Preparation and Properties
of Cellulosic Nanomaterials

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Abstract. What are the reasons for the effervescence and explosion of the scientific literature during the last decade in the field of cellulosic and other polysaccharide nanomaterials? First, the raw materials are abundant, available in a variety of forms, renewable, non-toxic, low density, and biodegradable. In addition, it is well known that unexpected and attractive properties can be observed when decreasing the size of a material down to the nanoscale. Different forms of cellulose nanomaterials, resulting from a top-down deconstructing strategy (cellulose nanocrystals – CNCs, cellulose nanofibrils – CNFs) or bottom-up strategy (bacterial cellulose – BC), can be prepared. Multiple mechanical shearing actions applied to cellulosic fibers release more or less individually the nanofibrils. A controlled strong acid hydrolysis treatment can be applied to cellulosic fibers allowing the selective dissolution of non-crystalline domains and disengagement of nanocrystalline cellulose regions. The mechanical modulus of crystalline cellulose is the basis of many potential applications. With a Young's modulus of the order of 100–130 GPa and a specific surface of several hundred m²·g⁻¹, these cellulosic nanomaterials have a significant capacity of reinforcement at low filler content. Several properties reviewed in this article are impacted by the nanoscaling process.

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Получение и свойства
целлюлозных наноматериалов

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Аннотация. Каковы причины резкого роста в последнее десятилетие научной литературы в области целлюлозных и других полисахаридных наноматериалов? Во-первых, сырье для получения этих материалов в изобилии, доступно в различных формах и из возобновляемых источников, нетоксично, обладает биоразлагаемостью и низкой плотностью. Кроме того, хорошо известно, что при уменьшении материала до наноразмера могут появляться необычные и привлекательные свойства. С использованием природной целлюлозы можно создавать различные формы целлюлозных наноматериалов: в результате применения стратегии деконструкции «сверху вниз» (нанокристаллы целлюлозы – CNC, нанофибриллы целлюлозы – CNF) или стратегии «снизу вверх» (бактериальная целлюлоза – BC). Многократные механические сдвиговые воздействия на целлюлозные волокна приводят к высвобождению отдельных нанофибрилл. Контролируемый кислотный гидролиз целлюлозы обеспечивает селективное растворение некристаллических доменов и разъединение областей нанокристаллической целлюлозы. Высокие механические свойства кристаллической целлюлозы открывают потенциал для ее использования во многих областях. Благодаря модулю Юнга порядка 100–130 ГПа и высокой удельной поверхности в несколько сотен м$^2\cdot$г$^{-1}$ целлюлозные наноматериалы обладают значительной способностью к армированию при низком содержании наполнителя. В статье рассматриваются свойства целлюлозы, изменяющиеся в процессе наномасштабирования.

Ключевые слова: нанокристаллы целлюлозы, нанофибриллы целлюлозы, целлюлозные наноматериалы, производство, характеристики.

Introduction

Cellulose is an organic compound belonging to the category of polysaccharides. It is the most important material of the plant cell wall. It is also biosynthesized by a number of living organisms including some amoebae, sea animals, bacteria, and fungi. Its chemistry and its structure determine its properties. The cellulose molecule is a monotone polymer made of glucose units linked in β-1,4 (Fig. 1). As a result of the β-1,4 glycosidic bond, the homologous functions of the monomers are alternately above and below
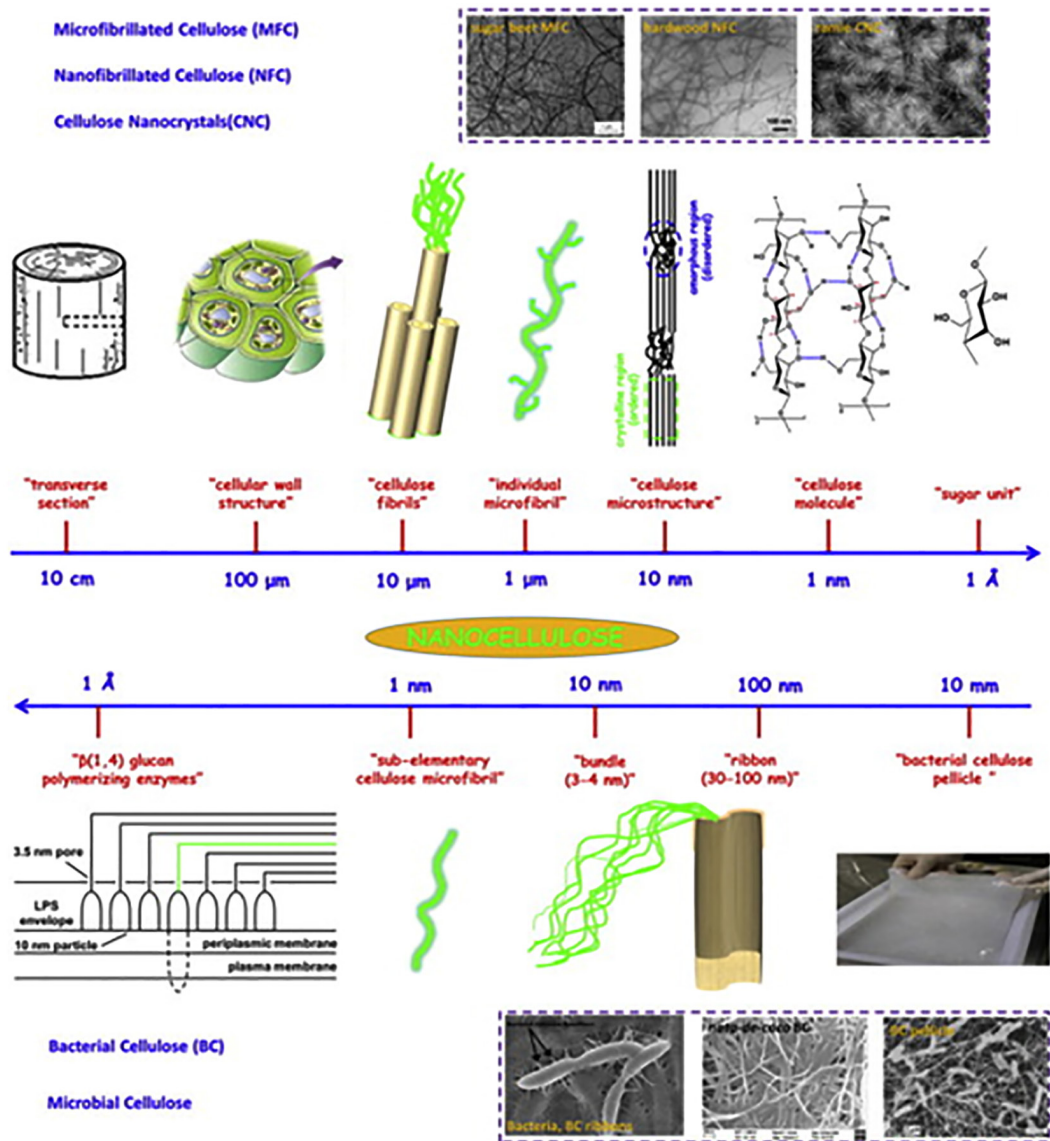
Fig. 1. Hierarchical structure and multi-level organization of cellulose; top image (from large unit to small unit): cellulose nanocrystals (CNC), micro/nanofibrillated cellulose (MFC and CNF/NFC); bottom image (from tiny unit to small unit): bacterial cellulose (BC) (Lin, Dufresne, 2014a)

the plane. The molecule is thus linear and its flexibility comes from the degree of freedom at each bond. Each glucose bears three hydroxyl groups, and their ability to form hydrogen bonds plays a major role in directing the crystalline packing and governing the physical properties of cellulose. The flexibility of the cellulose molecule is therefore limited by the regular formation of intramolecular H-bonds, and this linear molecule then becomes more rigid and resistant. Intermolecular H-bonds can also develop and allow the formation of numerous molecular assemblies (microfibrils) with diameters ranging from 2 to 20 nm, which are even more rigid and resistant. These intermolecular H-bonds are so strong that the glass transition and melting points of dry cellulose usually observed for semi-crystalline polymers occur at temperatures

higher than the degradation temperature. The degradation of cellulose occurs around 220 °C but its color already starts to become yellow-brown at 180 °C under ambient conditions because of a loss of chemical stability.

Cellulose acts as a structural element and provides rigidity to the plant cells. The high tensile strength of cellulose fibers present in the plant cell wall is responsible for maintaining the shape and rigidity of plant cells. It is due to such strong cellulose fibers in the cell wall that plant cells do not burst like animal cells when placed in a hypotonic solution. The purest form of plant cellulose is cotton, which contains around 98 % cellulose. Besides, cellulose is also present in wood obtained from the trees, which is approximately 40–50 wt% cellulose with about half in nanocrystalline form and half in non-crystalline form. Wood and plants are cellular hierarchical biocomposites designed by nature, basically consisting of an amorphous matrix composed of hemicellulose, lignin, waxes, extractives, and trace elements reinforced by semicrystalline cellulose microfibrils. Lignocellulosic fibers consist therefore of a cemented microfibril aggregate. The hierarchical struture and multi-level organization of cellulose is reported in Figure 1. The structure of plants spans many length scales, in order to provide maximum strength with a minimum of material. Cellulose has been used for centuries in different industries for the welfare of mankind. It is used to make paper, cardboards, and other paper products. In the textile industry, different clothes are made using cotton and other plant fibers. It is also used to make electrical insulation paper in the electric industry, bio-fuel, gunpowder. Cellulose can be used as a stabilizer in different drugs and as a stationary phase for chromatography in biological labs. More recently, the recognition that, by suitable chemical and mechanical

treatments, it is possible to produce fibrous materials with at least one dimension in the nanometer range from any naturally occurring source of cellulose has been emphasized and it opens the door to new applications because of specific properties in the nanoscale.

Preparation of cellulosic nanomaterials

Nanomaterials describe materials for which a size (in at least one dimension) ranges between 1 and 100 nm according to the usual definition of nanoscale. Biological systems often feature natural, functional nanomaterials. Accordingly, the synthesis method should allow controlling the size of the material within this range. These methods are usually divided into two main types, «bottom up» and «top down». Nanocellulose is often used as an umbrella and general term for the different types of nano- and micro-sized cellulosic particles (Lavoine et al., 2012). Based on their dimensions and preparation methods, nanocelluloses may be classified in three main subcategories (Table 1).

Top-down approach

In this approach, the starting material consists of micrometer lignocellulosic fibers. As for most cellulosic sources this material is intimately tied to other materials, removal of most of the non-cellulosic components from the natural fiber is generally performed. It usually involves an alkali extraction, during which soluble polysaccharides such as low molecular weight hemicelluloses and other extractives are dissolved in what is called the black liquor. Bleaching with sodium chlorite ($NaClO_2$) solution in a buffer medium under mechanical stirring generally follows to remove most of the residual phenolic molecules like lignin or polyphenols and proteins. This process converts the brown pulp to a white material. It is associated with a decrease

Table 1. The family of cellulose nanomaterials (adapted from (Klemm et al., 2011)

Type of nanocellulose	Synonyms	Typical sources	Formation and average dimensions
Cellulose nanofibrils (CNF)	Microfibrillated cellulose (MFC), cellulose nanofibers, nanofibrillar cellulose (NFC), nanofibrillated cellulose	Wood, sugar beet, potato tuber, hemp, flax	Delamination of the pulp by mechanical treatment after chemical or enzymatic treatment Diameter: 5–100 nm Length: several μm
Cellulose nanocrystals (CNC)	Cellulose crystallites, nanocrystalline cellulose, rod-like cellulose microcrystals	Wood, cotton, hemp, flax, wheat straw ramie, microcrystalline cellulose, tunicate, bacterial cellulose	Acid hydrolysis Diameter: 5–70 nm Length: 100–1000 nm
Bacterial cellulose (BC)	Bacterial nanocellulose, microbial cellulose, biocellulose	Low molecular weight sugars, alcohols	Bacterial synthesis Diameter: 20–100 nm

in the diameter of the fiber due to the removal of the cementing materials, an increase in the crystallinity index, and an increase in thermal stability due to the removal of poorly thermally stable hemicelluloses. This purified material can be subsequently submitted to a mechanically- or chemically-induced deconstructing treatment to decrease its size to the nanoscale.

Mechanically-induced deconstructing strategy. After the purification step, the cellulose fibers consist of fibril aggregates made of strongly interacting bundles of parallel glucan chains, which are the smallest discernable building blocks of cellulose I (native cellulose) as shown in Figure 1. A mechanically-induced deconstructing treatment involving strong multiple mechanical shearing actions can be applied to diluted aqueous dispersions of cellulose fibers in order to release more or less individually these fibrils. Different terminologies are used to describe the material resulting from the cellulose fiber fibrillation process, sometimes leading to misunderstanding and ambiguities. The resulting material was denoted microfibrillated cellulose (MFC) in the pioneering work reported in 1983 (Herrick et al.,

1983; Turbak et al., 1983). This terminology is now usually limited to materials with a broad size distribution of the fibers, from the nanoscale to bigger fibers, forming a network structure and interconnected to each other. Other terms, such as cellulose nanofibers, nanofibrillar cellulose, cellulose nanofibrils (CNFs), and nanofibrillated cellulose are used when the material is more in the nanoscale than in the microscale and exhibits a narrow size distribution.

Different equipment can be used to induce the fibrillation of cellulose fibers including homogenizing (Dufresne et al., 2000; Malainine et al., 2005; Zuluaga et al., 2007; Ferrer et al., 2012), grinding (Taniguchi, Okamura, 1998; Iwamoto et al., 2007), cryocrushing (Chakraborty et al., 2005), high-intensity ultrasonication (Cheng et al., 2007; Chen et al., 2011), aqueous counter collision (Kondo et al., 2014; Tsuboi et al., 2014), ball milling (Zhang et al., 2015; Nuruddin et al., 2016), and twin-screw extrusion (Cobut et al., 2014; Ho et al., 2015). A detailed description of these different techniques can be found elsewhere (Dufresne, 2017a). Among these different methods, homogenizing and grinding are the most commonly used for the preparation

of CNFs and the most effective for the scaling production of CNFs at present.

The yield of these processes is close to 100 %, but this production route through mechanically-induced deconstruction is normally connected to high energy consumptions associated with the fiber delamination. A renewed interest has emerged when different pretreatments were proposed to obtain fibers that are less stiff and cohesive, thus decreasing the energy needed for fibrillation, as detailed in (Lavoine et al., 2012). Three different strategies were basically proposed: (i) limiting the hydrogen bonding in the system, and/or (ii) adding a repulsive charge, and/or (iii) decreasing the degree of polymerization (DP) or the non-crystalline link between individual fibrils. The most popular pretreatments are enzymatic hydrolysis, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation, and carboxymethylation/acetylation. For the enzymatic hydrolysis pretreatment, it was reported that monocomponent endoglucanase is more efficient to facilitate the fibrillation of the pulp (Rosgaard et al., 2007). TEMPO-oxidation and carboxymethylation pretreatments induce negatively charged groups into cellulosic fibers, improving their delamination. The typical oxidation system for cellulose is TEMPO/NaBr/NaClO (Saito et al., 2006), which has been extensively used for the pretreatment of raw cellulose materials before mechanical disintegration. During the reaction, the primary alcohol groups are first oxidized to aldehydes and further converted to carboxyl groups. At the same time, the depolymerization phenomenon of cellulose occurs. TEMPO/NaClO/NaClO$_2$ system was also applied, which overcame the depolymerization (Saito et al., 2009). For carboxymethylation, it was shown that a pH higher than 10 is required to dissociate all the charges of the microfibrils (Wågberg et al., 2008). Other pretreatments such as periodate-chlorite oxidation (Liimatainen et al., 2012), oxidative sulfonation (Liimatainen et al., 2013), cationization (Aulin et al., 2010; Olszewska et al., 2011; Ho et al., 2011), ionic liquids (Li et al., 2012; Ninomiya et al., 2018), and deep eutectic solvent (Li et al., 2017) have been reported.

Morphologically, CNF occurs as a highly viscous suspension (Fig. 2a) and consists of long entangled filaments made of both individual nanofibrils and microfibril bundles as shown in Figure 2b. The particle diameter is generally in the range 5–30 nm, and the length, which is more difficult to determine, is supposed to be in the range 1–10 μm. MFC prepared without pretreatment of the initial pulp consists of coarser nanofibers with a diameter ranging from 10 to 100 nm forming a 3D network (Fig. 2c).

Chemically-induced deconstructing strategy. Cellulose nanomaterials can also be prepared through acid hydrolysis or enzymatic treatment of cellulose under controlled conditions. The acid hydrolysis process is based on the difference in accessibility of hydronium ions in the crystallized and non-crystallized zones of cellulose. It induces the dissolution of non-crystalline domains, due to the easier penetration of hydronium ions within the non-crystalline cellulosic regions, promoting the hydrolytic cleavage of the glycosidic bonds and release of individual crystallites (Nickerson, Habrle, 1947). Different descriptors are used to describe the material resulting from this process. It includes cellulose whiskers, cellulose nanowhiskers, nanocrystalline cellulose, and cellulose nanocrystals (CNCs), the latter being the most commonly used.

CNCs are generally obtained through mineral acid hydrolysis of cellulose pulp under very harsh reaction conditions, which usually require concentrated acid. Sulfuric acid is generally preferred as it produces negatively charged sulfate ester groups at the surface of released crystals,
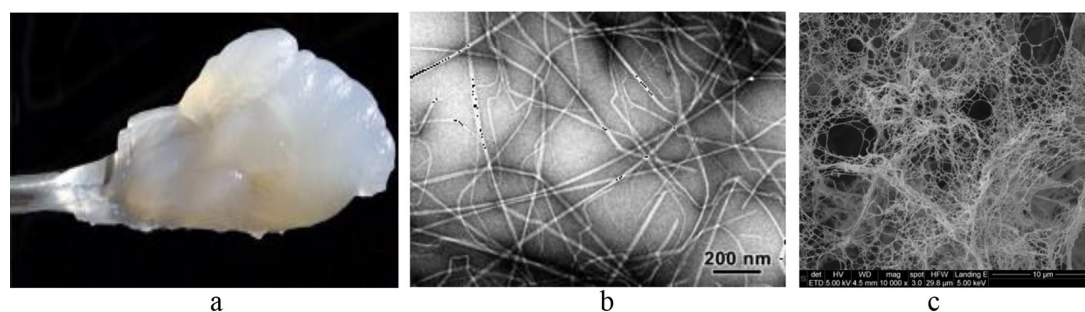
Fig. 2. CNF morphologically: (a) Appearance of a 2 wt% CNF suspension obtained from enzymatically pretreated eucalyptus showing its gel-like behavior (Lavoine et al., 2012); (b) TEM for CNF obtained by fibrillation of TEMPO-oxidized tunicin fibers (Saito et al., 2006); (c) SEM for MFC mechanically isolated from oat straw cellulose powder (Tingaut et al., 2011)

resulting in improved electrostatic stabilization of the suspension. At the same time, it decreases the thermal stability of the nanoparticles. In general, the hydrolysis process is performed at sulfuric acid concentration of 60–65 %, reaction temperature of 40–50 °C, and reaction time in the range 30–60 min. CNCs with increased thermal stability but a higher tendency to flocculation can be prepared using hydrochloric acid. Phosphoric (Camarero Espinosa et al., 2013), hydrobromic (Lee et al., 2009), nitric (Liu et al., 2010), phosphotungstic (Liu et al., 2014), and formic acids (Li et al., 2015) have also been reported for the preparation of CNCs. Using the mineral acid hydrolysis strategy to produce CNCs is a simple method that has been used at pilot scale and even in a demonstration plant. It has some drawbacks, such as the problem of corrosion of the equipment resulting in high production cost, and the generation of a large amount of residual acid and other pollutants during the acid hydrolysis process, which are very difficult to dispose of and recover. The enzymatic hydrolysis process for obtaining CNCs requires longer time. Other processes have been proposed for the preparation of CNCs. These include TEMPO oxidation (Hirota et al., 2010), hydrolysis with gaseous acid (Pääkkönen et al., 2018), ionic liquid (Man et al., 2011), ammonium persulfate oxidation (Leung

et al., 2011), periodate oxidation (Yang et al., 2013), ultrasonication-assisted FeCl$_3$-catalyzed hydrolysis (Lu et al., 2014), liquefaction (Kunaver et al., 2016), and acid deep eutectic solvents (Sirviö et al., 2016). The yield of CNCs prepared via acid hydrolysis is generally quite lower, in the order of 30 % (Dufresne, 2017a). Morphologically, CNC occurs as a suspension that exhibits the formation of birefringent domains when observed in polarized light between cross-nicols (Fig. 3a). This behavior results from two origins: (i) a structural form anisotropy of cellulose (anisotropic refractive index, $\Delta n\sim 0.05$) and (ii) a flow anisotropy resulting from the alignment of the nanorods under flow generally operated before observation. Each nanocrystal consists of straight rod-like or needle-like nanoparticles (Fig. 3b). The dimensions of these nanorods are governed by the source of cellulose, hydrolysis conditions, and ionic strength. The length is typically of the order of a few hundreds of nanometers and the width is of the order of a few nanometers.

Bottom-up approach

The bottom-up, or self-assembly, approach to nanofabrication uses chemical or physical forces operating at the nanoscale to assemble basic units into more complex and larger structures. For the production of nanocellulose,
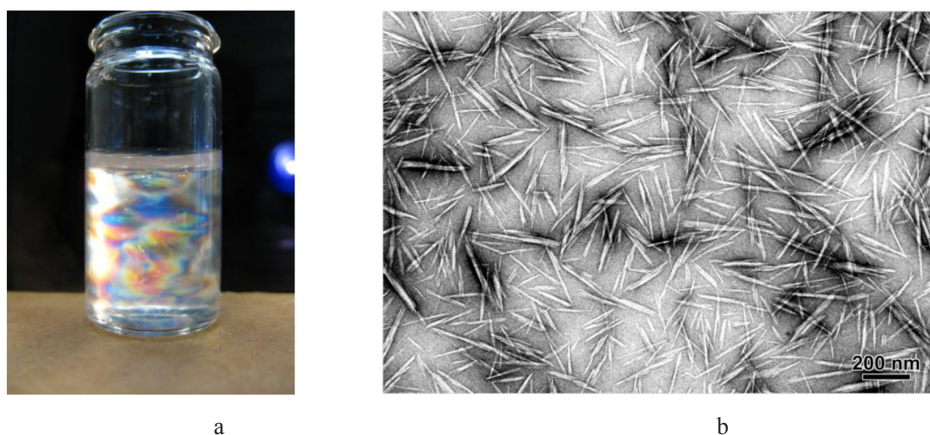
Fig. 3. (a) Photograph of a diluted aqueous suspension of CNC (0.50 wt%) obtained by H_2SO_4 hydrolysis of capim dourado fibers observed between cross-nicols showing the formation of birefringent domains (Siqueira et al., 2010); (b) TEM from a dilute suspension of CNC obtained by H_2SO_4 hydrolysis of ramie fibers showing both individual and laterally associated crystallites (Habibi et al., 2008)

it utilizes the ability of some bacteria to produce cellulose from a wide range of carbon and nitrogen sources. These include Gram-negative species such as *Acetobacter*, *Azotobacter*, *Rhizobium*, *Pseudomonas*, *Salmonella*, and *Alcaligenes* and Gram-positive species such as *Sarcina ventriculi*. The most effective producer of cellulose is *Acetobacter xylinum*. Historically, bacterial cellulose (BC) has been limited to the manufacture of Nata de coco, a South-East Asian food product (Iguchi et al., 2000).

The production of BC is based on a process involving dual couple steps, *viz.* polymerization and crystallization. Glucose residues polymerize to β-1,4 glucan linear chains in the bacterial cytoplasm and are extracellularly secreted. The developed chains crystallize into microfibrils, and then some microfibrils consolidate to materialize a highly pure 3D porous network of entangled nanoribbons 20–60 nm wide (Fig. 1). Compared to plant cellulose, BC is produced in a pure form, free of lignin, pectin, and hemicelluloses, and no purification treatment is needed. Under static culture conditions, these ribbons and associated cells form a 3D-nanofibrilar floating pellicle that allows the non-mobile, strictly aerobic bacteria

to grow in the top oxygen-rich interface of the growth medium. Under agitated and/or aerated conditions, BC is obtained in the form of fleeces with variable size.

**Properties of cellulose
in the nanoscale**

When decreasing the size of a material down to the nanoscale, some properties are altered compared to its microscale form. These modifications can strengthen the use of cellulose and broaden its applications to new markets. The main properties of cellulose that are amended in the nanoscale are collected in Table 2 and detailed in the following sections.

Specific surface area

The specific surface area of a solid material refers to the total surface area of a material per unit of mass. When decreasing the size of a material, it obviously increases due to the increase in the surface-to-volume ratio. It is usually measured by gas adsorption using the BET (Brunauer-Emmett-Teller) isotherm with nitrogen as adsorbate. However, this method requires completely dried samples, resulting in the collapse of the

Table 2. Properties of cellulose in the nanoscale

Property	Modification compared to microscale	Reason	Market
Specific surface area	Huge increase	Nanosize, high surface-to-volume ratio	Paper and cardboard, composites, packaging, pharmaceutics, membranes, hydrogels, aerogels
Stiffness	Improvement	Reduction of defects	Paper and cardboard, composites, packaging
Aspect ratio	Broad range	Different preparation techniques	Composites
Thermal properties	Lower coefficient of thermal expansion	Crystallinity, ability to form a dense network	Electronics, sensors
Rheological properties	High viscosity of the suspension, shear-thinning behavior	High specific surface area, high density of surface hydroxyl groups	Food, cosmetics, oil, construction, paper & cardboards, paints, coatings, inks
Optical properties	Transparency, iridescence	Nanosize, rod-like morphology, birefringence	Electronics, packaging, paper, cultural heritage, inks, coatings, cosmetics
Barrier properties	Improvement in dry conditions	Nanosize, crystallinity, ability to form a dense network	Packaging
Functionalization	Wide range	High density of surface hydroxyl groups	Composites, filtration, biomedical, hygiene

pores, irreversible hydrogen bonding, and hornification, leading to an underestimation of the specific surface area. Nuclear magnetic resonance (NMR) approach provides a good first approximation for the specific surface area of cellulose nanomaterials and overcomes the limitations of BET measurements for highly aggregated samples (Brinkmann et al., 2016). A method based on xyloglucan adsorption was also proposed (Moser et al., 2018). The specific surface area of cellulose nanomaterials can be estimated from the average geometrical dimensions of the nanoparticles, assuming a rod-like geometry and a density ρ of 1.5 g·cm^{-3} for crystalline cellulose. Figure 4 shows the evolution of the specific surface area as a function of the diameter of rod-like nanoparticles. A sharp increase is observed when the diameter drops below a value of 20 nm, which corresponds to the diameter range of most cellulose nanomaterials.

The specific surface area of cellulose nanomaterials plays a crucial role in determining the fiber-fiber interaction, which is an important parameter for the tensile strength of paper and for stress transfer from the matrix to the reinforcement in composite applications. It also affects the chemical reactivity and promotes an efficient surface functionalization. Active packaging where cellulose nanomaterials can serve as carriers of active substances such as antioxidants and antimicrobials can be developed.

This high specific surface area coupled with the low concentration of the suspensions allows the preparation of hydrogels and highly porous aerogels (by removal of the aqueous phase by e. g. freeze-drying), which can be used as porous templates. The aerogel network can be chemically modified to tune its wetting properties towards non-polar liquids/oils. It can also be impregnated with different precursors, which can readily
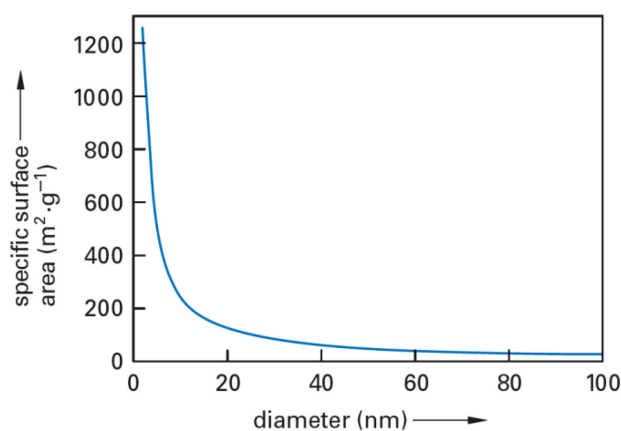
Fig. 4. Evolution of the specific surface area for cellulose rod-like nanoparticles as a function of their diameter, assuming a density of 1.5 g·cm⁻³ for crystalline cellulose (Dufresne, 2017a)

be transformed into functional nanoparticles. Nanopapers fabricated by filtration or casting-evaporation can be used in the sensors sector since they can maintain their 3D structure in water. They can also be used for the development of high capacity retention filters and membranes for the removal of contaminants.

Stiffness and strength

Cellulose serves as structural element in nature and confers mechanical properties to higher plant cells. Plant fibers have a length ranging from few mm to several cm and their diameter is in the order of 20–40 µm. The formation of defects in a material adversely affects its mechanical properties, but the probability of their occurrence decreases when the size of the material is reduced. The extraction of cellulose at the nanoscale is therefore beneficial to improving the stiffness and strength of the fiber. The mechanical modulus of cellulose nanomaterials is probably their main asset, and it is the basis of many potential applications, including the reinforcement of polymer composites and improvement of the durability and scratch resistance of water-based paints and varnishes. The tensile modulus and strength of single cellulose I crystal has been estimated

both experimentally and theoretically. Average values of 130 GPa and 10 GPa, respectively, were reported (Dufresne, 2017b). The tensile modulus is slightly lower (100 GPa) for CNF because of its lower crystallinity. Enhanced mechanical properties and fracture characteristics of concrete were reported, with the ability of cellulose nanomaterials to arrest micro-cracks formed during hydration and to prevent their further growth. In composite applications, density is also an important parameter to consider. It can be reflected through the specific tensile modulus, which is the ratio between the tensile modulus and the density. Considering a density around 1.5–1.6 g·cm⁻³ for crystalline cellulose, the specific modulus for CNC and CNF was found around 85 and 65 J·g⁻¹, respectively, much higher than for steel (25 J·g⁻¹) or glass (27 J·g⁻¹) (Dufresne, 2013).

Aspect ratio

The aspect ratio of rod-like particles is defined as the length-to-diameter ratio. This parameter is difficult to precisely determine for CNF due to its flexibility and difficulties associated with the determination of its length, but it is considered to be very high. It is easier to quantify for CNC, and its value is found to mainly depend on both the source of cellulose

and hydrolysis conditions. Low values around 10 are reported for cotton, and for most cellulosic sources, it ranges between 10 and 30 (Dufresne, 2017a). For specific sources of cellulose, higher aspect ratio CNCs have been obtained, e. g. close to 70 for tunicin (Anglès, Dufresne, 2000) or capimdourado (golden grass) (Siqueira et al., 2010). The value of the aspect ratio determines the anisotropic phase formation and reinforcing properties of CNC.

In composite science, the concept of critical aspect ratio is well-known and is an indicator of the amount of stress transferred to the fiber. Below this critical aspect ratio, insufficient stress is transferred and the reinforcement is inefficient. For cellulose nanomaterial reinforced nanocomposites, the impact of aspect ratio is even more relevant. It was shown in the pioneering work in this research area (Favier et al., 1995) that the mechanical behavior of these materials is linked to the formation of a rigid continuous network of H-bonded nanoparticles. Above a critical volume fraction, defined as the percolation threshold, whose value decreases as the aspect ratio of the nano-rods increases, an

unusual and exceptional strengthening effect was reported. A high value of the aspect ratio is therefore necessary to decrease the percolation threshold, which guarantees a high reinforcing effect for lower nanofiller contents. Moreover, it was shown that when increasing the aspect ratio of individual CNC, the stiffness of the percolating network increases (Bras et al., 2011), further increasing the mechanical reinforcement effect. These effects are illustrated in Figure 5, which shows the evolution of the storage modulus in the rubbery state of the matrix as a function of CNC content for nanocomposites obtained by mixing poly(styrene-co-butyl acrylate) (poly(S-co-BuA)) with CNCs extracted from *Posidonia oceanica* balls and leaves, with an aspect ratio of 35 and 75, respectively (Bettaieb et al., 2015).

Thermal properties

Compared to inorganic materials, organic compounds have limited thermal stability, due to the low polar character of C–C and C–H bonds. This can restrict the use of cellulose and manufacturing conditions of its composites at
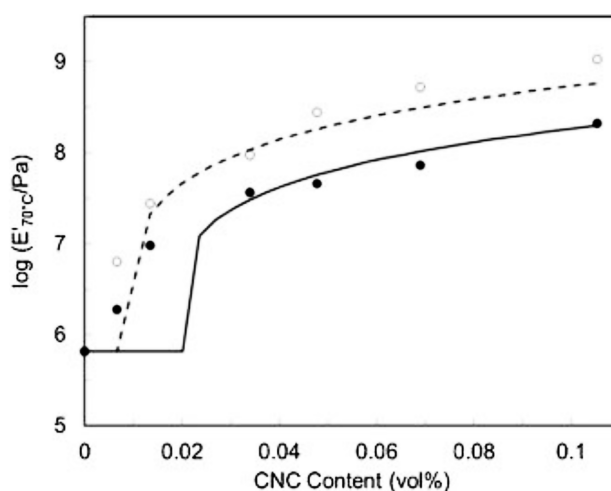

Fig. 5. Evolution of the logarithm of the tensile storage modulus at 70 °C (Tg + 40 °C) for poly(S-co-BuA) versus CNC content: experimental data for CNC extracted from *Posidonia oceanica* balls (●, aspect ratio 35) and leaves (○, aspect ratio 75), and predicted data from the percolation approach for CNC extracted from *Posidonia oceanica* balls (solid line) and leaves (dashed line) (Bettaieb et al., 2015)

high temperatures. This issue is even more critical for H_2SO_4-hydrolyzed CNC, for which some of the surface hydroxyl groups are substituted with charged sulfate groups ($-OSO_3^-$) that lower its thermal stability (Lin, Dufresne, 2014b). The amount of charged sulfate groups on the crystal surface can be controlled or changed in different ways, either during the sulfuric acid hydrolysis or afterwards.

An interesting thermal property benefiting from the size reduction of cellulose to the nanoscale is its very low coefficient of thermal expansion (CTE) when in film form. This is attributed to both the enhanced crystallinity and strength of the cellulose nanomaterial network interactions (Sheltami et al., 2017). This feature can be used to reduce the CTE of polymer nanocomposite sheets assuming that the strength of the network is strong enough to restrict the thermal expansion of the matrix (Yang et al., 2015).

This low CTE value of cellulose nanomaterial films associated with transparency, lightweight, resistance, and flexibility make them potentially useful in electronics and sensors applications to replace plastic of glass for flexible display panels and electronic devices, e. g. mobile phones, computers, TVs, touch sensors, solar cells, and paper-based generators.

Rheological properties

Cellulose nanomaterials are produced and commonly used in the form of aqueous dispersions, and highly viscous suspensions are obtained as shown in Figure 2a for CNF. This highly viscous behavior results from the high specific surface area of cellulose nanomaterials and ensuing huge amount of surface hydroxyl groups that can interact with the surrounding medium. In addition, the fibrils tend to form a continuous and strong network that resists flow effectively. A gel-like behavior of cellulose

nanomaterial suspensions at low solid content is observed. It has been found that the higher the concentration, the higher the viscosity. Cellulose nanomaterial suspensions can therefore be good stabilizing agents for emulsions or suspensions since they can trap particles or droplets in the network, preventing them from settling or floating.

The shear rheology flow curve for CNC suspensions is concentration-dependent and usually exhibits three distinct zones (Bercea, Navard, 2000; Ureña-Benavides et al., 2011; Shafiei-Sabet et al., 2012) as shown in Figure 6. At low concentrations, the viscosity is mostly constant, indicating a Newtonian behavior, and a slight shear-thinning behavior is observed when increasing the shear rate. At higher concentrations, where the suspensions become lyotropic, a typical behavior of liquid crystalline polymers in solutions is generally reported. Shear-thinning is first observed at the lowest shear rates, followed by a viscosity plateau region and then another shear thinning region at higher shear rates. The first shear thinning region has been attributed to the breaking of aggregated domains or clusters. The plateau region indicates that the microstructure of the CNC suspension remains unchanged until a sufficiently high shear flow is applied allowing the alignment of individual particles, which corresponds to the second shear thinning region. At higher concentrations (corresponding to a gel), the viscosity depends on the shear rate according to a power-law relation across the entire shear rate range, a typical gel behavior. Ultrasound treatment severely affects the viscosity of CNC suspensions as shown in Figure 6. Increasing the amount of applied ultrasound energy significantly decreases the viscosity of the sample.

The rheological behavior of CNF suspensions has also been studied, but since it consists of
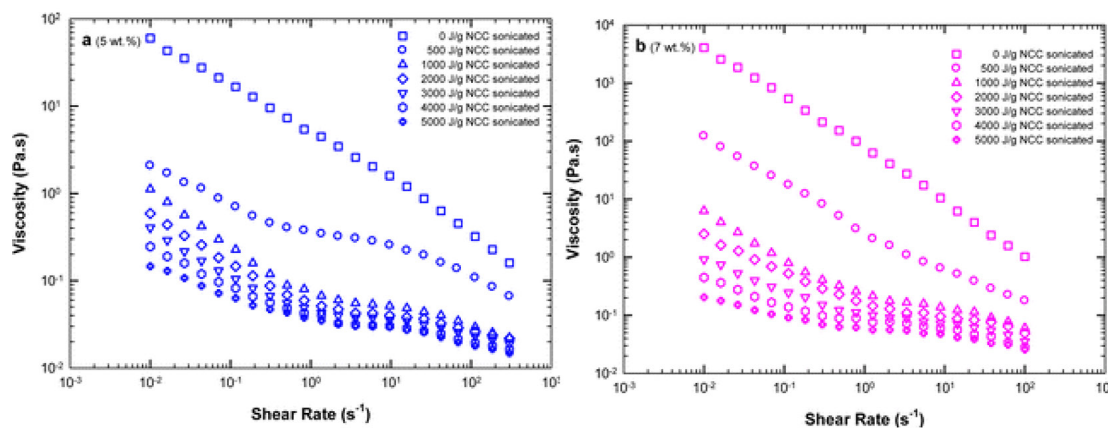
Fig. 6. Effect of ultrasound energy input (level of sonication) on the viscosity for (a) 5 wt% and (b) 7 wt% CNC suspensions prepared from black spruce kraft pulp (Shafiei-Sabet et al., 2012)

aggregated fibril bundles and long fibers of large size variations, it is therefore difficult to perform accurate and reproducible rheological studies (Pääkkö et al., 2007; Iotti et al., 2011; Schenker et al., 2019). Wall slip, heterogeneous flow, and flocculation may occur during the measurement process, which impacts the reproducibility and the reliability of the results (Nazari et al., 2016). The rheological behavior of cellulose nanomaterial suspensions associated with their natural origin opens up potential applications in various sectors. These include the food industry, where they can be used as rheological modifier and fat replacer and low-calorie substitute for carbohydrate additives used as gelling agents, flavor carrier, or stabilizer. In the cosmetics industry, they can be a valuable ingredient providing texture that improves a product's feel in facial and body applications. The rheological properties of cellulose nanomaterial dispersions can find potential applications in cosmetic products for hair, eyelashes, eyebrows, or nails. The paper and cardboard or coating industries can benefit from their ability to stabilize fillers and adsorb dyes. The addition of cellulose nanomaterials to cement and concrete mixes can accelerate the hydration process of cement cure and alter the rheology.

Optical properties

Due to the nanoscale of cellulose nanomaterials, transparent films (nanopapers) or coatings can be obtained if the nanoparticles are densely packed, and the interstices between the fibers are small enough to avoid light scattering. These optically transparent films can find applications in packaging, for flexible device substrates, or for conservation and restoration of cultural heritage serving for filling paper losses on cultural objects and a stabilizing agent for paper. Transparent composite films can also be obtained by impregnating the CNF/CNC film with a transparent resin or mixing if the difference in refractive index between both components is small and/or the domain sizes in the different phases are smaller than the wavelength of visible light. Examples of transparent composite films consisting of poly(lactide) (PLA) and CNC prepared from microcrystalline cellulose (MCC) are shown in Figure 7.

At sufficiently high concentrations, CNC suspensions self-organize into a chiral nematic (cholesteric) liquid crystal phase with a helical arrangement. After slow evaporation of the suspension, semi-translucent films that retain this self-assembled chiral nematic liquid crystalline order formed in the suspension can be produced,
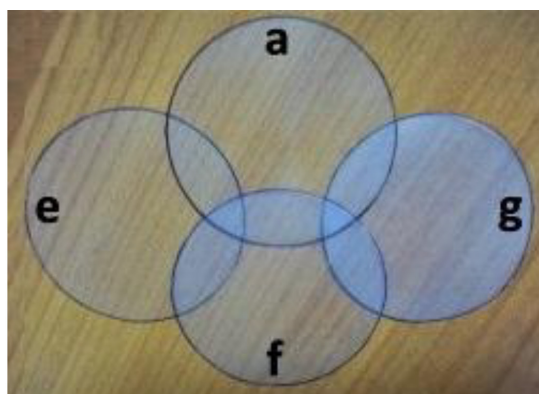
Fig. 7. Optically transparent composite films made of neat poly(lactide) (PLA) (a) and PLA reinforced with 2.5wt% (e), 7.5 wt% (f) and 15 wt% (g) CNC grafted by n-octadecyl-isocyanate (Espino-Pérez et al., 2013)
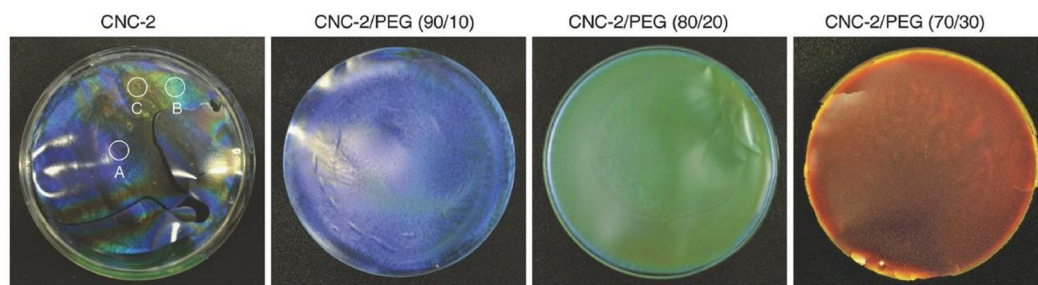

Fig. 8. Photographs of neat CNC and CNC/PEG (PEG content varying from 10 to 30 wt%) composite films showing various structural colors under white light illumination (Yao et al., 2017)

and then CNCs can form chiral nematic, iridescent, colored films. This chiral nematic organization of CNCs is always left-handed and thus, chiral nematic CNC films selectively reflect left-handed light and appear colorful when the helicoidal pitch is of the order of magnitude of the wavelength of visible light, giving a photonic band gap. The pitch can be controlled through ionic strength, temperature, concentration, relative humidity, sulfur content, and exposure to magnetic field or ultrasonic treatment, allowing modulating the film color. Photonic composite films with uniform brilliant structure colors from blue to red were also prepared by assembly of poly(ethylene glycol) (PEG) (Fig. 8). These iridescence properties can be exploited in security papers, birefringent inks, coatings, and cosmetics.

Barrier properties

Nanoscale dimensions and high specific surface area of cellulose nanomaterials can impart improved barrier properties when used as self-standing films, coating for polymers and paper, or reinforcement in polymer composites due to a tortuosity effect towards diffusing gazes. Their high crystallinity and ability to form a dense percolating network strengthen this effect. However, because of their inherent hydrophilic nature, they are generally poor moisture barrier. When exposed to water vapor, the water molecules adsorb in the material and increase the fractional free volume of the film serving as a moving carrier for gases. Under dry conditions (below 70 % RH), good oxygen barrier is observed. Improved performance of such materials can be optimized by tailoring the morphology and

surface chemistry of cellulose nanomaterials or sandwiching them with high moisture-resistant polymers (Wang et al., 2018). The edibility, flexibility, biodegradability, transparency, and possibility to develop active packaging, as cellulose nanomaterials can serve as carriers of some active substances such as antioxidants and antimicrobials, are additional motivations for their use in the packaging field. However, a key need is the achievement of an adequate resistance of cellulose nanomaterial-based packaging films to water vapor and moisture.

Functionalization

Since the cellulose molecule contains many reactive hydroxyl groups, it can be easily chemically modified to impart it specific properties. As a carbohydrate, the chemistry of cellulose is primarily the chemistry of alcohols, and it forms many of the common derivatives of alcohols, such as esters, ethers, etc. It is well-known that the hydroxyl group at the 6 position can react ten times faster than the other OH groups. In order to keep the structural integrity of cellulose nanomaterials, their functionalization needs to be limited to their surface. It is therefore necessary to perform the chemical grafting process in mild conditions, avoiding swelling media and peeling effect of surface-grafted chains inducing their dissolution in the reaction medium.

Because of the nanoscale dimensions of cellulose nanomaterials, the impact of surface functionalization is intensified by the prevalence of surface OH groups. A broad range of opportunities to develop new functional nanomaterials via a chemical reaction strategy, but also through physical methods may be considered (Lin et al., 2012). The surface of charged cellulose nanomaterials, e. g. H_2SO_4-hydrolyzed CNC, can also be tuned profitably using the charged groups through ionic adsorption. A broad range of functionalization methods, including coupling of hydrophobic small molecules, grafting of polymers and oligomers, and adsorption of hydrophobic compounds onto the surface hydroxyl groups of cellulosic nanomaterials, can be used. The most common surface covalent functionalization strategies of CNCs are reported in Figure 9.

The objective of these modifications is to make available cellulose nanomaterials that can be used as reinforcing agents in composite materials or can contribute to specific functions for the development of new nanomaterials, with the target of expanding their applications in the field of functional nanomaterials. Impacted sectors include filtration, biomedicine, and hygiene.

Conclusions

Cellulose is the most abundant polymer on Earth, and it has been widely used for centuries in industries such as paper, textile, chemical, and biomedical among others. The applications of this abundant and renewable bioresource can be further broadened by transforming it into a nanomaterial. Both mechanical and chemical methods can be used to prepare cellulose nanomaterials using a top-down strategy. A bottom-up strategy can also be applied. Cellulose nanomaterials exhibit specific properties, which are described in this manuscript, such as improved mechanical, thermal, and barrier properties, increased specific surface and aspect ratio, special rheological and optical properties, and magnification of the impact of surface functionalization. Individually or together, these distinguishable properties have the potential to provide new applications for cellulose. The industrial production and commercialization of cellulose nanomaterials are increasing rapidly, and several companies are already producing them at the scale of tons per day. Nevertheless, extraction of cellulosic nanomaterials remains
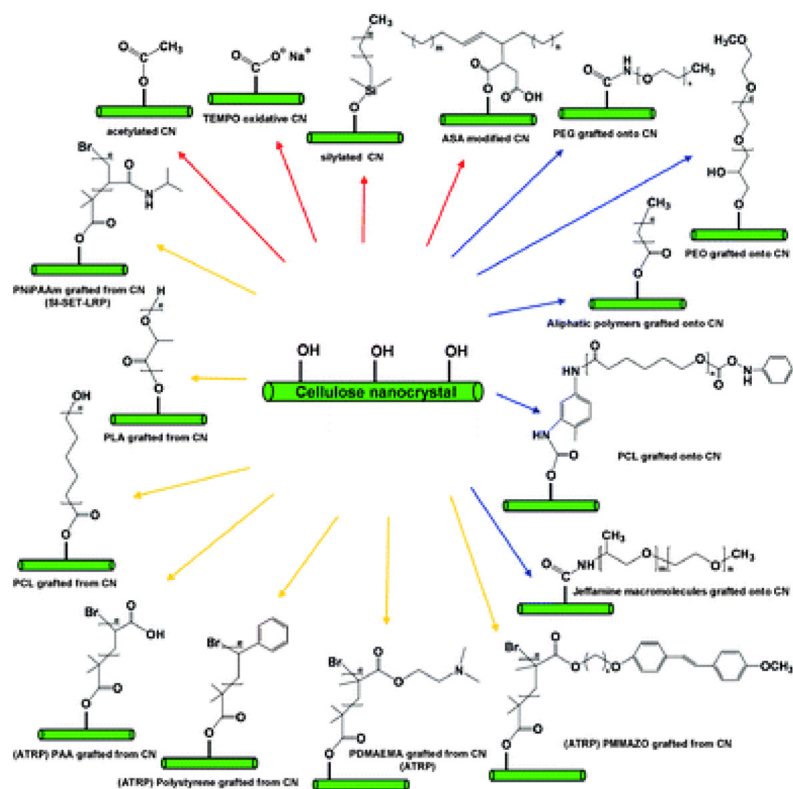
Fig. 9. Common surface covalent chemical modifications of cellulose nanocrystals. PEG: poly(ethylene glycol); PEO: poly(ethylene oxide); PLA: poly(lactic acid); PAA: poly(acrylic acid); PNiPAAm: poly(*N*-isopropylacrylamide); PDMAEMA: poly(*N, N*-dimethylaminoethyl methacrylate) (Lin et al., 2012)

an expensive and energy-consuming process. The challenges are mainly related to affordable large-scale production and cost-effective surface modification pathways.

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