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Nanocellulose Bio-Nanomaterial: A Review

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Abstract

Nanocellulose is a unique and gifted natural material with hierarchical structure of cellulose extracted from various natural cellulose sources like plants, animals and bacteria. Nanocellulose has gained a large amount attraction due to its remarkable properties like natural and renewable, biodegradability, biocompatibility, low cytotoxicity, high strength, modulus, high surface area, high aspect ratio, chemical functionality, dimensional stability, thermal stability, etc., Nanocellulose is available in three different types, viz cellulose nanocrystals (CNC), cellulose nanofibrils (CNF) and bacterial cellulose (BC). Due to its physical, surface chemistry and biological property it has been widely used in various biomedical applications (medical implants, tissue engineering, cardio vascular application, drug delivery), paper, packaging and electrical field. This article gives an overview about the nanocelluloses.

Keywords: Hierarchical; Cellulose; Nanocrystals; Biodegradability

Introduction

Cellulose is the most abundant linear polymer as cellulose chains occurring naturally on earth as lignocellulosic biomass. It is a high molecular weight homopolysaccharide complex having hierarchical structure. Cellulose structure is made by repeating β (1-4)-bound D-glucopyranose units with a degree of polymerization of 10000 to 15000 [1]. Linear cellulose chains combined with hemicelluloses and lignin, which forms the cell walls of the wood and higher plants. Cellulose is present in higher plants, certain types of bacteria and fungi as unidirectional parallel orientation chain having one reducing end and non-reducing end [2]. Cellulose is present as two forms such as crystalline and amorphous. In crystalline region the cellulose chains are arranged as highly ordered one (made of cellular hierarchical biocomposites) and in amorphous region the cellulose chains are arranged as disordered one (made of hemicelluloses, lignin, waxes, extractive and trace elements) [3,4]. Presence of three hydroxyl groups in each glucose unit is the important characteristic property of the cellulose. The hydroxyl groups are present in 2, 3 and 6 positions of the glucose unit. The hydroxyl group present in the 6th position is acts as a primary alcohol whereas the other two hydroxyl groups acts as secondary alcohol. The reactivity of the hydroxyl group are varies with its position. The hydroxyl group present in the 6th position can react 10 times father than the hydroxyl group present in position 2 and 3; the hydroxyl group present in the position two can react twice than the hydroxyl group present in the 3rd position [5,6]. Steric effect is induced in the cellulose by the attachment of the alkyl group in the hydroxyl groups. Cellulose chain is stabilized by the two types of hydrogen bonds such as intramolecular and intermolecular. In cellulose the intramolecular hydrogen bond is formed between the hydrogen borne by the OH group of the C3 carbon and ring oxygen of the adjacent glucose unit (O5), whereas the intermolecular hydrogen bond is formed between the hydrogen of the OH−6 primary hydroxyl and oxygen in position O3 in a cycle of a neighboring unit, as well as the hydrogen of OH−2 and oxygen in position O6 [2].

These hydrogen bonds are having an important role in maintaining the cellulose as hierarchical structure and increase the stiffness [7]. The hierarchical structure of cellulose [2] is shown in figure 1.

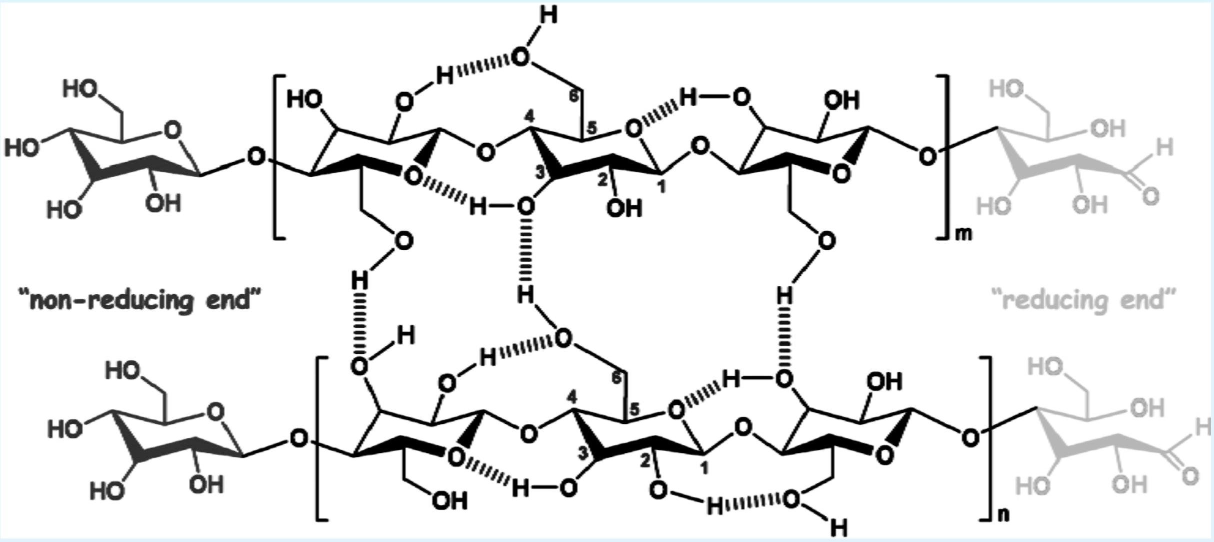

Figure1. Hierarchical structure of cellulose.

Various factors such as maturity, separating processes, microscopic and molecular defects such as pits and nods, type of soil and weather conditions under which they were grown are affect the fiber properties [4]. Nanocellulose is a product isolated from the natural cellulose which is present in the plants, animals and bacteria.

Due to its hierarchical structure and semi crystalline nature of cellulose, nanoparticles can be extracted either top-down mechanical process or chemical induced deconstructing strategy by converting the large units (cm) into the small unit (nm).

Nanocellulose is classified as three types. They are

1. Cellulose nanocrystals (CNC) – nanocrystalline cellulose, cellulose whiskers, nanowhiskers and nanorod
2. Cellulose nanofibrils - nanofibrillated cellulose, micro fibrillated cellulose (MFC), and cellulose nanofibers
3. Bacterial cellulose [8-9]

Cellulose nanocrystals refers to short and rigid rods; cellulose nanofibril refers to long, thread-like cellulose nanofibers and bacterial cellulose refers to ribbon-like bacterial nanocellulose (BNC).

Cellulose nanocrystals and cellulose nanofibrils can be extracted from various sources such as wood, cotton, hemp, flax, wheat straw, sugar beet, potato tuber, mulberry bark, ramie, algae and tunicin. Different nanocellulose types [2,10] are shown in Figure 2.

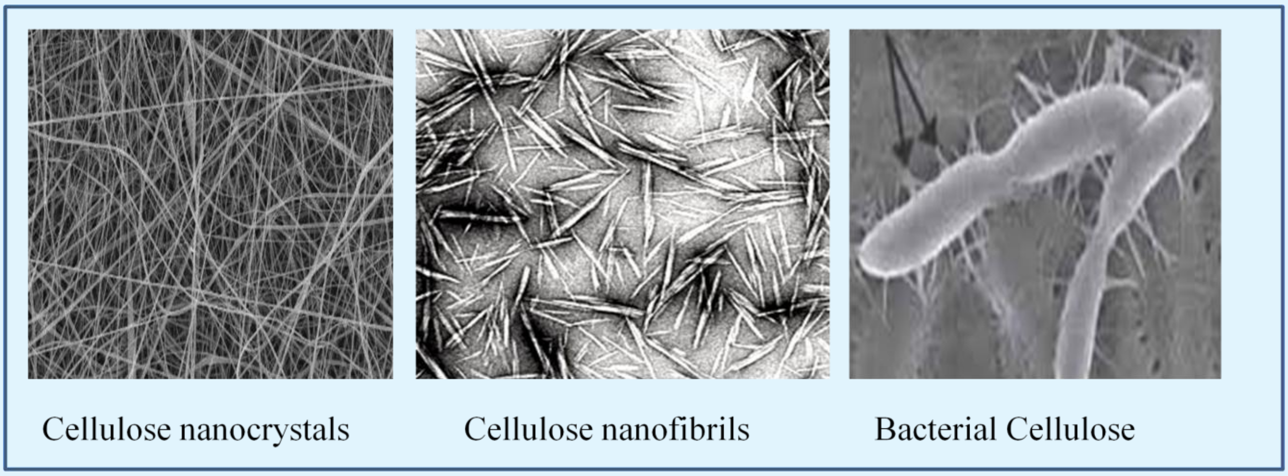

Figure2. Structure of different nanocellulose.

Isolation of Nanocellulose

Nanocellulose as Nanocellulose fibrils can be isolated from the natural source by various mechanical process like high pressure homogenization, high intensity ultrasonication, high pressure refiner, grinding and mechanical cutting with or without post enzymatic treatment.

Nanocellulose as crystalline nanocellulose can be isolated from the natural source by chemical reaction like acid hydrolysis, enzymatic pretreatment, introduction of charged groups through carboxymethylation reaction and oxidation by 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) [4,10-17].

Mechanical Methods

In mechanical method, multiple mechanical shearing actions are applied to the cellulosic fibers to delaminate the fiber effectively into more or fewer individual micro fibrils. The product obtained by mechanical method is not a single fiber so it is called as nanofibrils or micro fibrillated cellulose (MFC). Pre-treatment can also be done to introduce the electrostatic repulsion between the fibers and prevent the aggregation [18-21].

Chemical Method

In chemical induced destructuring method, acid hydrolysis is preferred. In acid hydrolysis method, strong acid is utilized for extraction of crystalline nanocellulose from natural cellulose by hydrolysis of the cellulose fibers, solubilizing and removal of amorphous regions and preserving the highly crystalline structure by longitudinal cutting of the micro fibrils. A range of acids such as sulphuric acid, phosphoric acid, hydrobromic acid, hydrochloric acid and nitric acid can be used for the acid hydrolysis; among the various acids sulfuric acid is preference one.

During acid hydrolysis, sulfuric acid is acting as hydrolyzing agent with the surface hydroxyl groups of the cellulose by esterification process and introducing the anionic sulfate ester group leads to form a negatively charged group induces the formation of a negative electrostatic layer on the surface of the nanocrystals. This negative electrostatic layer of the nanocrystals promotes the nanocrystals dispersion in water. The negative surface charge due to sulfate group on crystalline nanocellulose can be controlled through temperature and time duration of hydrolysis. Thermal stability of the nanocrystals prepared by acid hydrolysis method utilizing sulfuric acid can be improved by neutralization of the nanocrystals by sodium hydroxide [22-25].

Mechanism of Acid Hydrolysis

In the acid hydrolysis process, the hydronium ions from the acid penetrate the cellulose chains in the amorphous regions leads to cleavage of the hydrolytic linkage in the glycosidic bonds, leaving the crystalline segments intact. The cellulose as crystals can be released after suitable mechanical treatment [22-25].

Other Methods

Other methods for extraction of nanocrystals from native cellulose are

1. Enzymatic hydrolysis treatment
2. TEMPO oxidation
3. Hydrolysis with gaseous acid
4. Treatment with ionic liquids [4,26-29].

Bacterial Cellulose is typically synthesized by bacteria (such as Acetobacter xylinum) in a pure form which requires no intensive processing to remove unwanted impurities or contaminants such as lignin, pectin and hemicelluloses. During the biosynthesis of BC, the glucose chains are produced inside the bacterial body and extruded out through tiny pores present on the cell envelope. With the combination of glucose chains, micro fibrils are formed and further aggregate as ribbons (nanofibers) [2, 30].

Physicochemical Properties of Cellulose and Nanocellulose

Chemically both cellulose and nanocellulose are consists of β-anhydroglucose units, these anhydroglucose units are linked together by β-1-4 glycosidic bonds. Each anhydroglucose unit have two secondary hydroxyl groups at 2, 3 and primary hydroxyl group at 6^{th} position.

Physically both cellulose and nanocellulose are white in color, nontoxic, biodegradable, solid homopolymer, insoluble in water, soluble in organic chemicals, having high tensile and compressive strength [2].

Unique Properties of Nanocellulose Materials

Due to its nanometer size, nanocellulose materials have some unique properties when compare to its bulk raw material (cellulose).

The unique properties of nanocellulose includes

- Nanocellulose can provide extremely larger surface area to volume ratio, results to have very large surface dependent material properties.
- Special morphology
- Spatial confinement

- Crystallinity
- Liquid crystalline behavior
- Specific configuration
- High surface area and energy
- Large fraction of surface atoms
- Lack of imperfections
- Rheological properties
- Mechanical reinforcement
- Surface reactivity
- Biocompatibility, biodegradability and low cytotoxicity [2]

Mechanical Property

Mechanical property of the nanocellulose is based on the crystalline (ordered) and amorphous (disordered) regions. In nanocellulose the amorphous region is responsible for the flexibility and plasticity whereas the crystalline region is responsible for the stiffness and elasticity of the material.

The crystallinity of the nanocellulose is determined by

- Wave propagation
- X-ray diffraction
- Raman spectroscopy
- Atomic force microscopy [2]

Biocompatability and Biodegradability

Being a natural material, nanocellulose is biocompatible whereas biodegradability concern due to lack of cellulolytic enzymes in the cellulose, it is not readily degradable but slowly degradable. The degree of degradation, absorption and immune response may be affected by its unique properties like crystallinity, hydration and swelling [2,31-33].

Applications

Various applications of nanocellulose are

Biomedical

1. Tissue bioscaffolds for cellular culture
2. Drug Excipient and drug delivery
3. Blood vessel and soft tissue substitutes
4. Skin and bone tissue repair materials
5. Antimicrobial materials
6. Medical implants
7. Tissue engineering
8. Wound-healing
9. Cardiovascular applications
10. Coating applications

Others

1. Paper and board strength enhancement
2. Porous nanocellulosic materials for insulation and packaging
3. As flocculants and retention aids
4. Rheological modifiers
5. Flexible energy storage devices (Batteries and super capacitors)
6. Adaptive, biomimetic nanocomposites [2,4,7,34-54]

Conclusion

In recent years, there has been an intense research to focus on the use of natural polymers (biomass) as a renewable energy source materials. Natural polymers are abundantly available on the variety of natural organisms with the specific properties to meet its needs in the earth. Cellulose in the plant cell wall has been considered as a basic structural matrix. Among the range of polymer materials nanocellulose has gained much attention among the researchers. Numerous availability and nanocellulose material unique properties, created a wide extended variety of applications in the different field. Among the different applications nanocellulose materials are widely utilized in the biomedical applications due to its physical stability, outstanding mechanical property, biocompatibility, low cytotoxicity, high strength, surface area, thermal stability and low degradation rate of cellulose in the human body. Certainly nanocellulose is a gift provided by nature and its biomedical application is still in its first phase. But in near future nanocellulose will provide a good solution for some of the undefeatable challenges of biomedical application field.

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