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Review

A Review of Applications of Nanocellulose to Preserve and Protect Cultural Heritage Wood, Paintings, and Historical Papers

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Abstract: Due to several of their characteristics, such as their renewability, sustainability, and eco-friendliness, nanocellulose-based materials are arousing growing interest from researchers in various fields of study and applications. The purpose of this review article is to provide an overall view of the most recent applications of these innovative bio-nanomaterials in the field of cultural heritage. First, an introduction of the different classes of cellulose nanomaterials and their synthesis and characterization methods is presented. After that, many consolidation treatments based on nanocellulose structures for the recovery of degraded and archeological wood, the stabilization of damaged painting canvases, and the deacidification of historical papers are shown in order to underline the advanced potential of nanocellulose for the conservation of artistic heritage and the respect for the environment.

Keywords: nanocellulose; cultural heritage; degraded wood; painting canvases; ancient paper; stabilization; reinforcement; strengthening; deacidification

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1. Introduction

In recent years, the application of green, renewable, and sustainable materials has become increasingly important for the realization of various added-value products with a low environmental impact. In this context, considering that artworks constitute a worldwide priceless good, conservation scientists, restorers, curators, and researchers who deal with this field are trying to develop innovative solutions for the conservation and recovery of cultural heritage, taking into account environmental compatibility and sustainability [1]. Therefore, for this purpose, the research is focused on using nanotechnology to obtain more sustainable solutions; among these, nanocellulose, or cellulose in the form of nanostructures, has proved to be one of the most important biomaterials of modern times, and also easily usable in the field of cultural heritage given its compatibility with many types of artistic substrates, which mainly consist of cellulose [2–4].

This innovative bio-nanostructure can be obtained from cellulose extracted from different natural sources, such as plants, algae, small marine animals (tunicate), seeds (cotton), cane (bamboo, bagasse), straw (rice), and some bacteria, by several processes that are necessary for separating cellulose from the other components present in the sources, such as hemicellulose and lignin in the case of wood, or pectin, waxes, and other hydrosoluble components in starting materials of different nature [5].

Due to all of the shapes that nanostructured cellulose can take, they have resulted in being an attractive alternative solution to non-renewable sources that are in continuous decline, to environmental pollution, to global warming, and to the energy crisis, as well as to the frequent use of invasive synthetic products for the preservation of artistic works [6].

The differences between several types of nanocellulose (NC), which are cellulose nanocrystals (CNCs), cellulose nanofibrils (CNFs), and bacterial nanocellulose (BNC), concern their dimensions and crystallinity; in fact, CNCs are nano-scale materials and correspond to the crystalline part of cellulose, therefore having a higher degree of crystallinity, whereas CNFs and BNC can be nano- or micro-scale materials [7].

The advanced characteristics of cellulosic nanomaterials make them materials that are widely usable for various applications, also including the restoration and recovery of cultural heritage, according to their eco-friendly properties and versatility [3].

For example, CNCs have a high Young's modulus, for which being relatedto the Kevlar material, and are thus used for the production of highly robust materials [8]. Moreover, their biodegradability and biocompatibility make crystalline nanocellulose non-toxic for humans and useful for the reconstruction of body tissues or for drug delivery as reported by Mali and Sherje [9]. Nanocellulose has fire retardant properties and can be used as a UV shield [10]. It can also be inserted in a polymer matrix as an additive or applied on the surface of natural or synthetic textile fibers to improve their properties [11,12]. According to Omran et al., these nanomaterials are also renowned for the possibility of modifying their surfaces with various functional groups that enhance their compatibility with polymers to obtain multifunctional composite materials [13]. The enormous quantity of hydroxyl groups on the nanocellulose surface allows for its interaction with organic compounds and heavy metals present in the waste waters, acting as a filtering membrane [3,14]. Additionally, thanks to its antimicrobial action, it can be used as wallpaper for hospitals or as food packaging materials and water filters [10]. In the field of cultural heritage, nanocellulose can be used in combination with some additives [15], such as silver nanoparticles (AgNPs) [16] or ZnO [17], thus providing an antibacterial and antifungal activity against common fungi usually found in archives or museums, and bacteria more present in common life. If nanocellulose is used to realize composite materials for the electronic industry, it is able to enhance flexibility and conductivity. As an example, polyaniline nanocellulose composite film is widely used as conductive adhesives, paper-based sensors, flexible electrodes, and in electronic device fabrication [10].

Focusing on cultural heritage, it should be emphasized that many collections of objects and artifacts of world artistic patrimony are made of cellulose-based materials such as wood, paper, archaeological fabrics, and painting canvases, and a large part of these requires an intervention of recovery and restoration due to the chemical acidification processes caused by primers, paints, and glues; the absorption of acid gases present in the atmosphere to which they are subjected; or the biological attacks by xylophagous insects and microorganisms that digest cellulosic substances, deteriorating the material [18]. For these reasons, nanocellulose-based innovative materials with many fascinating characteristics, such as a high specific surface area, non-toxicity, light weight, high elastic modulus (140–150 GPa), gas impermeability, high aspect ratio, high stiffness, and interesting mechanical properties, are very important for the recovery and conservation of cultural heritage, because an intervention with these materials certainly gives better results compared to synthetic products, and, moreover, they do not alter the optic effect of artistic surfaces. In fact, beyond the similar chemical nature of the consolidant and the treated materials, the nanometric dimension of cellulose enhances the physicochemical interaction between the consolidant and the substrates, providing more effective actions than the synthetic consolidants that are usually used [19]. In this context, nanocellulose can not only be used as a consolidating agent or structural reinforcement, which are actions related to its penetrating power, but also as an antibacterial agent due to the possibility of being functionalized thanks to the availability of numerous free hydroxyl groups. For all of these reasons, scientists and art curators all over the world believe that nanocellulose will be one of the most important materials for the entire technology and engineering world [10,13,20].

In this review paper, the description of different types of nanocellulose is first reported, and then several characterization methods used to analyze them. Finally, the most recent applications of these innovative nanomaterials in the artistic context have been collected; nanocellulose has proved to be useful for several purposes, such as: ancient and degraded wood consolidation, wood reinforcement coating, the consolidation of waterlogged wooden artifacts, and structural reinforcement for canvases degraded by aging [18,19,21–25]. The novelty of this review, which aims to offer an interesting overview about the use of nanocellulose for the recovery and conservation of cultural heritage, lies in having collected the latest applications of this bio-nanomaterial for the treatment of several artworks in a single paper. To achieve this, Scopus and WOS databases were used. The information collected and mentioned in this paper about nanocellulose applications was selected in a timeframe ranging from 2013 to 2022, focusing on the last five years. Earlier articles, dating from 1985 to 2012, have been mentioned in the more theoretical paragraphs in relation to nanocellulose extraction processes, its classification, and the recovery and conservation methods used in the past.

2. Cellulose Nanomaterials

Cellulose is the most abundant renewable source on Earth; it can be found in plants, algae, microorganisms, such as some bacteria, and other natural sources. In fact, its annual production is approximately 1.5×10^{12} tons [20,26]. Chemically, it is composed of a linear polysaccharide produced from ringed glucose monomers linked together through β-(1,4) glycosidic bonding, and its microscopic morphology corresponds to alternating regions of crystalline and amorphous zones, which, together, form the characteristic macroscopic fibrous structure of cellulose (Figure 1) [5,27].

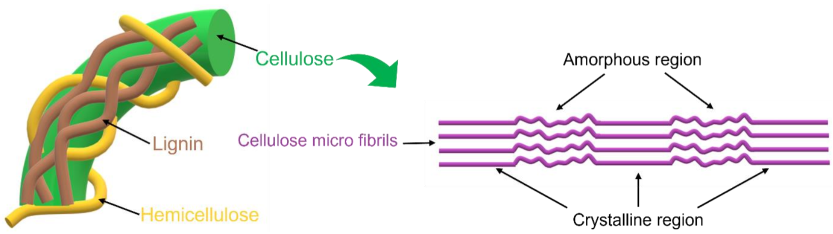


Figure 1. Amorphous and crystalline regions of cellulose micro fibrils.

The ordered crystalline domains are more resistant to chemical, mechanical, and enzymatic treatments and thus have a higher resistance to degradation compared to the amorphous ones; these crystalline regions are held together by hydrogen bonds that make cellulose stable, but decrease its solubility in water and other solvents [5,7].

The hierarchical structure of cellulose is described in Figure 2.

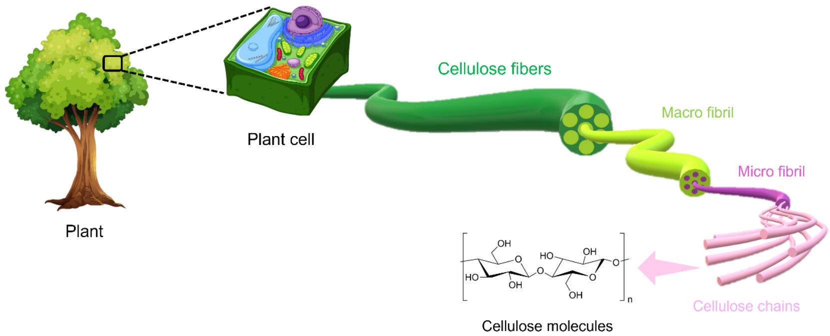


Figure 2. The hierarchical structure of cellulose. Reproduced under terms of the CC-BY license [6]. Copyright © 2020, The Authors, published by Front. Chem.

This polymer, seen as an inexhaustible source of raw materials and, consequently, all of the nanocellulose materials obtained from it, has gained increasing interest thanks to its attractive characteristics, such as its ease of availability, high surface area, good mechanical properties, renewability, and biocompatibility [6,28].

To define cellulose nanomaterials, the nomenclature established by the Technical Association of the Pulp and Paper Industry (TAPPI) of the Nanotechnology Division must be considered, and, from the standardization TAPPI WI 3021, it is possible to define nanocellulose as the crystallite or cellulose fiber possessing at least one dimension in the nanoscale range (1–100 nm) [6].

The class of nanocellulose materials includes all those derived from cellulose with several shapes, dimensions, chemical surface, and properties. Therefore, from the separation of cellulose fibers, different types of nanoscale cellulose can be obtained; in particular, through the function of their sources, the degree of crystallinity, and the extraction and production method, if a bottom-up or top-down technique is used, it is possible to distinguish three categories of nanocellulose: cellulose nanocrystals (CNCs), nano-fibrillated cellulose (CNF), and bacterial nanocellulose (BNC). CNCs consist of cylindrical, elongated, inflexible, and rod-like nanoparticles with dimensions of 4–70 nm in width and 100–6000 nm in length and a crystallinity index of around 54–88%; they are usually obtained by hydrolysis. Nanofibrillated cellulose (CNF), commonly obtained by mechanical treatment, with a braided network structure, is composed of longer and flexible fibers with dimensions of 20–100 nm in width and >10,000 nm in length and a low crystallinity index (<50%). Finally, bacterial nanocellulose (BNC), also known as microbial nanocellulose, is the most promising and cost-effective biomaterial, especially for the biomedical industry, with its highest crystallinity index > 88% [20]. The BNC consists of ultrafine nanofibers that are 20–100 nm in diameter and micrometers lengths that form an identifying 3D network [6,20,29]. All of these categories of nanocellulose are related to each other because they can all be obtained from the same natural sources, and each can form stable structures in a liquid medium or matrix via hydrogen bonds. In fact, nanocellulose contains a great number of hydroxyl groups (-OH) that can form hydrogen bonds either between different chains (intermolecular bonds) or in the same chain (intramolecular bonds), making this material highly hydrophilic and allowing us to modify it via different chemical and physical strategies [4]. Its hydrophilicity can sometimes be a drawback, especially in the case of applications where humidity can be a problem [10]. Consequently, chemical modifications on hydroxyl groups are often carried out in order to decrease the hygroscopicity of nanocellulose [30].

However, these nanomaterials can also cause compatibility problems with the matrix that incorporates them, such as hydrophobic polymers in the case of nanocomposite materials [31]; therefore, their dispersibility must be guaranteed. For CNCs, this problem does not exist, because it has special self-assembling behavior that makes it highly interesting for the study and the development of advanced materials [27].

2.1. Cellulose Nanocrystals (CNCs)

The term cellulose nanocrystals, or even crystalline nanocellulose (CNC), describes the rod-like shaped nanoparticles obtained from different sources, such as cotton, wood pulp, plant residue, etc., and this is the most common type of nanocellulose [3].

These nanostructures are produced with an extraction process consisting of two successive steps: the initial pre-treatment of the raw material and the following hydrolysis into CNCs. In the first step, raw materials are treated to remove the impurities and all other chemical constituents present in cellulose sources, such as hemicellulose and lignin; to achieve this, alkaline and bleaching treatments are carried out [32]. Then, hydrolysis is carried out to obtain the nanocellulose crystals; this step is based on a strong acid process that uses especially sulfuric acid (H_2SO_4), hydrochloric acid (HCl), or phosphoric acid (H_3PO_4), [27]. The acid hydrolysis is useful for removing, under controlled conditions, the disordered and amorphous regions of the cellulose fibers, leaving the crystalline domains, which then take on the characteristic crystalline shape, with a crystalline index of 54–88% [6,33]. Sulfuric acid hydrolysis is the most efficient and widely used extraction method and, during the isolation treatment, it allows for a better dispersion of cellulose crystals in polar solvents due to the introduction of sulfate half ester groups on the cellulose chain, which, with a negatively charged surface coating, enhance intermolecular repulsive interactions [10].

Cellulose nanocrystals have many interesting properties, such as a good stability, wide surface area, higher tensile strength (10 GPa), high elastic modulus (140–150 GPa), and several optical qualities.

Their dimensions depend on the nature of the starting material, but they are certainly in the nanometer range. In particular, the length and width differ depending on temperature, time, and purity of the cellulose source [7,9]. For example, CNCs obtained from plants have a diameter of 3–5 nm and length of up to 100–300 nm, whereas the CNCs collected from tunicates have a diameter of 10–20 nm and length of up to 500–2000 nm [9]. The morphological characteristics of CNCs are studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) or dynamic light scattering (DLS) [3].

Table 1 shows the dimensions of cellulose nanocrystals as a function of the acid used for the hydrolysis and the source, highlighting the various parameters.

Table 1. Dimension of nanocellulose with respect to the various parameters. Reproduced with permission [7]. Copyright © 2018, Elsevier.

Method	Source	Remarks
H_2SO_4 hydrolysis	Bacteria	L (nm) = 100–1000; W (nm) = 10–50; Aspect ratio (L/D) = 2–100.
H_2SO_4 hydrolysis	Valonia	L (nm) = 1000–2000; W (nm) = 10–20; Aspect ratio (L/D) = 50–200.
H_2SO_4 hydrolysis	Ramie	L (nm) = 70–200; W (nm) = 5–15; Aspect ratio (L/D) = ~12.
H_2SO_4 hydrolysis	Wood	L (nm) = 100–300; W (nm) = 3–5; Aspect ratio (L/D) = 20–100.
H_2SO_4 hydrolysis	Sisal	L (nm) = 100–300; W (nm) = 3–5; Aspect ratio (L/D) = ~60.
H_2SO_4 hydrolysis	Tunicates	L (nm) = >1000; W (nm) = 10–20; Aspect ratio (L/D) = ~100.
HCl hydrolysis	Bacteria	L (nm) = 160–420; W (nm) = 15–25; Aspect ratio (L/D) = 7–23.
HCl hydrolysis	Cotton	L (nm) = 100–300; W (nm) = 3–5; Aspect ratio (L/D) = 20–100.

2.2. Cellulose Nanofibrils (CNFs)

Cellulose nanofibrils, also called nano-fibrillated cellulose (CNF), are primarily obtained from wood with a mechanical treatment of wood pulp, but they can also be extracted from sugar beets, potato tubers, hemp, and flax [13].

Their characteristic structure is formed by an entangled network of long and flexible fibers, with dimensions of 20–100 nm in width and >10,000 nm in length [6].

This type of nanocellulose presents the same amount of amorphous and crystalline regions; the mechanical treatments are the most common methods used to produce it, such as mechanical defibrillation or disintegration caused by mechanical forces. The main disadvantage of these methods is the significant energy consumption. For this reason, and mainly to prevent the aggregation of the micro and nanofibrils in the final product, the mechanical treatments are usually combined with enzymatic and/or chemical treatment, such as the catalytic 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation method, which allows us to obtain nanofibrils by mechanical disintegration, generating CNFs with a uniform size. This approach, moreover, does not change the crystallographic forms of the cellulosic fibers while increasing the surface charge due to the carboxyl groups introduced by TEMPO, which is an interesting advantage for the production of nanocellulose composite materials [34–36]. Nevertheless, the mechanical production methods of this type of nanocellulose remain the most advantageous; in fact, they do not require additives, do not modify the surface charge compared to the starting material, and give excellent yields [37].

CNFs have many interesting properties, such as their mechanical strength and rigidity, that make them an alternative to artificial fillers used for the reinforcement of plastic composite materials; moreover, the low thermal expansion and limited oxygen transmission rate permit their application in electronic devices, food packaging, and printing. Furthermore, the easy functionalization of CNFs also allows for their use in hydrophobic matrices with which they would have little affinity [10].

2.3. Bacterial Nanocellulose (BNC)

Nanocellulose produced by bacteria is called microbial cellulose or bacterial nanocellulose (BNC), and its purity is higher than other kinds of nanocellulose [38,39]. This type of nanostructured cellulose is produced by a bottom-up method consisting of assembling low-molecular-weight sugars by means of microorganisms; the single fibers that are achieved have a thickness of a few nanometers. Usually, two culture methods are used to produce BNC: static and stirred techniques; through the function of the chosen technique, it is possible to modify different characteristics, such as the surface morphology and physical and mechanical properties of the BNC and, therefore, to use it for several applications [26]. The main properties of BNC are its high crystallinity (80–90%), high purity, high flexibility, high water content (approximately 99% in the hydrogel structures inside the network of nanocellulose), and high mechanical and thermal resistance.

Moreover, due to its biocompatibility, bio-functionality, and nontoxicity, bacterial nanocellulose is a very promising material in the fields of medical implants and biotechnology, as well as for the applications of engineering tissues reconstruction or regenerative medicine. However, the principal challenge to be faced is the scale-up of industrial BNC production, which, today, is difficult to achieve due to the low productivity, highly expensive culture media, and high fermentation costs [3].

One way to overcome these problems can be the use of industrial wastes as extraction sources, which have a low cost and are readily available, and can also be processed with clean technology approaches, thus promoting not only a reduction in disposal costs of waste for the industries that supply the raw materials, but also the protection of the environment [40].

In conclusion, Table 2 shows the comparison between the different types of nanocellulose.

Table 2. Comparison between the different types of nanocellulose [29].

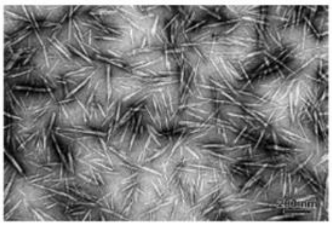
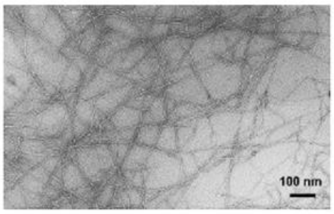
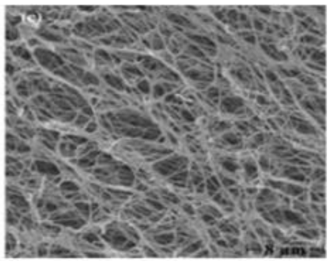
	Cellulose Nanocrystals (CNCs)	**Cellulose Nanofibrils (CNFs)**	**Bacterial Nanocellulose (BNC)**
Images	 Transmission electron microscope (100 nm)	 Transmission electron microscope (100 nm)	 Scanning microscope (8 μm)
Synonyms	Crystallites, whiskers, nanowhiskers, cellulose nanocrystals, rod-like cellulose microcrystals	Microfibrillated cellulose, nanofibrils, microfibrils, cellulose, nanofibers	Biocellulose, bacterial cellulose, microbial cellulose
Common source	Wood, cotton, hemp, flax, rice straw, wheat straw, ramie, avicel, mcc, tunicin, algae, bacterial cellulose, pea hull fibers, branch-bark of mulberry, black spruce and eucalyptus, tunicate, valonia, kraft wood, pine and spruce, palm oil, pineapple leaf fibers, grass, swede root, chardonnay grape skins, coconut fibers, softwood wood flout, kenaf fibers, rice husk, sabdariffa fibers, wood fibers, corncob.	Pea hull, kenaf, hardwood and softwood pulp, cotton linter, cotton, cassava bagasse, sugarcane bagasse, cotton, algae (valonia), tunicate cellulose, bacterial cellulose, sugar beet pulp, wheat straw, date palm tree (rachis/leaflets), coconut husk fibers, recycled pulp, acacia pulp, banana, capimdourado, mulberry, flax, hemp, *luffacylindrica*, mengkuang leaves, curauna.	Low molecular weight sugar, alcohols, several bacteria species such as gluconacetobacter, agrobacterium, pseudomonas, rhizobium, and sarcin.
Formation process	Chemical or enzymatic treatment prior to delamination or wood pulp by mechanical pressure, acid hydrolysis	Acid hydrolysis, integration of mechanical shearing process via high pressure homogenization and enzymatic hydrolysis, TEMPO-mediated oxidation	Bacterial synthesis and cultivation in aqueous culture media present by glucose, oxygen and phosphate.

Table 2. *Cont.*

	Cellulose Nanocrystals (CNCs)	Cellulose Nanofibrils (CNFs)	Bacterial Nanocellulose (BNC)
Average size	Diameter: 5–80 nm Length: 100–250 nm	Diameter: 5–70 nm Length: 100–250 nm (from plant); 100 nm to several micrometer (from cellulose of tunicates, algae, bacteria)	Diameter: 20–100 nm Length: 1.0–5.0 µm Different types of nanofibers networks
Tensile Strength	2–6 GPa	2–4 GPa	200–300 MPa
Young's modulus	50–143 GPa	15–150 GPa	15–35 Pa
Crystallinity Index	54–88%	<50%	>88%

3. Characterization Methods of Cellulose Nanomaterials

Usually, cellulose nanomaterials are studied and characterized with several techniques in order to evidence different properties, such as the surface morphology, size, dimensions (length, diameter, and aspect ratio), shape, thermal stability, surface charge, crystallinity, and the most important properties within the cultural heritage, such as mechanical or optical characteristics [7].

The properties of nanocellulose change in function of its type, if crystalline or fibrous, and, thus, they depend on the production process, the starting natural source, and the final application. In this context, there are many characterization methods for NC; among them, more complex, time-consuming, and off-line methods are usually used in the laboratory, requiring high capital investments and skilled staff. On the other hand, in the industry field, the methods used have to be simple, less time consuming, and designed for online measurements. For the characterization of nanocellulose, once applied on an artistic substrate, the techniques used to evaluate the effectiveness and characteristics of the nanostructured bio-consolidant obviously cannot be the same as those used on the consolidant before its application, since an art object or ancient artifact cannot be replaced or consumed and damaged for analytical purposes, and, for these reasons, in this case, non-destructive techniques should be used in order to preserve the aspect of the object before and after the treatment [41].

Table 3 shows the main properties and characterization techniques for NC, including those used in the field of cultural heritage for the analysis of nanocellulose-based consolidants [42–45].

Table 3. Main properties and characterization techniques used for nanocellulose [42–45].

Property	Characterization Techniques	Acronym	Advanced Research	Industrial Environment	Cultural Heritage [43–45]
Size and morphology: • Length (L) • Width (w) • Diameter • Aspect ratio (L/w) • Average particle size/size distribution	Atomic force microscopy	AFM	X		X
	Scanning electron microscopy	SEM	X		X
	Transmission electron microscopy	TEM	X		X
	Optical microscopy	OM		X	X
	Fiber analyzer			X	
	Fractionators			X	
	Gel point (for aspect ratio)	GP	X	X	
	Viscosity (for aspect ratio)		X	X	
	Light scattering techniques: - Dynamic light scattering - Depolarized DLS	DLS DDLS	X	X	

Table 3. *Cont.*

Property	Characterization Techniques	Acronym	Advanced Research	Industrial Environment	Cultural Heritage [43–45]
Physical properties: • Crystallinity (mainly for NCC) • Degree of polymerization (DP) • Specific surface area (SSA) • Density	Crystallinity and dimensions of cellulose crystals: - X-ray diffraction - Raman spectroscopy - Infrared spectroscopy - ^{13}C nuclear X-ray diffraction magnetic resonance - Solid-state nuclear magnetic resonance	XRD ^{13}C NMR ssNMR	X		X
	Viscosity method		X	X	
	Determination of SSA: - N_2 adsorption, Brunauer–Emmett–Teller isotherms - Congo Red method - Small-angle X-ray scattering	BET SAXS	X		
	Network density (on nanopapers): - Air permeability (Vase de Mariotte, Bendsen) - Porosity (calculation from basis weight and thickness) - Transparency		X	X	X
Elemental analysis (EA)	Carbon hydrogen nitrogen elemental analysis	CHN CHNS CHNSO CHNSOX	X		
	Secondary ion mass spectrometry	SIMS	X		
	X-ray photoelectron	XPS	X		X
	Auger electron spectroscopy	AES	X		
	Energy dispersive X-ray spectroscopy	EDS (or EDX)	X		X
	Inductively coupled plasma: - Mass spectrometry - Atomic emission spectroscopy	ICP-MS ICP-AES	X		
Water retention	Water retention value	WRV	X	X	
Fibrillation degree (for NFC)	Atomic force microscopy	AFM	X		
	Scanning electron microscopy	SEM	X		
	Transmission electron microscopy	TEM	X		
	Optical microscope (for low fibrillation degree)	OM		X	
	Mechanical fractionation by combination of sieves and membranes		X		

Table 3. *Cont.*

Property	Characterization Techniques	Acronym	Advanced Research	Industrial Environment	Cultural Heritage [43–45]
	Field/tube flow fractionation		X		
	Centrifugation		X	X	
	Transmittance by UV-vis spectroscopy Turbidity		X X	X X	
Dissolved and colloidal substances (amount and quality)	Atomic force microscopy	AFM	X		X
	Scanning electron microscopy	SEM	X		X
	Transmission electron microscopy	TEM	X		X
	Gel permeation chromatography	GPC	X		
	Size-exclusion chromatography	SEC	X		
	High-performance liquid chromatography	HPLC	X		
Surface charge and chemistry: • Surface modifications • Charge determination	Surface chemically modified by adsorption: - Fourier-transform infrared spectroscopy - Elemental analysis	FTIR EA	X		X
	Surface chemically modified by covalent bonding: - Fourier-transform infrared spectroscopy - Solid-state nuclear magnetic resonance - X-ray photoelectron spectroscopy - Elemental analysis	FTIR ssNMR XPS EA	X		X
	Inverse gas chromatography	IC	X		
	Conductimetric titration		X	X	
	Charge determination: - Cationic demand - Zeta potential	CD ZP	X	X	
Rheology: • Viscosity • Yield stress • Gel point • Aspect ratio	Low shear viscosity by viscometers		X	X	
	Gel strength, viscoelastic properties by rheometers		X	X	
Mechanical and thermal properties	Tensile testing		X	X	X
	Flexural testing		X	X	X
	Compression testing		X	X	X
	Dynamic mechanical analysis	DMA	X		X
	Raman spectroscopic		X		X

Table 3. *Cont.*

Property	Characterization Techniques	Acronym	Advanced Research	Industrial Environment	Cultural Heritage [43–45]
	Thermogravimetric analysis	TGA	X	X	X
Other properties	Health characterization (i.e., eye irritation, skin irritation, genotoxicity, toxicokinetic testing, systemic testing, ecotoxicity . . .)		X		X
	Safety characterization (i.e., deflagration index . . .)		X		X

For example, Kumar et al. [33] show the use of field emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM), and transmission electron microscopy (TEM) techniques for the morphological and topographic analyses of nanocellulose; instead, chemical and physical analyses were carried out by Fourier transform infrared spectroscopy (FTIR).This is a very interesting technique for evaluating the surface functionalization of NC, which is a very significant aspect for the analysis of nanocellulose composite solutions used for the conservation of artworks, for which, it is important to evaluate the successful functionalization, which is useful for different purposes; moreover, the elemental analysis was carried out by X-ray diffraction (XRD) and energy dispersive X-ray analysis (EDX).

In particular, XRD was used to determine the crystallographic structure of CNC and, therefore, the crystallinity degree of nanocellulose; finally, the thermal stability and thermal response to a change in temperature were evaluated by thermogravimetric analysis (TGA), derivative thermogravimetry (DTG), and differential thermal analysis (DTA), which are techniques that allow us to evaluate the thermal stability of the consolidants [46,47].

Huang et al. [48] report the use of the same characterization techniques for nanocellulose extracted from cotton source. In particular, thanks to the SEM and TEM analyses, they managed to distinguish the morphological differences of the four polymorphic nanocelluloses obtained with four different treatments.

In their review paper, Mishra et al. [7] show the use of other techniques for the study of the nanocellulose morphology, such as dynamic light scattering (DLS), small-angle neutron scattering (SANS), small-angle X-ray scattering (SAXS), and wide-angle X-ray scattering (WAXS), to analyze the particles dimension distribution. Moreover, they also discussed the use of Raman analysis to evaluate the structure and the crystallinity of NC. This type of technique is widely used in the field of restoration because it is non-destructive, has a high resolution, and can carry out in situ surveys for both inorganic and organic materials [43].

The DLS technique, also called photon correlation spectroscopy [49], is mentioned by Singh et al. [50], who used it for the particle size analysis of isolate microcrystalline cellulose. In fact, the problem related to the DLS technique is that this model, based on light scattering, works well when it describes spherical particles with a single and constant rate of diffusion, but, for the nanocellulose structures, which have high aspect ratios and different parallel and perpendicular translational diffusion constants, accurate particle size measurements are not always obtained in terms of the length or cross-section of the particle. Therefore, this technique provides a hydrodynamic "apparent particle size" used to evaluate the aggregation and dispersion of NC suspensions and, to have a more accurate analysis, it is necessary to combine the results obtained with DLS with those obtained from other techniques, such as microscopy analyses [42]. Du et al., in their recent work on the functionalization of CNCs with P- and Si- for the fabrication of composite nanomaterials, used FTIR, TG-DTG, XRD, and SEM-EDS to demonstrate the successful surface modification of nanocellulose [12].

Moran et al. [51] introduce, in their contribution, the contact angle measurement of starch films functionalized with nanocellulose in order to analyze the influence of chemical modifications on the surface polarity due to the nanocellulose. This is a significant aspect because, with this measurement, it is possible to evaluate the variation in the hydrophilic character of nanocellulose coatings, which affects the behavior of the treated artistic substrate [51,52]. In addition to the above-mentioned techniques, Gond et al. [49] used UV/visible spectroscopy to measure the optical properties of nanocellulose. In the conservation of cultural heritage, the appearance of works of art depends on the optical properties; unfortunately, UV light can also destroy covalent bonds in organic materials present on the artwork, causing many undesirable degradation effects, such as in polymers, woods, dyes, and pigments, leading to the photodegradation of the works themselves. For these reasons, it is important to evaluate the behavior of the consolidants against the UV radiation [53]. Moreover, in the same work of Gond et al., the antibacterial analysis performed against Bacillus and E. coli bacteria using the disc diffusion method is reported [49]. In the case of artworks, it is very important to perform this analysis on the consolidants in order to ensure that irreparable damages due to bacteria do not occur. The antimicrobial activity of nanoparticles or other nanomaterials, such as nanocellulose, is usually carried out by optical and electronical microscopy [54].

Beyond that, the toxicity and cytotoxicity of nanocellulose are other important aspects to analyze, especially for applications in the medical and biotechnology fields, but also for the protection and health of operators working in the field of fine arts. To achieve this, four different approaches can be used: the first method consists of the assessment of cell damage in function of its morphology; the second one measures the cell damage; the third measures the cell growth; and, finally, the last method measures specific metabolic activities. Roman [55] reported that most of the studies on the cytotoxicity of NCs do not show harmful effects on cells and there are not even adverse dermal or oral toxicity effects for the human health; however, the presence of surface functional groups and cytotoxic impurities due to the origin of the cellulose source, the preparation procedure, and the post-processing or sample preparation may be harmful; for these reasons, further studies and the development of new characterization methods of nanocellulose are required [9].

All of these investigation techniques allow us to obtain very interesting information about these innovative materials and to visualize the differences between each type of nanocellulose, starting from their shape and morphology up to their concentration of carbon and oxygen, the main elements present in nanocellulose. Therefore, the techniques previously mentioned are the most used for the first characterization of nanocellulose, but also for the analysis of nanocellulose-based consolidants applied for the recovery and conservation of cultural heritage [4,16,17,24,34,36,56–61]. The description of all of these techniques and their principles of operation were recently reported by Varshney et al. [62].

Certainly, the development of new, faster, and reliable characterization techniques that are able to carry out less destructive and in situ analyses would allow for the spread of nanocellulose at an industrial level, and this is the challenge that we are trying to overcome, even if, for the application in the artistic patrimony conservation field, the nanocellulose mass available is currently sufficient for sustaining these uses [15,42].

4. Applications of Cellulose Nanomaterials in Cultural Heritage

Cultural heritage is an inestimable patrimony of society: it encloses potentially all of the artifacts, artworks, objects, and intangible assets designated by each state as fundamental, containing values of archaeology, literature, art, science, folklore, ethnology, or anthropology.

Therefore, cultural heritage constitutes a priceless good; thus, it is mandatory to protect it from degradation mechanisms and the course of time in order to continue cultural and intellectual progress while preserving and transferring the ancient traditions and knowledge to future generations [1,4].

In the last few years, new technological and innovative materials based on nanotechnology science have been designed and synthesized to enhance the performance and technical sustainability of materials used in the field of cultural heritage conservation and, therefore, to obtain non-destructive and non-invasive cleaning treatments, a reliable consolidation, or long-lasting selective conservation [63,64]. At the same time, new sophisticated techniques for the characterization of these materials are optimized to understand the chemical and physical properties and the interaction between the nanostructures and artworks [1].

The collections of objects and artifacts that belong to our world artistic patrimony are largely made of cellulosic-based materials, such as paper, painting canvases, archeological fabrics, and wood, and all of the world historical memory and anthropological values are associated to them; for these reasons, the preservation of cellulose-based artworks is a crucial topic in the conservation science of cultural heritage [4]. The variety of the degradation phenomena that concern artworks reflects the vast range of materials used in humankind heritage, and their prevention results in being advantageous for different artworks, such as books, manuscripts, maps, drawings, and textiles, as well as wooden artifacts such as sculptures or shipwrecks. A significant amount of these artworks requires an urgent intervention of restoration due to several factors to which they are subjected; moreover, those situated outside are particularly irreparably exposed to several agents of degradation, such as humidity, temperature, microorganisms, and air contaminants, all of which are responsible for the natural aging of art materials [4,24,63]. Among these, the acidity mechanism causes a decrease in the polymerization degree and, consequently, the loss of the mechanical properties; the degradation by sulfur dioxide and nitric oxides from air pollution makes cellulosic fibers increasingly brittle; another problem is the thermal degradation due to photolysis, microorganisms, and fungi [24].

Moreover, almost all of the materials used in the past restoration treatments are acidic or may develop acidic products upon aging, thus degrading the works of art; they also must be removable or must at least leave the object retractable, but this is not always possible with traditional consolidation products [18].

Therefore, due to the variety of artistic substrates, conservation science has explored different pathways, developing several technical approaches for solving conservation problems, and nanocellulose-based materials are one of these solutions [63].

Recently, efforts are being made to develop ecological and green approaches to address the above problems, which are also thanks to nanotechnology. For example, Semenzin et al. [65] proposed a sustainable alternative approach for designing new nano-based consolidants in order to support the development of safer nanostructures for conservation whilst preserving their functionality. This very innovative flowsheet consists of several consequential steps, where each affect one aspect of the process, such as the study of the state-of-the-art, the initial formulation of the consolidant, the screening of the hazard assessments and, therefore, the eventual optimization of the product, and, finally, the evaluation of its safety and sustainability [65].

This framework takes into account the current EU legislative context (i.e., CLP and REACH regulations) and the requests of the conservators and restorers, with the aim to promote the selection and use of more sustainable and ecological nanomaterials in different conservation fields [63,65].

In this context, nanocellulose, with its very attractive properties and advantages, is very important and useful for the conservation treatments of cellulose-based artworks for many reasons: thanks to the dense hydrogen bonding network provided by this nanomaterial, it is possible to obtain an improvement in the mechanical properties of the treated cellulose-based object with the simple addition of functional groups for a more specific conservation action; moreover, nanocellulose-based consolidants can create transparent films that produce barrier effects towards oxygen, water and water vapor, and oil, which could damage artistic substrates, without altering the visual appearance of works of art; and, finally, another great advantage is the reversibility of these restoration strategies, which is achievable with the simple application of hydrogels, without causing any damage to the works [15,59]. For the sake of clarity, Table 4 summarizes some advantages and disadvantages of nanocellulose applications for wood, paintings, and paper conservation.

Table 4. Some advantages and disadvantages of nanocellulose applications for wood, paintings, and paper conservation.

Artistic Application Field	Advantages	Disadvantages
Wood	• Compatibility • Good penetration • Increase in compression strength • Good adhesion • Increase in stiffness • Eco-friendly • Transparency • Flexibility • Tensile strength • Stability • Easily cleanable	• Decrease in adhesiveness • Possible coating deformations after drying • Irreversibility • Brittleness • Shine
Painting Canvases	• Compatibility • Eco-friendly • Increase in interaction with substrates • Increase in Young's modulus • Reversibility • Lower weight increase • Stability • Resistance to humidity	• Slight yellowing
Historical Paper	• Compatibility • Eco-friendly • Adhesion • No optical effect • Stability • Low coating thickness (compared to Japanese paper) • Better legibility (compared to Japanese paper) • Decrease in wettability • Decrease in air permeance • Reversibility • Coating uniformity	• Not always mechanical reinforcement (depending on the solvent used) • Slight yellowing

Here, several examples of different applications of nanocellulose are reported, such as the consolidation and reinforcement of ancient degraded wood [21], the chemical modification of wood adhesive [66], the preparation of cellulose and lignin nano-scale consolidants for waterlogged archaeological wood [18], the consolidation of cotton painting canvases [24,25,67], the combined stabilization and deacidification of cellulosic materials [61], and the increase in watercolor painting efficiency on paper [68].

4.1. Wood

In the past, wood was one of the most used materials for buildings, furnishings, and artworks [69].

It is basically an organic, hygroscopic, and anisotropic material. Its porous and fibrous structure is mainly composed of cellulose fibers, a lignin matrix, and hemicellulose; this composition makes wood, and therefore wood artifacts, highly sensitive to moisture, which can promote attacks by microorganisms and fungi. This type of degradation induces a dramatic decrease in the mechanical properties of wood due to the loss in density and cellulose content. To prevent this problem, an urgent consolidation intervention is needed, where the consolidants must have specific properties and characteristics, such as the correct penetration degree, in order to re-establish the cohesion between the wood fibers.

Usually, the most common treatments utilize synthetic polymers that are soluble in acrylic, aliphatic, and aromatic resins, which decrease the porosity and improve mechanical properties; otherwise, in the past, natural oils or resins were also used for wood consolidation, therefore introducing a hydrophobic coating that reduces the moisture absorption and stabilizes the wood [60,70]. However, in addition to the chemical nature of the consolidant, there may be other factors influencing the final performance of wood treatments, such as the method used to apply the consolidant, the use of pre-treatments or post-treatments, and the environmental conditions [69].

Beyond the restoration of mechanical properties, it is also important to recover the appearance of historical wood; different materials are used to achieve this, including epoxy and polyester resins as reported by Moise et al. [71], but also cellulose derivatives as described by Hamed and Hassan [21], who demonstrated how the nanocellulose-based consolidants can be used to enhance the hydroxypropyl cellulose (Klucel E) properties, usually used for this purpose, without changing the color of the treated wood but increasing the compression strength and adding advantages in terms of increasing penetration within the wood.

In the work of Basile et al. [60], a suspension of CNC was used as such or mixed with lignin and/or siloxane derivatives (PDMS) to treat rotten wood samples of Norway spruce belonging to the roof of an ancient 17th century villa in northern Italy; from the mechanical analysis of these samples, it was demonstrated that the CNC treatment was immediately effective, confirming a considerable improvement in the stiffness even after a few impregnation cycles.

Cataldi et al. [47] proposed the use of nanocellulose-based fillers as renewable reinforcing agents in a polymeric matrix, mainly used as a barrier protection against water absorption, which can cause internal stresses due to changes in pressure or temperature inside wood artifacts. Thanks to the bonds with the polymer chains, these nano-fillers can reduce the diffusivity of liquids, increasing the path tortuosity. Moreover, cellulose nanocrystals showed the highest increment in the stiffness and enhancement of the hydrophobicity of the starting matrix compared to the cellulose microcrystals, which, conversely, provided a less effective coating.

The choice of a suitable adhesive is another important aspect in the conservation of wooden artworks, since a wrong adhesive can irreversibly damage the object both aesthetically and mechanically. Therefore, when choosing the right and most adequate adhesive, several parameters should be evaluated, including the stability, reversibility, color, hardness, brittleness, sensitivity to relative humidity, bond strength, cost, and ease of application [72].

In this context, Vineeth et al. [66] addressed the use of nanocellulose for wood adhesive, claiming that the inclusion of nanocellulose inside the usually used polymeric adhesives could reduce the use of non-renewable petroleum sources and enhance the use of eco-friendly wood adhesives. Despite this, nanocellulose does not improve the adhesion properties of the adhesive resins, but this problem is easily overcome with the crosslinking approach and functionalization of this nanomaterial, possibly thanks to the availability of free hydroxyl groups on the surface of nanocellulose [73]. Usually, in order to improve several properties of wood adhesives, a small amount of nanocellulose is required as reported in the literature [74,75].

Another work that involves a different use of nanocellulose for the treatment of wood is the one proposed by Camargos et al. [52], who describe the synthesis of new green protective coatings, trying in this way to extend the lifetime of the artistic objects without affecting their original integrity.

The use of CNF for these coatings allows us to obtain several advantages, such as transparency, flexibility, and tensile strength, but also the disadvantage of a possible deformation of these films after drying. On the other hand, the use of CNC provides a high crystallinity and chemical stability of these coatings, but more brittle and shiny films. Consequently, a blend of CNF and CNC turned out to be the better solution to overcome these problems and to obtain new stable composite coatings, with a high compatibility with wood, able to preserve the roughness and the morphology of the treated material and prevent the degradation of wooden artworks. Moreover, IR-analysis showed another important characteristic of these coatings: their reversibility by means of water-loaded cleaning hydrogels.

Regarding the consolidating coatings for wood, Vardanyan et al. [76] also suggested the addition of CNC to improve the mechanical properties of these films without a significant modification of their optical characteristics, such as their color, optical transparency, and sheen.

Shipwrecks and waterlogged wood from land waterlogged sites or from submerged archaeological sites are often among the most common wooden archaeological findings. In these cases, the water fills the pore spaces, including capillaries and microcapillaries, changing the dimension and shape of wood [77]. Subsequently, many chemical and biological factors can cause the decay of the wooden artworks; for example, the salinity of sea water or a biological attack of degraders, such as the erosion or tunnelling bacteria, lead to a loss of mass and an increase in the porosity and permeability of the wood, thus weakening the material [78]. Also in the case of waterlogged wood, the consolidation treatments should provide integrity and stabilization of the wood after the drying procedures, required for the musealization of these wooden objects. Moreover, the consolidants should be stable, resistant to the biotic and environmental attacks, eco-friendly, and, where possible, reversible. Historically, the most used chemical methods provided alum treatment [79] and polyethylene glycol [80]; otherwise, most recent studies showed the use of several materials able to consolidate the decayed wood, such as natural resins [81], sugars [82], and polysaccharides [21], therefore also including nanocellulose.

In fact, different kinds of nanocellulose-based materials were recently investigated by Antonelli et al. [18], such as bacterial nanocellulose (BNC) and cellulose nanocrystals (CNC), for the consolidation of the degraded cell walls of waterlogged wooden artifacts, obtaining successful results in terms of consolidation and interactions with the wood ultrastructure, although the two types of consolidants acted differently, one penetrating little into the wood in the case of CNC, and the other forming a compact layer on the surface in the case of BNC.

Regardless, the best result can be obtained by combining the use of the two types of nanocellulose, one more filamentous and the other composed of more spherical nanoparticles, to increase the adhesion of nanofillers with the cell walls of the wood ultrastructure.

Figure 3 shows the SEM micrographs of untreated and treated samples, where it is possible to observe how the cellulose nanoparticles were penetrated inside the wood.

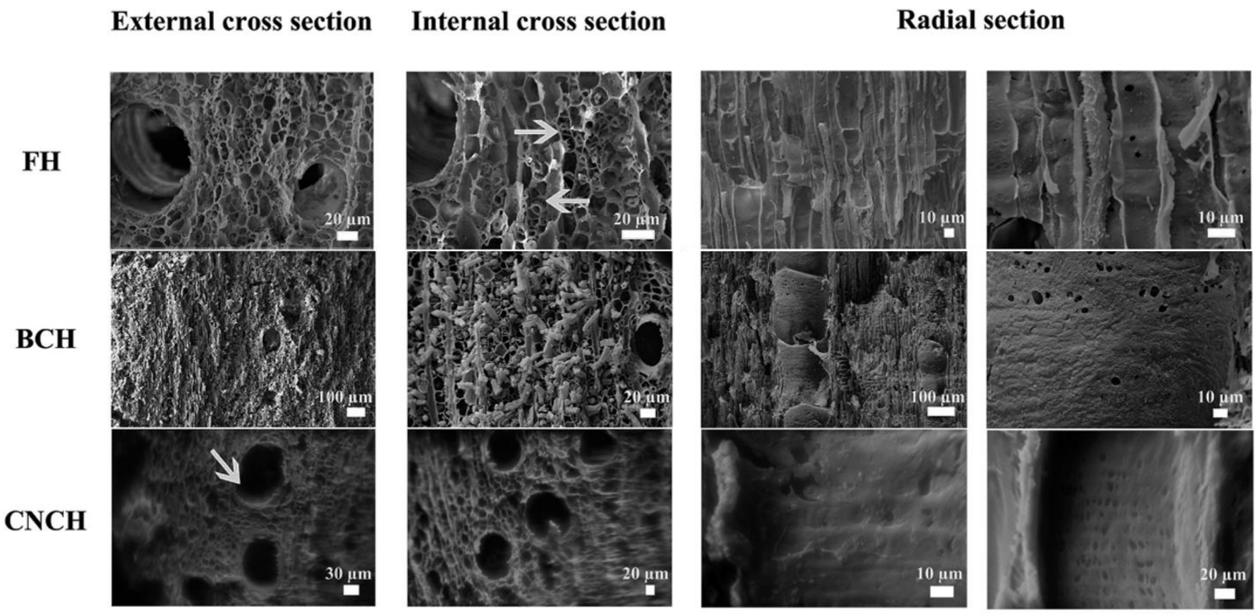


Figure 3. SEM images of freeze-dried control wood (FH) and blocks treated with bacterial nanocellulose (BCH) and cellulose nanocrystals (CNCH). **External and internal sections:** for FH cell, lumens are empty and secondary cell walls appear almost completely detached; for BCH sample, some of cell lumens are filled with consolidant, which creates sporadic superficial deposits; finally, for CNCH-treated wood, the cell lumens are empty and there is a thin layer of consolidant but it is not everywhere. **Radial section:** the fiber walls of sample FH appear smooth and the channels that they form are clearly visible; in BCH sample, there is a homogeneous and compact layer of consolidant, visible on the cell walls; in the CNCH sample, cellulose nanocrystals form a compact and homogeneous coat completely covering the pits. Reproduced under terms of the CC-BY license [18]. Copyright © 2020, The Authors, published by Front. Chem.

One of the future research areas will surely be in the field of nanocellulose in order to reach increasingly environmentally friendly, sustainable, and renewable consolidants, which nanocellulose-based materials have proven to be.

4.2. Painting Canvases

Traditional painting canvases present a multi-layered structure made of the canvas, the preparation made by adhesive and inert charge, the paint layer consisting of the pictorial medium and pigments, and the varnish, consisting of a mixture of natural or synthetic resins, which is not necessarily present on all canvases. All of these layers that constitute a painting artwork have different compositions, roles, and chemico-physical characteristics. The painting canvases can be made by different materials, but the natural fibers linen and cotton have always been the favorite surfaces for artists. These canvases have a woven structure that comprises two thread directions, which are defined as warp and weft.

This characteristic structure of the canvases is responsible for their anisotropic behavior and directional-dependent properties. Moreover, in a painting, the canvas plays a fundamental role of mechanical support for the tensile stresses to which it is subjected to over time and, for this reason, it is the focus of the work on painting structural consolidation [83,84].

The first canvas consolidants were applied in the XVII century, when the support of the first oil paintings started to show signs of degradation. Between the XVII and XX centuries, lining treatments gained the attention of the artistic community and were carried out increasingly frequently. Currently, minimal possible intervention is required in the field of cultural heritage conservation in order to preserve the original aspect of the painting canvases. For this reason, even if it is rarely possible, attempts are made to obtain stabilizing products with a double effect of both deacidifying and consolidating in order to prevent the chemical and mechanical degradation of the canvases. The most important degradation mechanism of these artworks is acid-catalyzed hydrolysis, which leads to a decrease in the polymerization degree (DP) and, as a result, in a decrease in the mechanical resistance of the materials. Another characteristic result of canvases degradation is aging, which is caused by several reactions taking place in the material and phenomena such as temperature and humidity variations that produce the cracking of the paint layer, resulting in irreversible damages of the painting [25,61,85]. Even the biodeterioration of canvas paintings is a frequent problem that involves the inorganic materials, and it is produced by microorganisms and bacteria that are present in the textile supports due to different environmental conditions such as pH, the presence or absence of oxygen, temperature variations, light, and pollution, which, in turn, can affect their growth. Among these, the percentage of cellulose also influences the resistance to microbiological attacks; in fact, the higher this is, the more resistant the canvas [86].

Further, the mechanical stress itself can also trigger the chemical degradation of the canvas, and both mechanical and chemical processes make the painting canvas increasingly brittle. To prevent this problem, it is common to replace the full lining and to use a localized consolidation treatment with the application of an adhesive strip in the degraded zone of the canvas [83].

However, as mentioned before, among the most important properties of any consolidation treatment and, therefore, adhesives for canvases, are its reversibility, compatibility, and stability, which are all factors that the materials used in the past did not always possess. From this perspective, conservators are still searching for novel consolidation strategies based on more eco-friendly materials, but this search has started with the framework of the EU Nanorestart project 2020 [52,67].

With the introduction of nanocellulose in conservation, these problems have been overcome [67].

In fact, nanocellulose is a material that is chemically similar and thus more compatible to the canvas, unlike the traditional vinyl and acrylic-based resins. Moreover, nanocellulose, with its nano-scale dimension, allows us to obtain a higher physicochemical interaction with the canvas substrates to be treated [19].

In fact, this bio-nanomaterial has the potential to improve and/or modify the properties of various polymers used as a matrix to produce glues or consolidants in preservation when mixed as a filler.

Bridarolli et al. [19] were among those who developed and evaluated an alternative approach to structural painting consolidation, which provided the use of natural materials such as nanocellulose. Among the aims of their research was the assessment of the consolidants' response to relative humidity (RH) variations, which is useful for defining the suitability of these materials for canvas consolidation purposes. For this experiment, an aqueous dispersion of cellulose nanocrystals (CNCs) and nanofibrils (CNFs) was applied to the surface of a modern cotton canvas, which was then subjected to aging. The first consideration was that the nanocellulosic treatments did not visibly modify the canvas color; moreover, the mechanical properties of treated samples showed an improvement with an increase in the Young's modulus and, in particular, the best performances were obtained with CNCs, which might result from the greater mass coverage measured for these nanostructures. To evaluate the impact of consolidation treatments on the mechanical properties, RH dynamic mechanical analysis (DMA-RH) was carried out. Overall, this study demonstrated that the CNC treatment is the best in terms of reinforcement and long-term stability compared to the CNF treatment. However, Figure 4 confirms that, with these consolidation treatments, a continuous surface layer was obtained, preserving the topology of the canvas, and, in particular, in the case of CNFs, a network similar to the natural fiber structure was formed across the cotton fibers.

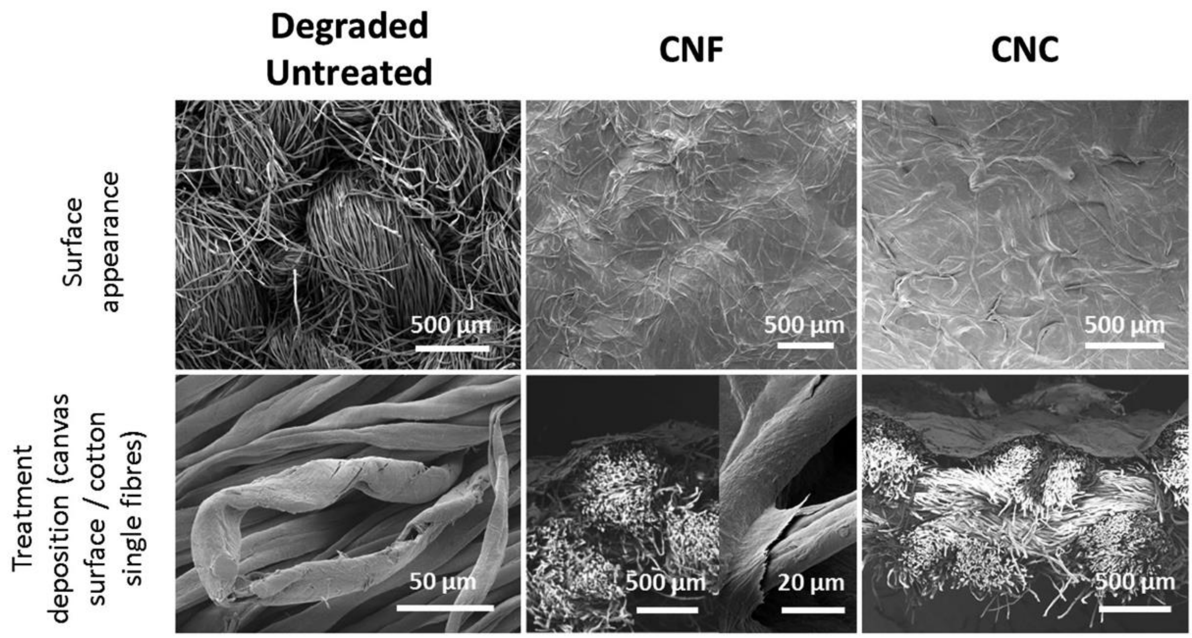


Figure 4. SEM images showing the canvas surface topography before and after treatment. Reproduced with permission [19]. Copyright © 2018, Taylor & Francis.

In addition, Nechyporchuk et al. [23] demonstrated for the first time that stabilization due to the use of different types of nanocellulose is more effective than that of the wax-resin formulation Beva 371 commonly used. To achieve this, mechanical tests in the elongation region were carried out to evaluate the response of treated canvases to static and periodic uniaxial stress at different relative humidity values, and the results obtained show that the nanocellulose-based consolidants gave better performances than the traditional consolidant Beva 371. Another important aspect highlighted in this work is the formation of thin films of nanocellulose, with a structure that depends on the type of nanocellulose used—if fibrous or crystalline—which is an aspect that ensures the reversibility of these bio-consolidants since the films are superficial and do not penetrate into the bulk of the canvases as shown in Figure 5.

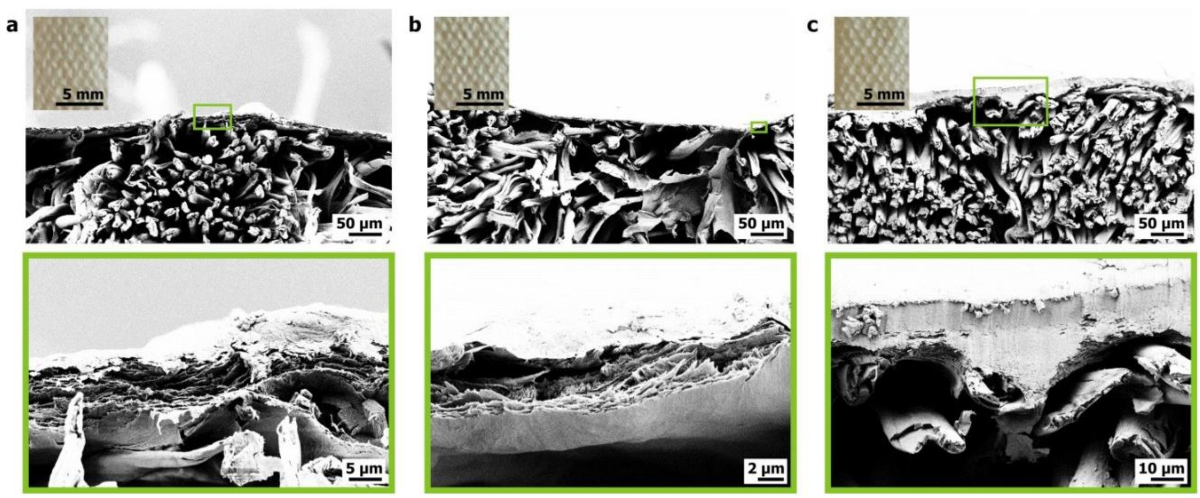


Figure 5. SEM images of aged cotton canvases coated 3 times with: (**a**) CNF; (**b**) carboxymethylated CNF; and (**c**) CNC, with optical microscopy images as insets (left top). Reproduced with permission. [23]. Copyright © 2018, Elsevier.

Moreover, from Figure 5, it can be seen that CNCs tended to form denser structures compared to CNFs and functionalized CNF coatings due to the better packaging ability of nanocrystals than flexible nanofibrils.

Palladino et al. [61] reported an interesting research work about an alternative method for the strengthening and deacidification of cellulose-based materials with nanocellulose and inorganic nanoparticles, which was already addressed in different previously published works [87,88]. In detail, calcium carbonate nanoparticles were used to neutralize the acidity, whereas stabilization was approached through a combination of nanocellulose and silica nanoparticles to obtain synergic effects of fiber stiffening and structural reinforcement. In the specific case of iron-tannate inks or dyes, they trigger severe degradation in cellulosic substrates, causing the acid-catalyzed hydrolysis of cellulose; in addition, iron ions not involved in the formation of complexes produce further oxidation. All of the results obtained from this research work demonstrated that the combination of nanocellulose and silica nanoparticles was efficient as a multiscale reinforcement, which is very important for canvases consolidation.

The main advantage of this treatment is the lower weight increase: approximately 2.5% compared to a weight increase of 200% for traditional lining. Overall, this study also demonstrated that CNCs were more effective than CNFs because this type of nanocellulose gives the possibility of using higher concentrations in the aqueous dispersion, allowing for a higher strengthening after the equivalent number of coatings and smaller mechanical changes in RH variations. Moreover, CNCs have a higher degree of crystallinity, which makes the treatment much more stable.

More recently, Böhme et al. [24] conducted a study on the use of CNCs for the consolidation and deacidification of a highly degraded acidic model cotton canvas and canvas from real paintings.

Usually, the restoration treatments of a painting canvas are concentrated on the face of the painting, whereas the consolidant is applied to the back of the canvas due to aesthetic reasons; in fact, in this case, the treatment was also applied to the back side of the canvases in order to avoid the formation of cracks and disruption, which endanger the paintwork of the artwork (Figure 6).

Figure 6. Application of nanocomposite consolidants on original paintings. Reproduced under terms of the CC-BY license [24]. Copyright © 2020, The Authors, published by Springer Nature.

Another problem related to this is the extreme sensitivity of canvases and paintworks to any type of solvents, whether polar or non-polar; this can be overcome with a short contact time of the solvent and the canvas; otherwise, a very low solvent amount or a solvent with a high volatility can be used.

In this context, this research work studied the behavior of polar components such as CNCs in water and non-polar compounds obtained by the silylation of CNCs to allow for its solubility in non-polar solvents as heptane. Therefore, cellulose nanocrystals were mixed in the polymer matrices, obtaining numerous advantages, such as an increase in the tensile strength of the canvas material, a greater chemical compatibility of the consolidant to the substrate, an easier and homogeneous applicability to the canvas, an unchanging appearance of the canvas and painting, impenetrability through the paint layer, and, finally, a sufficient reinforcement to the canvas. In addition to these advantages, these consolidation nanocomposite systems offer the possibility of carrying out both the consolidation and deacidification of the paintings together thanks to the addition of nanoparticles of calcium carbonate or magnesium oxide.

Figure 7 demonstrates that the optical changes were minimal; there was only a slight yellowing of the material.

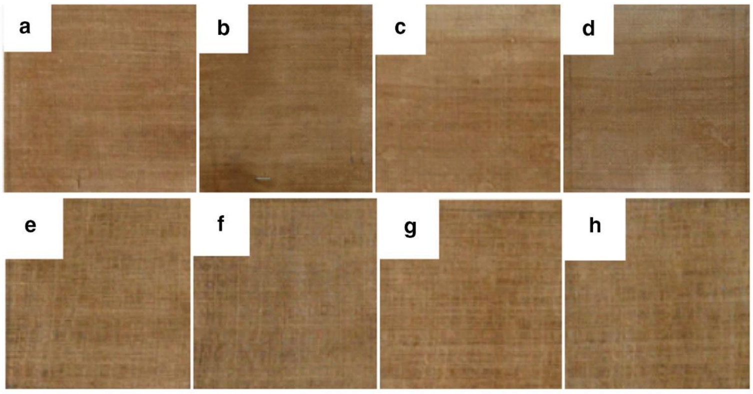


Figure 7. Real linen canvas with high-density weaving before (**a**) and after (**b**) treatment with polar nanocomposite and before (**c**) and after (**d**) treatment with non-polar nanocomposite; real linen canvas with low-density weaving before (**e**) and after (**f**) treatment with polar nanocomposite and before (**g**) and after (**h**) treatment with non-polar nanocomposite. Reproduced under terms of the CC-BY license [24]. Copyright © 2020, The Authors, published by Springer Nature.

All of the results obtained in the reported work were also expanded by the most recent study of Bridarolli et al. [67], in which, some canvases treated with the same previously tested and synthesized nanocomposite consolidants were mounted in a custom-made closed cell and underwent programmed cycles of relative humidity (RH) at a controlled temperature while exposed to a neutron beam in order to understand how rapidly moisture can diffuse into the untreated and nanocellulose-consolidated cotton canvases and to validate the effectiveness of the treatment carried out. The neutron radiography technique showed that the CNC treatment has a better protective action than the CNF treatment, increasing moisture diffusion across the canvas and allowing for the formation of a homogeneous superficial layer of moisture.

All of the results of these research works are the basis for the development of innovative systems based on new eco-friendly nanomaterials that are easy to handle and able to be used in the field of canvas conservation.

4.3. Historical Papers

Paper is the most used material for transmitting knowledge, and it represents most of the world artistic heritage. The degradation of historical papers in museums, libraries, and archives is due to different factors such as humidity, light, air, pollution, and bacteria attacks; moreover, this type of artworks is often subject to mechanical damage in terms of cracks, cuts, and deformations, especially in the borders, and is more exposed to atmospheric agents that induce the lowering of mechanical properties of paper. However, regarding the other cellulose-based artworks discussed before, in this case, the main degradation process is also acidic hydrolysis, which produces a considerable decrease in the mechanical strength of cellulose fibers [16,89–91]. To provide a structural reinforcement of paper, many strategies have recently been developed using both synthetic and natural materials [92]. For example, among the synthetic materials, we find 3-aminopropyl-methyl-diethoxysilane (AMDES) and 3-aminopropyl-triethoxylsilane (APTES); however, they give stability problems [93]. On the contrary, natural materials such as nanocellulose are better solutions due to their compatibility with paper and eco-friendliness.

In this context, many studies were conducted on the potential of nanocellulose for the stabilization and reinforcement of ancient papers. Among these, Perdoch et al. [94] recently described how the mechanical properties of treated paper change with the nature of nanocellulose: if crystalline or fibrous. In fact, the mechanical behavior depends on the bonding of fibers inside the paper and on the forces that provide these interactions between the fibers, which are especially hydrogen bonds, van der Waals bonds, and frictional forces. Therefore, the introduction of nanocellulose with many hydroxyl groups on the surface and a very small size promotes the formation of hydrogen bonds between fibers and cellulose nanoparticles, thus increasing the strength of paper. In this specific case, CNCs and CNFs were suspended in two different solvents, water and ethanol, to assess the possible consequences on tested properties, including the tensile index, elongation coefficient, and bending strength. Additionally, the CNF was also functionalized with carboxyl groups in order to value the penetration of nanocellulose inside the paper structure.

From this study, Perdoch et al. were able to conclude that nanocellulose did not always improve the mechanical properties of paper; in addition, the medium in which it is suspended can be crucial because its polarity influences the strength of hydrogen bonds and thus the paper strength.

Völkel et al. [89] discussed the possibility of using nanocellulose-based suspensions for the treatment of damaged historical papers. Usually, Japanese paper additions are used to rehabilitate damaged areas of these artworks, with a minimum acceptable alteration in the surface aspect and visual changes, since they are especially applied on very fragile paper [95]. However, the use of these very thin Japanese tissue papers and glues to attach these little fragments of papers to the damaged artwork involves several problems, such as the difficult control of humidity and influence of moisture. For this reason, Völkel et al. focused their attention on nanocellulose because it is the same material as the matrix to be treated; in fact, cellulose nanofibers bond with fibers of the papers and stabilize the fibers of the artwork without the addition of anchoring materials such as adhesives. In particular, in this research work, both bacterial (BNC) and fibrillated nanocellulose (CNF) were studied since they have different characteristics regarding their morphology (Figure 8), crystalline and polymerization degrees, and purity level. In the function of the type of nanocellulose used and the modification performed to decrease the content of the water of the two suspensions, the results obtained were different: for example, the substitution of water with ethanol gave a faster absorption and greater aggregation for the CNF suspension, making the application of the consolidant more complicated. On the other hand, the freeze-drying modification of the BNC suspension caused a loss of viscosity and, in this case, agglomerations were formed.

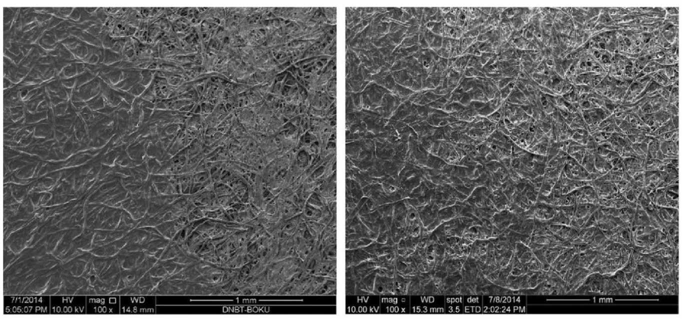


Figure 8. Left: paper treated with BNC; a clear borderline between the treated (**left**) and the untreated (**right**) areas is visible. **Right:** paper treated with CNF; the borderline between the treated (**left**) and untreated (**right**) areas is not as clear as with BNC. Reproduced under terms of the CC-BY license [89]. Copyright © 2017, The Authors, published by Springer Nature.

Otherwise, in both cases, the modification performed with the addition of gelatin increased the stability of nanocellulose film but left the treated surface very sensitive to the moisture and stickier compared to the nanocellulose suspensions without gelatin. However, with these treatments, the damaged areas of paper were consolidated, as visible in Figure 9, and the results of the application of BNC and CNF suspensions were comparable with the adhesive consolidation; they did not alter the visual appearance of ancient papers, even in the long term, and permitted an innovative approach for paper stabilization.

Figure 9. Cracks and leakage of damaged paper before treatment (**left**). After a direct application of nanocellulose, the cracks are closed (**right**) and the damaged paper is consolidated and stabilized. Reproduced under terms of the CC-BY license [89]. Copyright © 2017, The Authors, published by Springer Nature.

Other research works, such as those reported by Gomez et al. [96] and Santos et al. [97,98], showed the use of bacterial nanocellulose (BNC) for the paper reinforcement as a replacement of the usual Japanese paper coating method, obtaining excellent results in terms of the minimum thickness of the coating and better legibility of the characters after processing, although with a slight yellowing of the surface due to the aging process. Moreover, the treatment with BNC decreased the wettability due to the reduction in air permeance, an important aspect that prevents the formation of mold. Hence, bacterial nanocellulose is a promising material for the restoration of paper because it preserves the cellulose fibers of paper against degradation agents such as atmospheric pollutants and humidity, with results similar to those obtained for Japanese paper consolidation treatment.

A similar study conducted by Dreyfuss-Deseigne [99] compared nanocellulose coatings with different kinds of Japanese paper and confirmed that nanocellulose provided a better consolidating film that was able to withstand aging, light, and temperature.

Bergamonti et al. [16] proposed a new treatment for the conservation and consolidation of ancient papers based on the use of cellulose nanocrystals (CNCs) with the addition of silver (Ag) nanoparticles in order to obtain both a consolidating action due to nanocellulose and biocidal activity by Ag nanoparticles (Figure 10).

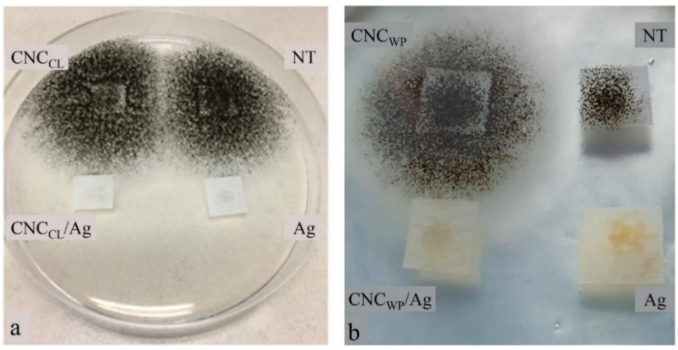


Figure 10. Growth inhibition of Aspergillus niger on Whatman paper samples, not treated (NT) and treated with CNCs obtained from different sources (CNC$_{CL}$ from cotton linter and CNC$_{WP}$ from waste paper), CNCs/Ag and Ag nanoparticles. (**a**) CNC$_{CL}$ (**b**) CNC$_{WP}$. Reproduced with permission [16]. Copyright © 2019, Elsevier.

The main advantage of this new approach is the absence of alterations in the appearance of original papers, even after adding the Ag nanoparticles to the CNCs suspension. Moreover, the CNCs coating was tested by mechanical stresses, and it was demonstrated that it increased the interaction between fibers, allowing for the stress to transfer into the material, thus obtaining a greater resistance.

Jia et al. [17] suggested the use of nanocellulose-based composites containing metal nanoparticles, which are commonly used for the conservation of paper collections. In particular, in this work, ZnO nanoparticles were used as an antimicrobial agent in order to increase the resistance to the biological degradation of paper due to some fungal strains present in archives or museums and to improve its chemical stability, including under UV radiation. In fact, once exposed to UV light, cellulose, which paper is made of, undergoes oxidative degradation due to the formation of hydroxyl radicals and carbonyl groups, which promotes the yellowing of the paper. However, these nanoparticles need stabilizers that avoid their agglomeration and, to achieve this, cellulose nanocrystals were used, thus increasing the tensile strength and folding strength of degraded paper. In this way, Jia et al. demonstrated how the ZnO/CNCs nanocomposite system can simultaneously act as a consolidating agent and bacteria, fungi, and UV light protection.

Another innovative treatment of damaged ancient paper that makes use of nanocellulose was shown by Operamolla et al. [59]. First, they demonstrated the reversibility of their studied treatment thanks to the use of a hydrogel suitable for removing nanocellulose, such as Gellan gel. This is a very important aspect of consolidation treatment because, in the field of cultural heritage, the reversibility is a fundamental goal for all restorations. Moreover, in this research work, the importance of the surface functionalization of cellulose nanocrystals was underlined to evaluate the influence of surface functional groups on their behavior as paper consolidants. In particular, it was observed that the presence of sulfate groups (S_CNC) affected aggregation properties and the aging response of treated materials, worsening the conservation in the long-term. This behavior is related to the pH of paper treated with S_CNC, which is lower compared to that of paper treated with uncharged CNC. For this reason, S_CNC suspension requires the addition of deacidifying agents to eliminate the acidity excess and to prevent paper depolymerization. On the contrary, a neutral CNC suspension did not compromise the pH and mechanical properties of the treated paper and therefore seemed to be the best solution between the two treatments. Finally, from the visual analysis of the Breviarium pages treated with the two types of CNCs (Figure 11), it is possible to observe how transparent CNC films do not alter the characteristics of the written parts since they remain clearly legible in all samples.

Figure 11. Images of pages and details from Breviarium romanum ad usum fratrum minorum treated with (**A**) water (pristine); (**B**) S_CNC; and (**C**) CNC. Reproduced under terms of the CC-BY license [59]. Copyright © 2021, The Authors, published by American Chemical Society.

Xu et al. [100], in their work, proposed an interesting solution for providing both consolidation and deacidification for the degraded papers with a single-step treatment, thus reducing the risks and stresses usually associated with a conservation intervention. To achieve this, they grafted cellulose nanocrystals with oleic acid to improve their dispersibility in organic solvents, such as ethanol, and then added alkaline nanoparticles of $Ca(OH)_2$ or $CaCO_3$, thus obtaining an ethanol-based "hybrid" system able to improve the mechanical properties of the paper and increase its pH, hindering further cellulose depolymerization. Figure 12 shows the graphical schematization of the conservation proposal made by Xu et al.

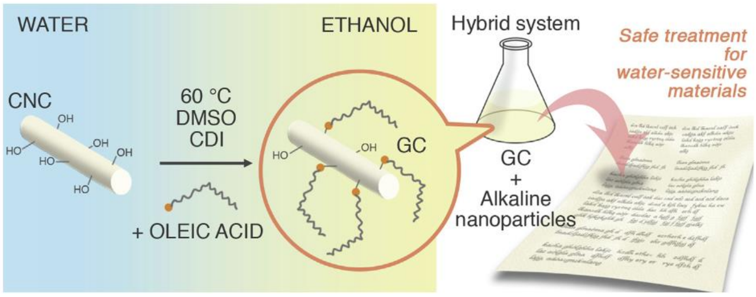


Figure 12. Schematization of conservation proposal by Xu et al. Reproduced with permission [100]. Copyright © 2020, Elsevier.

Ma et al. [92] showed a new treatment based on the suspension of crystalline nanocellulose and polyhexamethylene guanidine (PHMG) to reinforce paper and to hinder the mold growth on ancient books. In fact, mold is another important factor that, by producing acidic compounds, may cause the acidification of paper cellulose fibers and, moreover, with the production of mycotoxins, may endanger human health [101]. For this reason, Ma et al. studied the new polymer PHMG, which, due to its high biocidal activity, antibacterial power, and low toxicity, as well as its contribution to the formation of hydrogen bonds with nanocellulose, turned out to be a very interesting material for improving the mechanical properties of paper. From this research work, many promising results were obtained: the mechanical tests demonstrated an improvement in the folding strength, even after an aging period; moreover, the biocidal activity of the nanocellulose-based compound resulted in being significant.

Another type of paper damage is corrosion due to iron gall ink, a frequent phenomenon in medieval manuscripts, already mentioned above, since it also concerns the degradation of the painting canvases.

As mentioned before, this ink is not stable, and it is responsible for the degradation of paper by two mechanisms: the acid hydrolysis of cellulose due to the high acidic content and the oxidation of cellulose fibers related to free iron ions [102]. To overcome these problems, Völkel et al. [103] proposed a solution that provided two processes: a chemical treatment for deacidification, and the complexation of free iron ions. Furthermore, ink corrosion is usually matched with the mechanical damage of paper, and, for this reason, Völkel et al. proposed the use of nanocellulose to prevent the decrease in mechanical properties. The synergic effect of these two types of consolidation and stabilization was demonstrated, and the results obtained from this study once again highlighted the great effectiveness of nanocellulose as a bio-consolidant. Obviously, the use of nanocellulose can be further optimized to also obtain better results in terms of the optical stability and uniformity of the coating, as is possible to see from Figure 13.

Figure 13. Sample of damaged paper before (**I**) and after (**II**) mechanical stabilization by CNF. After the application of CNF, the fractures and cracks were stabilized. Reproduced under terms of the CC-BY license [103]. Copyright © 2020, The Authors, published by Springer Nature.

Finally, Imchalee et al. [68] proposed a new use of crystalline nanocellulose to improve the efficiency of watercolor paint on paper, which is usually faded to light. From the results obtained by SEM analysis, mechanical tests, and an evaluation of color fastness, CNCs resulted in being an excellent solution not only for the improvement in the efficiency of watercolor paint but also for their positive influence on the mechanical properties of paintings, once again proving to be an excellent eco-friendly and sustainable alternative to commonly used products. From the SEM micrographs (Figure 14), it is possible to conclude that CNCs mixed with watercolor paint can stabilize the watercolor painting, preventing damages due to the absorption of gas or liquid molecules on the paper surface.

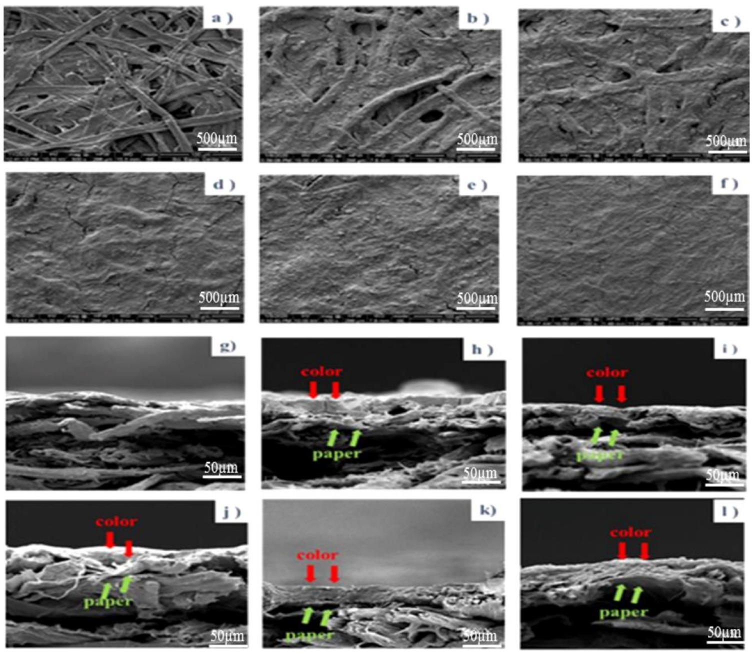


Figure 14. SEM image of the watercolor paint mixed with CNC painted on surface paper: (**a**) paper, (**b**) control, (**c**) 1% CNC, (**d**) 3% CNC, (**e**) 5% CNC, and (**f**) 7% CNC, and cross section image of (**g**) paper, (**h**) control, (**i**) 1% CNC, (**j**) 3% CNC, (**k**) 5% CNC, and (**l**) 7%CNC. Reproduced with permission [68]. Copyright © 2021, Elsevier.

Therefore, all of the collected studies demonstrated the enormous possibility of nanocellulose to substitute the synthetic products used for paper conservation and stabilization thanks to its numerous interesting surface characteristics and advantages, such as not having to use stickers [89].

The future challenge will be to make nanocellulose a more commercial product in the field of cultural heritage, with the aim of developing new, innovative, non-invasive, and more efficient bio-consolidants for paper artworks.

5. Conclusions

In this review, the structure and properties of all cellulose nanomaterials were first shown; then, the three types of nanocellulose—crystalline, fibrous, and bacterial—their synthesis processes, their peculiarities, and, finally, their characterization techniques, were summarized. Moreover, these nanomaterials have also demonstrated to be good substitutes for synthetic products in the field of the conservation and recovery of cultural heritage, where they can be used for several applications. Here, the most recent developments, results, and findings about nanocellulose-based consolidants were presented, with particular attention on the recovery and reinforcement of degraded wood and stabilization of painting canvases and historical papers.

In the case of wooden artifacts, one of the most important results obtained is the possibility of reducing the use of non-renewable petroleum sources and enhancing the use of eco-friendly wood adhesives, reached with the easy functionalization of nanocellulose. In addition, for waterlogged wood, nanocellulose-based consolidants have also achieved excellent results in terms of consolidation and interactions with the structure of wood, comparable to those obtained with synthetic consolidants.

For the painting canvases, nanocellulose is gradually taking the place of synthetic resins usually used as consolidant, thus providing better results both in terms of mechanical properties and stability toward moisture changes, also sometimes allowing for a very innovative approach that simultaneously provides a consolidating and deacidifying action without affecting the visual appearance of the artwork thanks to the addition of nanoparticles of calcium carbonate or magnesium oxide.

Finally, regarding the degradation of paper, the primary medium for recording information throughout the world, all nanocellulose types are better solutions due to their compatibility with paper and eco-friendliness. The use of Japanese paper, which, despite its good results, creates considerable thickness and does not reach the legibility of the characters after processing obtained with nanocellulose-based treatments, can be overcome. Moreover, with the addition of specific metal nanoparticles in the nanocellulose suspensions, it is also possible to reach antibacterial activity, thus hindering degradation due to the formation of mold and bacteria attacks, or also an UV light protection.

The future challenge of these research works concerns the study of the variability of nanocellulose properties, which are influenced by the type of nanocellulose, the manufacturing processes, and the natural sources from which it is extracted. However, the study of large-scale nanocellulose production processes will definitely need to be deepened in order to make it an easily available and low-cost material, obviously taking into account the "green" aspect and therefore the bio-compatibility and eco-sustainability of the synthetic procedures, coping with the dictates of the EU Green Deal. All of these improvements will allow us to use these nanomaterials and their composites in different fields of applications, including that of cultural heritage, where the use of cellulose nanomaterials would avoid synthetic consolidating agents harmful to both artworks and the health of operators working in the field of fine arts. This will only be possible with an interdisciplinary research work that aims toward the study and improvement of nanocellulose materials with a low environmental impact and high technological content for increasingly advanced and sustainable applications in order to benefit from the knowledge preserved in the cellulose artworks for as long as possible.

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Abbreviations

CNCs, cellulose nanocrystals; CNFs, cellulose nanofibrils; BNC, bacterial nanocellulose.

Vocabulary Section

Cellulose nanomaterials: crystallite or cellulose fiber containing at least one dimension in the nanoscale range (1–100 nm).

Cellulose nanocrystals: cylindrical, elongated, rigid, rod-like nanoparticles with dimensions of 4–70 nm in width, 100–6000 nm in length, usually obtained by hydrolysis.

Cellulose nanofibrils: commonly obtained by mechanical treatment, are composed of longer and flexible fibers with dimensions of 20–100 nm in width and >10,000 nm in length and a low crystallinity grade.

Bacterial nanocellulose: consists of ultrafine nanofibers that are 20–100 nm in diameter and micrometers lengths and form an identifying 3D network.

Acidification: the degradation process that promotes cellulose depolymerization phenomena, resulting in the loss of the typical mechanical properties of the material.

Consolidation: the restoration work aimed at recovering the compactness of the material, which is obtained by filling the gaps inside the material itself.

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