester groups of nanocellulose and textile materials (PET and nylon). This additive was compared to the action of a copolymer of glycidyl methacrylate (GMA) and oligo(ethylene glycol) meth-acrylate (OEGMA) (P(GMA-OEGMA)), able to enforce the hydrogen bonding network and cross-link the fibers, and of a commonly used cellulose-crosslinker, a polycarboxylic acid (PCA) agent. Wet and dry tests run on nanocellulose coatings deposited on polymer films revealed that the highest nano-cellulose adhesion was achieved on nylon, cellulose, and cellophane surfaces. The lowest nanocellulose adhesion was achieved on PET. The coatings' stability was improved by the introduction of PEI and of a reactive P(GMA-OEGMA) copolymer. These additives promoted the formation of a cross-linked network. When P(GMA-OEGMA) was added, the highest coating adhesion and stability were observed. Alternatively, the coating can be reinforced by cross-linking of nanocellulose with polycarboxylic acids. Overall, CNC coatings demonstrate higher adhesion to all substrates with respect to CNF coatings.

A 100% polyester substrate was treated with nanocrystal suspensions prepared from scraps of viscose rayon fibers and dyed with a direct dye such as Congo red BDC. Optical microscopy performed on the coated samples revealed the presence of red color (Figure 14). CNCs treatment enhanced the color strength of the polyester fabric and improved the fastness against soaping. The study showed also that the application of CNCs to polyester fibers causes an improvement in their resistance to load. The improvement in physical and mechanical properties was attributed to the mechanical interlocking caused by the presence of CNCs in the intermolecular pores of polyester.[203]

Nanocellulose coating is, by definition, able to improve the mechanical properties of a coated textile. This characteristic, combined with nanocellulose intrinsic biocompatibility and health harmlessness, allows envisioning CNF coating for intelligent textile used for medical devices, like lumbar belts.[204] This protective equipment is useful to prevent and mitigate risks of spine injuries during work time, caused by a too intense workload or scarce care from the workers during the execution of their duties. An ideal intelligent fabric should display an adaptive behavior depending on the use conditions in terms of pressure, load, humidity, temperature, etc. Poly(ethylene terephthalate) (PET) samples were coated with CNFs and potato starch gel. In this case, starch was used to improve the adhesion of the CNF coating to the polyester substrate. The coating was

water-soluble, therefore not suitable for protective garments, mainly due to the solubility of starch. However, traction tests indicated that the textile underwent a great increase in elasticity when impregnated with nanocellulose and starch, therefore the CNF coating reveals to be an appealing method for improving the mechanical properties of the intelligent fabric, provided that a correct way to anchor them on synthetic fibers like PET can be defined.

A field of application that seems more mature concerns the relevant use of nanocellulose to reduce the large volume of wastewater in the dyeing phases of cotton.[205,207] A conventional discharge dyeing method utilizes an exhaustion dyebath with a copious amount of dye solution. The fabric is dipped into the dyeing solution until the color is developed. For the application of exhaustive dyeing to cotton, a large volume of salts must be added to the dyebath, to mitigate, through the increased ionic strength, the electrostatic repulsion between fibers and reactive dyes. During the NFC-based dyeing, a hydrogel of nano-fibrillated cellulose, containing reactive dyes and dye auxiliaries (salt and alkali), is applied as a viscous slurry on the surface of a fabric by printing. This new technology is expected to reduce the use of water and chemicals in fabric dyeing by an order of magnitude, with dyeing and coloring performance comparable to that of conventional discharge dyeing. Furthermore, it generates a much lower number of effluents. Figure 15 shows samples of cotton fabrics colored by Reactive Red 120, a substantive dye for cotton. Samples c) were colored by the NFC-based dyeing technique. The colored hydrogel application allowed saving water, dye, and auxiliaries with respect to the traditional dyebath application, preserving the application efficiency with satisfying results observed also after the standard accelerated laundering tests (AATCC 61-2013, 2 A). The covalent interaction between Red 120 and cellulose is shown in Scheme 4. Cellulose's hydroxyl groups residing on the surface of nanofibers will react with chlorotriazine functional groups of the reactive dye. This anchors the dyes on the hydrogel. The same mechanism works between the fabric and the dye during traditional discharge coloring. However, CNFs display a much-enhanced specific surface area and the capacity to chemically bind a higher amount of reactive dye molecules, improving the efficiency of the dyeing technology and decreasing dye losses.[205]

Indigo is a dye profusely used by the denim manufacturing industry. During the application of vat-dyeing, indigo is reduced to leuco-indigo by sodium hydrosulfite at alkaline pH (10-12). Leuco-indigo is oxidized to indigo in atmospheric oxygen, after deposition onto the textile. The industry of denim is one of the most polluting since indigo is flammable during storage and corrosive to wastewater pipelines.[214] During the wastewater treatment process, sodium hydrosulfite can form toxic hydrogen sulfides from the sulfates dissolved in the wastewater.[215] The presence of dyes in wastewater may be responsible for skin diseases.[216–218] Indigo-dyeing of cotton fabrics was achieved by the CNFs technology applied by screen printing.[206] The coated fabrics were treated with an aqueous solution of chitosan to improve the adhesion and stability of the coating. The whole procedure is described in Figure 16. The process involves a

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mixture of natural indigo particles (extracted from *Indigofera tinctoria*) and 1% NFC hydrogel, which is deposited on the surface of the cotton fabric by a screen-printing technique or on the yarn by a continuous flow padding process. Dyeing one pair of blue denim jeans by the traditional exhaustive dyeing technology on average consumes 50 to 100 liters of water containing alkali and toxic reducing agents. The CNF technology reduces water consumption up to a factor of 25 and eliminates the use of any reducing agent or alkali. Therefore, the new CNF-based technology drastically reduces effluents in wastewater. The considerable efficiency of the CNF dyeing process, indeed, allows the use of natural indigo particles, which, being more expensive than the synthetic leuco-indigo, cannot be used in exhaustive dyeing. Remarkably, the CNF technology guarantees that over 90% of the dye is fixed to the fabric, against 70–80% yield of conventional dyeing. A further advantage consists of the possibility to avoid multiple (up to 8) dips of the textile into the dyeing solution to achieve different shades: with the nanocellulose technology, lighter and darker shades can be achieved in only one step simply by the deposition of a CNF hydrogel loaded with fine natural indigo particles and chitosan over the cotton denim fabric or yarn.

The CNF dyeing technology has several benefits, including the flexibility of the coating, which conforms to the morphology of the fabric after water evaporation. In the coating, the CNFs form a braided network with a random mesh size distribution scalable with the diameter of the fibrils. Even if positively evaluated, the procedure is affected by the presence of hemicellulose in the hydrogel: hemicelluloses can conjugate reactive dyes, forming washable complexes that will have to be disposed of. This problem can be overcome by grafting hemicellulose-dye conjugates onto the surface of NFC nanofibers and cotton fabric using polycarboxylic acids (PCA) as cross-linkers. This will improve color fixation and reduce color contaminants (unreacted dyes) in wastewater.[205]

Textile coating with UV-protection properties can be useful to safeguard people from skin cancer diffusion, providing garments able to protect skin against the harmful effects of sunburnt. Coating with UV protection properties often contains a transparent layer of materials absorbing UV light. This UV-absorbing layer may be organic or inorganic. Strong absorption (high extinction coefficient) is required in the UV range from 290 to 360 nm. The UV protection factor (UPF) and sun protection factor (SPF) are the parameters usually taken into consideration to assess the goodness of a protective garment. Nanostructures and natural materials are among the most effective protective coating. With this respect, nanomaterials display high activity, while natural materials are the most benign for human health and for the environment. Cellulose nanocrystals can yield an anti-UV layer if combined with UV-blocking additives. Three types of CNCs with different particle sizes were applied as a potential UV blocking layer to cotton fabric.[208] Also, in this case, chitosan (CS) was used as a dispersant and binder of CNCs to form a biodegradable and biocompatible nanocomposite system. The cotton fabrics were dipped into CS/CNCs solutions. This treatment was followed by padding. The two steps were repeated several times to increase

the coating efficiency. Then, the padded fabrics were dried and cured at 90 °C for 10 minutes to fix the CS/CNCs nanocomposite on the surface of the cotton fabrics. Tannic acid, as shown in Figure 17, was used as a plasticizer and cross-linker due to its polyphenolic structure. All additives (chitosan and tannic acid) had the property to enhance coating UV protection.

The profiling of bacteria and microbes on surfaces leads to the need for a more consistent and passive form of tissue sterilization.[219] Research is heading towards the discovery of natural biocides with low-risk cytotoxic characteristics since microorganisms have become more tolerant to antibiotics. Recently, nanocellulosic antimicrobial materials and composites have been developed for various applications such as wound dressings, drug carriers, packaging materials, filter/adsorbent materials, textiles, and paints.[220]

The incorporation of enzymes into functional paper or textile coating is a still rather unexplored topic. An antibacterial coating was prepared by incorporating lysozyme from chicken egg white and allicin into a suspension of CNC.[209] The nanocellulose was prepared by acid hydrolysis and then modified by citric acid esterification to introduce on its surface pending carboxyl groups, able to bind amine-modified allicin. 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) was used as a condensing agent to conjugate the modified nanocellulose and amine allicin and isolate the conjugate (ACNC). Cellulose nanocrystals were, in a second step, coated with bovine serum albumin (BSA) and used as a binder between the cellulose nanoparticles and lysozyme. The conjugation of BSA and lysozyme was carried out by the EDC method. BSA is a large molecule, and several units of lysozyme can bind to one molecule of BSA. The bioconjugate of nanocellulose with lysozyme was named LCNC. Afterward, the bioconjugates were characterized by scanning electron microscopy, dynamic light scattering, and Fourier transform infrared spectroscopy. The reaction pattern is summarized in Figure 18a-b.

The antimicrobial susceptibility of allicin (A), lysozyme (L), nanocellulose (CNC), and the bioconjugates like allicin-nanocellulose (ACNC), and lysozyme-nanocellulose (LCNC) was evaluated by broth microdilution on four standard microbial strains (*Candida albicans, Aspergillus niger, Staphylococcus aureus*, and *Escherichia coli*).[209] Results showed that the pure nanocellulose has some antifungal and antibacterial activities, but is not enough effective against them. Indeed, nanocellulose alone can only perform a nonspecific function, and cannot target and destroy the cell wall, cell membrane, or active enzymes of bacterial and fungal strains. Free allicin, as well as ACNC (allicin covalently anchored on CNCs), performed potent antibacterial and antifungal properties. Native lysozyme could not inhibit *E. coli*, but LCNC (lysozyme immobilized on CNCs) was able to inhibit their growth. In this case, the authors speculated that the activity of lysozyme is modified by bioconjugation with BSA and nanocellulose. LCNC can bind to *E. coli* compartments, leading to cellular damage. Figure 19c-f shows dose-response plots at different concentrations of nanocellulose, LCNC and lysozyme, added separately to *C. albicans, A. niger, S. aureus* and *E. coli*. The knowledge of the

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antimicrobial mechanism of conjugated nanocellulose will be useful for developing new antimicrobial agents in the future.

CNFs, BNC, and CNCs, may also find interesting application in the field of safeguarding archaeological textiles or historical canvases. CNF or CNC layers may be successfully applied to archaeological textiles for conservation and preservation purposes. Silk belongs to one of the most precious and, at the same time, most vulnerable parts of China's Cultural Heritage. During the Shang Dynasty (1600 B.C.–1046 B.C.E.), silk reeling technology was invented in China, and silk textiles were fabricated as a symbol of luxury. Archaeological silk has invaluable importance in Cultural Heritage transmission and needs safeguarding from aging and microbial attack. A bacterial cellulose (BNC) film was used to reinforce vulnerable historical silk textiles for conservation and display purposes, in place of the traditionally used synthetic polymers. The historical silk textiles had been excavated from the Han Dynasty tomb in Xiejiaqiao, Hubei, China. Modern woven natural silk textiles were used for comparison after exposure to UV lamps (254 nm) for 12 days. The bacterial cellulose restoration was applied to aged artificial silk (AAS) and pristine historical silks (PHS). Beyond assessing the improved resistance to degradation, it is of fundamental importance in the preservation of cultural relics to preserve their appearance.[213] Figure 19 shows photographs of PHS and AAS and their bacterial nanocellulose treated counterparts, demonstrating a good effect of the conservation treatment on sample appearance with the exception that the sample colors became somewhat paler after nanocellulose application. It was also shown that bacterial nanocellulose could be removed from silk samples with little damage to the original fiber properties. Therefore, as a degradable, environmentally friendly, solvent-free and resource-abundant material, bacterial nanocellulose is promising for the conservation of silk fabric.

The latest developments in historical paper and archaeological textile conservation have encouraged the extension of the consolidation treatment with nanocellulose to other historical cellulosic artworks, such as cotton pictorial canvases.[210–212] The restoration of pictorial canvases is a complex problem that, due to the hierarchical nature of the canvas, requires interventions at different length scales.[212] The first investigation on nanocellulose-based consolidation of canvases has addressed the comparison between different nanocellulose-based formulations in the consolidation of model-aged canvases.[210] The authors investigated the film-forming properties of nanocellulose on canvas and their response to static and periodic uniaxial stress at different relative humidity values. The strengthening effect of the nanocellulose application to canvas was compared to the reinforcing effect achieved by the application of traditional consolidants. Mechanically isolated cellulose nanofibrils (CNF), carboxymethylated cellulose nanofibrils (CCNF), and sulfated cellulose nanocrystals (CNC) were applied to the canvases as water suspensions using a plastic serigraphy squeegee. These were compared to three different adhesives, animal glue, Klucel G and Paraloid B72, traditionally used as canvas consolidants. The morphology of nanocelluloses on degraded cotton canvases is shown in Figure 20. The three nanocellulose samples were different not

only for the morphology and aspect ratio, but also for their surface charge: CCNF and CNC were negatively charged, and this could enhance dispersibility influencing their penetration capacity into canvases. Conversely, the presence of acid functional groups may negatively influence the pH stability of canvases and require a deacidifying additive for neutrality preservation. In the SEM images of cross-sections for the canvas samples coated with three layers of CNFs, CCNFs and CNCs, respectively, the nanocellulose coatings are barely seen. Furthermore, they did not penetrate much into the canvas bulk pointing at fast water evaporation during deposition.

CNCs tended to form denser structures due to their rod-like shape, able to produce a film with the limited occurrence of voids, compared to the flexible nanofibrils. While CCNF showed the best reinforcing results per coated weight, their intrinsic water retention and lower dispersibility required higher amounts of water for the deposition, hampering their beneficial effect. Conversely, CNCs showed the smallest reinforcement per gained weight but the highest reinforcement per equivalent number of coatings: this advantage was generated by the use of higher solids content in the aqueous dispersion, enabled by CNCs surface charge and lower overall molecular weight. The introduction of a cationic polymer, polyamidoamine-epichlorohydrin (PAAE), as an intermediate layer between the canvas and the nanocellulose was used to promote adhesion between coating and substrate.[211] Morphological, chemical, and mechanical evaluation of canvas samples at different relative humidity (RH) levels showed that the quality of adhesion of the PAAE layer was crucial for the consolidation process. PAAE-treated canvases were also displaying a higher mechanical response to moisture absorption and desorption. Overall, this study shows the complexity of such systems and, consequently, the importance of using a multiscale approach for their analysis. An alternative is an approach that combines silica nanoparticles treated with polyelectrolytes (SNPs) and cellulose nanofibrils.[212] CNF can form a film on the surface of the canvas that increases ductility. The SNP penetrated deeper and strengthened at the fiber level, resulting in increased stiffness. The two effects can be balanced by varying the SNP/CNF ratio to achieve adequate reinforcement. This approach offers an alternative to conventional treatments based, for example, on relining with a new ply or applying film-forming synthetic compounds.

Freestanding nanocellulose/carbon nanotubes (CNTs) transparent thin films could be used as components for anti-theft systems for Museums. A transparent paper-based flexible generator (TPFG) can be used as a pressure sensor and applied to historical canvases or artefacts, as shown in Figure 21a. The transparent paper-based anti-theft system does not alter the appearance of the artwork and is also sensitive to external pressure sensing.[221] The anti-theft system is composed of a CNF nanopaper combined to a CNT layer and a PE support. The CNF nanopaper represents the external layer of the device, that would potentially contact the artefact. The CNTs used for the device displayed lengths of tens of micrometers and were deposited uniformly on the transparent surface of the nanopaper. A similar system with a PE covering layer could be

instead engineered for transparent smart mapping of packaging or important documents.

5. Conclusion

Coating of paper and textile is a very promising field of application for nanocellulose, both in the form of nano- or microfibers and in the form of nanocrystals. These materials are biocompatible, biodegradable and edible, transparent, and can be easily functionalized. However, there are several issues to solve before their massive use in industrial manufacture can be achieved. These limits are mainly posed by the nanocellulose availability, at present still limited by the energy required for their large-scale production. Less energy-demanding isolation methods are necessary to achieve this goal. However, nanocellulose mass availability does not represent a problem for narrower applications, such as Cultural Heritage conservation, paper electronics, or specialty paper coating, since the present worldwide capacity to produce nanocellulose is sufficient to sustain these applications. Another limit remains in the use of softwood as a source of cellulose nanomaterials, which is the same source used to fabricate many other cellulose-based products, like paper. Methods for successful and productive separation of cellulose nanofibers or nanocrystals from non-edible and waste biomass on a large scale are necessary to enable access to large feedstocks of nanocelluloses. In this perspective, if each territory will be able to isolate nanocellulose from local biomass, there will be a further worldwide economic advantage, with additional sustainability for the local manufacturers. On the other side, a considerable research effort is still necessary to definitively understand the different properties between CNFs and CNCs films, their features, and limits. Their adhesion to paper and textile will also need to be the object of investigation. It is likely that both typologies of nanocellulose will confirm interesting capabilities in coating flexible substrates. With this respect, research cannot discard any form of nanocellulose or biomass for future consideration. Furthermore, greener methods for nanocellulose surface functionalization are required. Indeed, in literature reports often nanocellulose functionalizations adopt non-green chemicals or solvents. From a perspective of a holistic approach to sustainable materials, this surely needs further work. The research work will need especially to be addressed to answer questions such as how the best performing materials, like perfluorinated alkyl substances, can be replaced by greener bio-based alternatives.

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

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