Chapter 2

NANOCELLULOSE AS GREEN PLATFORM FOR FUNCTIONAL HYDROGELS/AEROGELS

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INTRODUCTION

Sustainable nanomaterial synthesis and their materialization is the outset of modern nanotechnology. Nanocellulose, for the last decades, has become the active area of research for being the greenest material that could be derived from inexhaustible bioresources, possessing invincible properties.The unique combinations of properties by virtue of adaptive functionalities makes them tunable platform that outperform most of the present days synthetic material for myriad of applications.

MACROCELLULOSE TO NANOCELLULOSE

Nanocellulose is a general terminology used for cellulose having at least one dimension in nano regime. The source could be a plant or its any part (bast, fruit, seed, leaf, *etc*), some marine organisms, like certain algae, tunicates etc. and even obtained from certain bacteria as their extracellular product. The morphological level understanding of cellulose mainly unravels how the elementary cellulose bundles or ensembles are arranged within the cell wall. Apparently, as the size approaches to the macro level, the structural interpretation becomes more complex. In native cellulose, the fibrillar units are organized in layers with varying textures. Simply stated, a macro structured cellulose fiber comprises of a well-organized architecture of cellulose fibrils. The supramolecular level structure of cellulose broadly covers the arrangements/ assembly of individual linear chains in the native structure. An elementary fibril is considered to be the smallest morphological unit, which bundle into microfibrils (nanocellulose fibers, NCF) with size ranges around 3-25 nm (vary source-to-source). An illustration of the hierarchical architecture of cellulose fibrils is given in **Figure 1.** These microfibrils are again arranged in an even complex way along with various non-cellulosic cementing agents within the cell wall. A typical hierarchical arrangement of NCF bundles within the cell wall along with lignin, pectin, hemicellulose, etc. are schematically represented in **Figure 2.** Thus, the isolation of NCFs from lignocellulosic fibers involves the removal of all the above-mentioned residues.

TYPES OF NANOCELLULOSE

Nanocellulose, based on its isolation methods, cellulosic source, aspect ratio,etc. vary in their structure, properties and functions. Based on these factors they are variously termed as nanocrystals, nanowhiskers, nanorods, microfibrils or nanofibers, microbial cellulose, etc. Each microfibril consists of statistically alternated crystalline and non-crystalline regions (**Figure 3**). The cellulose chain orientation in these regions are mainly governed by the spatial interactions like hydrogen bonding, Van der Waals interaction, *etc*. and is largely vary depending upon the origin and modes of isolation.

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NC is mainly classified into three subcategories, nanocellulose crystals (NCCs), nanocellulose fibers (NCFs) and bacterial cellulose (BC) (**Figure 3**). NCC is a rod/whisker-like material derived from native cellulose by removing amorphous regions leaving behind the crystalline parts, whereas, NCFs retain most of its amorphous part during the cleavage of hydrogen bonds resulting in nano-sized fibers with high aspect ratio. While both NCCs and NCFs are obtained by top-down synthetic approaches, BC is produced by bacteria *via* a bottom-up approach. *i.e*, BC is biosynthesized by certain bacteria in the form of high aspect ratio nanofibers/nanoribbons entangled at the water/air interface under favourable culturing conditions.

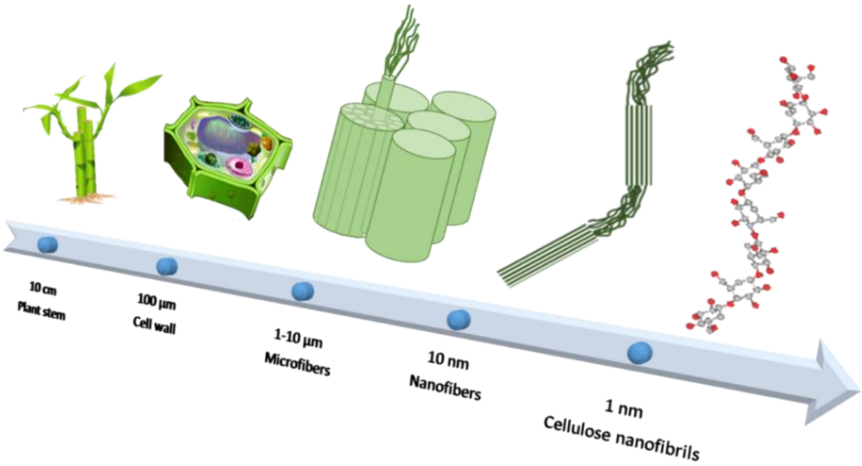

Figure. 1. Figurative illustration of existence of cellulose in plants.

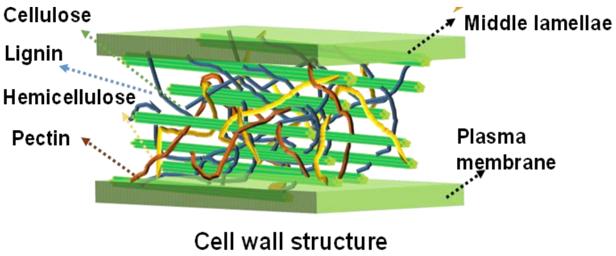

Figure 2. Schematic illustration of the hierarchical structure of plant cell wall.

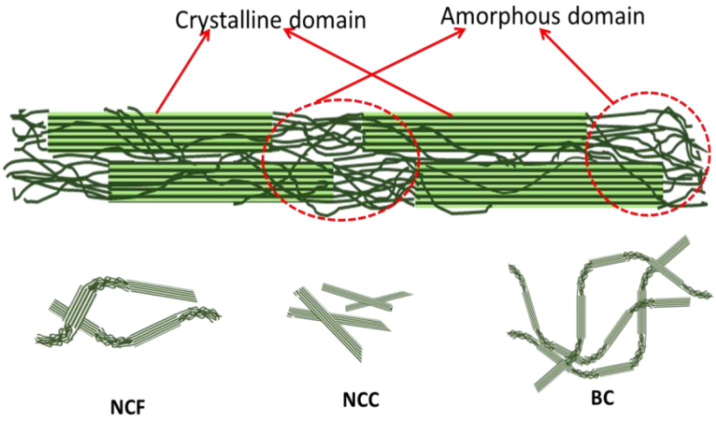

Figure 3. Schematic representation of typical semicrystalline nature of native cellulose with three variations of NC forms, *viz.* NCF, NCC and BC.

SCOPE OF NANOCELLULOSE

The ancient usage of cellulose was mainly limited in textiles and paper board industries where cotton cellulose and wood pulp had been utilized. As time progressed, cellulose has also been exploited as raw material for various commercial polysaccharides and many derivatives such as rayon, cellophane, etc. Later, by the discovery of NCs, it has been disclosed that when the lateral size of cellulose is reduced to the nanoscale, the material can replace many synthetic materials available in the market in terms of their strength, barrier properties, tunability and most importantly biocompatibility. Consequently, the nanoscopic features and properties of NCs have been exploited worldwide in a broad range of applications including, biomedicine, composites, nanoparticle synthesis, sensors, environmental monitoring, pollution control, etc. However, selecting the appropriate characteristics/properties of the cellulose material is vital for NC to be applied in different applications.

NANOCELLULOSIC HYDROGELS/AEROGELS AS FUNCTIONAL MATERIALS

The prime properties of cellulose microfibrils are its flexibility and propensity for entanglement owing to its high aspect ratio nanofibers and a greater extent of hydrogen bonding. An aqueous slurry/suspension of NCC/NCF/BC above a critical concentration can form three dimensional networks that hold water in their matrix called hydrogel. This gel upon removal of the solvent results in fine porous structured light-weight materials called aerogels. Hydrogels and aerogels of NCC/NCF/BC provide ideal platforms that could be materialized for various applications in environmental, energy and biomedical field. It should be taken into account that a regular oven drying leads to collapsed network structures by the capillary induced shrinkage of pores resulting in xerogel formation. Therefore, the removal of solvents from hydrogels often carried out by means of lyophilization or supercritical drying, which involves sublimation of water. Solvent exchange by less polar solvents followed by oven drying is an alternative to these two methods[11]. All these approaches help to maintain the three-dimensional skeletal structures intact more or less, avoiding capillary effect to a great extent.

An NCF/BC hydrogel can find potential applications in biomedical fields as drug-delivering agent, wound dressing material, tissue regeneration scaffold, bioimplant, *etc*, whereas, the corresponding aerogels are widely employed where potent captivation of external nanomaterials and molecules, barrier properties, *etc* are necessitated. The barrier properties of NCF/BC aerogels include thermal and acoustic insulation. These properties are greatly affected by the density, pore structure, and alignments of NCF/BC microfibrils. It has been found that NCF has thermal conductivity ranges in 0.2–0.5 W m^{-1} K^{-1} whereas, the aerogel made out of the BC can have thermal conductivity as low as 0.031 W m^{-1} K^{-1} (almost similar to that of silica aerogel), indicating that they are highly suitable for thermal insulation applications. This is because of the inclusion of a large volume of air (sometimes >99%) within the porous channels.

Since NCF based aerogels can attain specific surface area exceeding 300 m^2/g, it could be used as high class and green absorbents in environmental remediation applications. Additionally, the charged interfaces of NCFs are highly useful for making functional hydrogels such that they can accommodate a variety of functional nanomaterials. High aspect ratio NCFs can also impart flexibility and transparency to the fabricated device as per the need. NCF/BC could be employed either single-handed or in combination with various functional nanomaterials for the removal of many airborne and waterborne pollutants like heavy metals, organic dyes, oils, toxic gases, *etc*.

CONCLUSION

This chapter summarizes the basic concepts of nanocellulose materials and their implications as promising hydrogels/aerogels scaffolds in selected areas. Nanocellulose is known to be the future's greenest nanomaterial derived from almost inexhaustible bioresources, possesses unique combinations of properties, such as high entangling nature, excellent biocompatibility, flexibility, mechanical properties, etc. High aspect ratio NC microfibers are known to form biocompatible and flexible organic hydrogels/aerogels capable of accommodating various functional entities, which would otherwise outperform most of the existing products. Owing to their high porosity and surface area along with tunable surface properties and barrier properties render NC/BC-based hydrogel/aerogel a potential candidate to be used in biomedical fields as well as in energy and environmental remediation sectors, as they could be tailored into biocompatible functional scaffolds for various implants, wound dressing, drug delivering agents, customized sorption or filtrating systems for different contaminants *etc*.

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