



Tuning supramolecular interactions of cellulose nanocrystals to design innovative functional materials



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ABSTRACT

Cellulose nanocrystals (CNCs) are obtained from controlled hydrolysis of cellulose microfibrils. They consist in crystalline nanorods that have attracted much attention due to their biocompatibility, biodegradability, renewability and mechanical properties but also in reason of their interaction capacities. This review gives some insights into the versatile applications of CNCs arising from the non-covalent interactions they can establish to build and tune CNC-based supramolecular assemblies. The paper describes the use of (i) electrostatic interactions, (ii) van der Waals and hydrogen bonds and (iii) the uneven exposition of chemical groups due to crystalline organization of nanorods and their various form factors as approaches for the elaboration of functional materials. The interaction capacities are reported by emphasizing the specificity of CNCs and selected examples of CNC-based materials are described to illustrate each type of interaction.

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1. Introduction

Cellulose is one of the most abundant natural polymers produced in the biosphere and its use has very long history since it is involved in many applications and industrial products. The main sources of cellulose are wood and plant fibers but other sources are also possible including algae, fungi bacteria and even some marine animal (tunicates for instance). Regardless its origin, cellulose is a high molecular weight homopolymer of β -1,4-linked anhydro-D-glucose. The condensation reaction between two glucopyranoses in their β forms leads to the creation of a C₁-O-C₄ linkage and the disaccharide cellobiose that is the repeating unit of the cellulose structure (Fig. 1A). Cellulose chains are organized as compact semi-crystalline fibrils due to the formation of intra- and inter-chain hydrogen bonds and van der Waals interactions. The aggregation of cellulose chains is related to the biosynthesis process. Cellulose is synthesized at the surface of the plasma membrane by rosette-shaped enzymatic complexes comprising cellulose synthases (CESAs). (Vincent, 2002) Polymerization and extrusion of cellulose chains is closely followed by their aggregation to form the crystalline structure. Biosynthesis process imposes a directional asymmetry yielding in the location of hemiacetal groups on one end of the microfibrils (reducing end) while at the other

end, the hemiacetal groups are involved in glycosidic linkages to form the non-reducing end. Regarding the dimensions, microfibrils have nanometric sizes and, depending on the biological origin, the cross-section might vary from 2 to 50 nm (Fig. 1C). Some constraints may occur during the biosynthesis process inducing the formation of less ordered zones (amorphous zones) distributed all along the elementary fibrils. When controlled hydrolysis of the microfibrils is performed, the crystalline parts are released to produce stiff nanorods, referred as cellulose nanocrystals (CNCs) (Fig. 1B). They have been the subject of intense research since their discovery in the early 50's (Rånby, 1949; Rånby, 1951; Rånby and Ribl, 1950) yielding numerous reports that have tremendously increased in the two last decades (Charreau et al., 2013; Habibi et al., 2010; Klemm et al., 2011; Lin et al., 2012; Ni et al. 2016). The impressive interest for these nanoobjects is of course due to their biocompatibility, biodegradability, renewability and mechanical properties but also in reason of their capacity to afford to cellulose chemists a large panel of interaction possibilities. Thus supramolecular interactions through low energies forces can be a powerful tool to implement new and attractive materials. Indeed, due to their chemical structure and their intrinsic organization, CNCs can interact with other components through (Fig. 1D):

- Electrostatic interactions due to the occurrence of ionic moieties on the crystal surface usually arising from preparation procedures.

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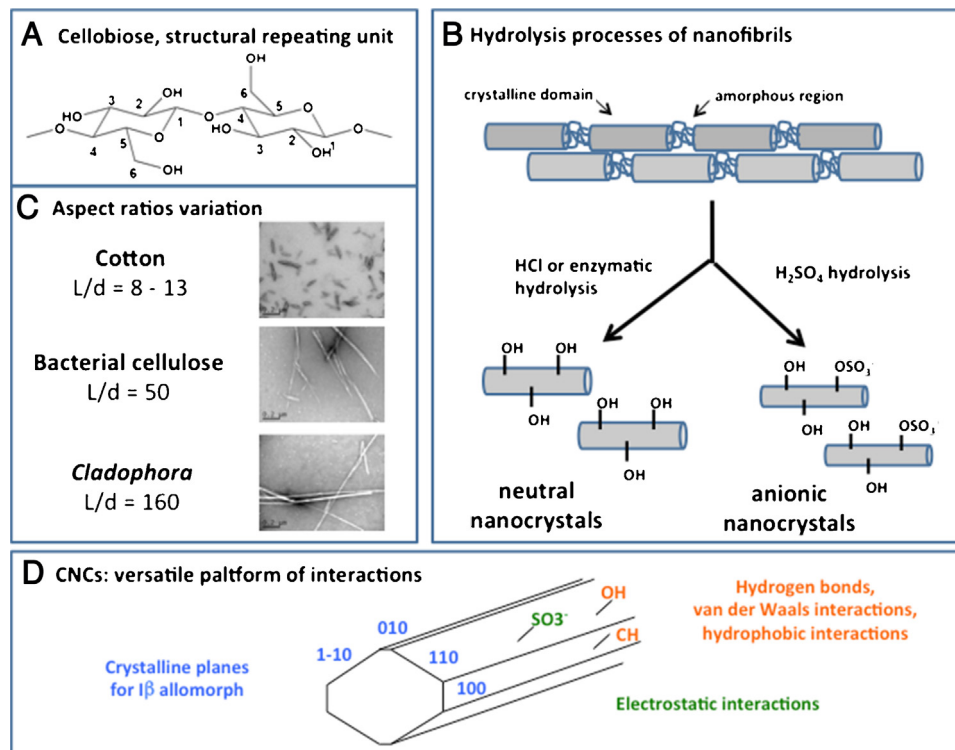


Fig. 1. Schematic representation of (A) the chemical structure of cellobiose, the repeating unit of the cellulose, (B) the isolation methods for CNCs from cellulose fibers, (C) TEM images (les images ne sont pas visibles pour moi !) of CNCs from different sources and the average aspect ratio (Length/diameter), and (D) schematic depiction of crystalline faces of CNCs and potential interactions.

- Hydrogen bonds or van der Waals interactions thanks to the hydroxyl or aliphatic groups of glucose monomers.
- Uneven exposure of chemical functions on the crystal faces resulting in hydrophobic or hydrophilic character of the faces.

The aim of this review is to give more insights into the interaction capacities of CNCs by emphasizing their specificity and their use as versatile platforms through non-covalent interactions to build and tune supramolecular assemblies based on CNCs. Selected examples of CNC-based materials are described to illustrate each type of interactions.

2. Preparation and characterization of CNCs

CNCs, which are also referred as cellulose whiskers, cellulose nanorods or nanocrystalline cellulose, are obtained by controlled hydrolysis of cellulose with harsh acids, generally sulfuric (H_2SO_4) or hydrochloric (HCl) acid. The first report of preparation of stable colloidal suspensions of CNCs was achieved in the early 1950's (Rånby, 1949; Rånby, 1951; Rånby and Ribí, 1950). The occurrence of CNCs was demonstrated by the combination of transmission electron microscopy (TEM) that detected rod-shaped nanoparticles, and electron diffraction that confirmed the crystalline structure of the nanoobjects. Since that time the interest for CNCs has increased due to their possibility to act as model surfaces for studying cellulose structure and properties. These biobased nanoobjects have been the matter of tremendously increasing interest that culminates during the two last decades, due to their amazing properties and the rising interest for biobased materials (Araki, 2013; de Souza Lima and Borsali, 2004; Isogai, 2013; Lin and Dufresne, 2014; Peng et al., 2011). Acid hydrolysis involves the diffusion of acid molecules (hydronium ions) into cellulose fibers, and subsequent cleavage of glycosidic bonds. Amorphous regions have a less ordered structure and are less densely packed, and as they

are more susceptible and available to acid molecules, these non-crystalline domains break up releasing the individual rod-shaped and nanometer-sized crystalline particles. Different strong acids have demonstrated to successfully degrade non-crystalline regions of cellulose fibers such as phosphoric (Camarero Espinosa et al., 2013), hydrobromic (Sadeghifar et al., 2011), nitric acid, and a mixture composed of hydrochloric and organic acids (Habibi et al., 2010). This acid hydrolysis step is followed by centrifugation, dialysis, and ultrasonication.

CNCs can be prepared by acid hydrolysis from a wide variety of sources such as cotton (Araki et al., 2001; Dong et al., 1998; Miller and Donald, 2003), tunicate (De Souza Lima et al., 2003; Favier et al., 1995; Kimura et al., 2005; Terech et al., 1999), algae (Hanley et al., 1992; Revol, 1982; Roman and Winter, 2004), bacteria (Grunert and Winter, 2002; Revol et al., 1992; Tokoh et al., 1998), wood (Araki et al., 1998; Beck-Candanedo et al., 2005; Fengel and Wegener, 1984; Revol et al., 1992) and microcrystalline cellulose (Araki et al., 1999). CNCs generally retain their native cellulose I polymorph after hydrolysis. (Bondeson et al., 2006; de Mesquita et al., 2011; Elazzouzi-Hafraoui et al., 2008) Nevertheless, their properties can be strongly impacted by the processing hydrolysis conditions, i.e. acid concentration, acid-to-fiber ratio, hydrolysis time, hydrolysis temperature, sonication time or ultrasonic irradiation intensity (Beck-Candanedo et al., 2005; Bondeson et al., 2006; Dong et al., 1998; Elazzouzi-Hafraoui et al., 2008; Lin and Dufresne, 2014). The geometrical dimensions (length, L and diameter, d) depend strongly on the starting material. Thus, CNCs with different aspect ratios can be produced, e.g. 200 nm long and 5 nm in lateral dimensions (Fengel and Wegener, 1984) from cotton and up to several microns long and 15 nm in lateral dimensions (Favier et al., 1995; Terech et al., 1999) from tunicate. In fact, there is a direct correspondence between the length of the CNCs and the LODP (Level Off Degree of Polymerization) of the initial fibers, as demonstrated by Nishiyama et al. (2003). The hydrolysis treatment with sulfuric

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