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Review

# Progress on nanocrystalline cellulose biocomposites

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ABSTRACT

Nanocrystalline cellulose (NCC) a rigid rod-like nanoscale material, can be produced from cellulosic biomass including wood and non-wood based materials in powder, liquid or gel form by acid and chemical hydrolysis. Owing to its unique and exceptional renewability, biodegradability, mechanical, physicochemical properties and characteristics of abundance, the incorporation of a small amount of NCC to the materials matrix (polymer, ceramic and/or metal) enhances the mechanical strength of the latter by several orders of magnitudes. Besides, NCC as a material derived from natural sources has no serious environmental concerns, providing further impetus for the development and applications of this green and renewable biomaterial to fabricate lightweight and biodegradable composites. Surface functionalization of NCC remains the main focus of NCC research to tailor its properties for dispersion in hydrophilic and hydrophobic media. It is of uttermost importance to develop tools and protocols for imaging of NCC in a complex matrix and quantify its reinforcement, antimicrobial, stability, hydrophilicity and biodegradability effect. This review highlights NCC biocomposites, preparation, modification, and potential applications.



**Contents**



## 1. Nanocellulose

One of the most important natural polymers, cellulose, is an inexhaustible raw material, and a main source of sustainable materials on an industrial scale [1–5]. Despite the high global quantity of 700,000 billion tons, only 0.1 billion tons of cellulose is currently being used for the production of paper, textiles, pharmaceutical compounds and others [2–3]. About 36 individual cellulose molecules are brought together by biomass which consists of cellulose, hemicellulose and lignin's into larger units known as elementary fibrils or microfibrils, which are packed into larger units called microfibrillated cellulose [2–4].

Other than renewability and biodegradability, the production of cellulosic fibers in nanodimensions adds promising properties, such as high mechanical performance, hydrophilicity, broad chemical modification, formation of versatile semicrystalline fiber morphologies, large surface area and low density [2–5]. Therefore nanocellulose could

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cover on many range of applications (Fig. 1). On the basis of their dimensions, preparation methods and functions, depend chiefly on the cellulosic source and on the processing conditions [3]. Thus, nanocellulose is generally categorized into three main groups (Table 1).

Recently, the pre-treatment, characterization and search for applications of novel forms of cellulose included crystallites, nanocrystals, nanofibers, nanofibrils and whiskers [2–3]. Novel methods for their production range from top-down methods involving enzymatic/chemical/physical methodologies for its isolation from cellulose sources [6–7]. Meanwhile the bottom-up production of nanocellulose is from raw glucose by bacteria [4].

### 1.1. Nanocrystalline cellulose (NCC)

Nanocrystalline cellulose (NCC) is generated by removal of amorphous sections of a purified cellulose source by acid hydrolysis, often followed by ultrasonic treatment [6]. Cellulose sources are variable, and their degree of crystallinity strongly influences the dimensions of the liberated crystals [2,3]. NCC crystals showed different geometries, depending on their biological sources (Fig. 2). For example, algal cellulose membrane displays a rectangular structural arrangement, whereas both bacterial and tunicate cellulose chains have a twisted-ribbon geometry [9].

The novel NCC opens up the strongly expanding fields of sustainable materials and nanocomposites, as well as medical and life-science devices [10]. The dimensional of NCC structure results in a high surface area hence the powerful interaction of the NCC with surrounding matrices to form a well compatible nanocomposites [10,11]. Sources of NCC are including wood, straw, bagasses, coconut husk, bacteria and sea animals, are widely diverse, providing a wide range of potential nanocomposites properties. In addition, NCC provides the potential for significant surface modification using well-established carbohydrate chemistry, that's why NCC is suitable for advanced applications that take advantage of their high surface area [12]. The reason behind using of NCC is that, its axial Young's Modulus reached to 137 GPa, similar to Kevlar [12,13]. Rather than that, much attention focused on NCC due to its appealing intrinsic properties including nanoscale dimensions (length 200 to 400 nm, diameter less than 10 nm), high surface area, high Young Modulus, low density as well as being available, renewable and biodegradable [14].

Addition of NCC caused composite stiffness and ultimate tensile strength to increase, with a reduction in the elongation at break. It also found that, the addition of NCC generally possesses a relatively low thermal resistance which in consequence did not decrease the composite's thermal stability [10]. Moreover, the biodegradability performance of the NCC composites is dependent on and controlled by the volume of NCC addition [13]. For example, NCC widely applied to reinforce polymer matrices, included polypropylene, poly(vinyl chloride), polycaprolactone, polylactic acid, polyurethane and others. These studies showed that NCC has thermoplastic reinforcing effects [11]. However, the dispersibility of the NCC in the polymer matrix and the compatibility between the composite components still need to improve. Thus, a lot of work done to modify the hydrophilic surface of NCC via functionalization, grafting, crosslinking and use of surfactant.

## 2. Extraction of NCC

### 2.1. Acid hydrolysis

The NCC could be produced via the acidic catalytic hydrolysis approach. Basically, strong acids are oxidizing agents and would dehydrate and redistribute the biopolymers in lignocellulosic materials. The effect of acid hydrolysis on the crystallinity of NCC is also studied and their results showed that, with an increase in acid concentrations, the crystallinity index decreased rapidly [12]. The most common acid catalyst used is sulfuric acid ($H_2SO_4$) [15–17]. The attachment of sulfate groups on the surface of nanocellulose results in negatively charged surfaces above acidic pH [16]. This anionic stabilization via the repulsion forces of electrical double layers was shown to be very efficient in preventing the aggregation of NCC [15]. In addition, the presence of NaOH decreased the crystallinity index of α-cellulose because sodium hydroxide penetrates and swells the cellulose fiber [17].

Greater concentration $H_2SO_4$ enhanced the hydrolysis degree of NCC, including amorphous component and crystalline component of NCC [18,19]. In addition, the amorphous component of NCC more easily decomposes in the presence of $H_2SO_4$ catalyst than a crystalline component of NCC due to their disorder microstructure [19]. Thus, the hydrolysis degree of amorphous NCC rises with $H_2SO_4$ concentration increasing and benefits to its yield productions [20]. However, the crystalline component of NCC is gradually hydrolyzed with acid concentration further increasing, which often leads to lower production yield. For example, the conventional process for preparation of NCC involves the use of 63.5% (w/w) $H_2SO_4$ for the hydrolysis of microcrystalline cellulose (MCC) which results in the whiskers NCC with a length between 200 and 400 nm, having a width lesser than 10 nm and a yield of 30% [21].

However, the conventional acid hydrolysis process for the production of NCC may be environmentally hazardous due to the effluents generated in their production and also the resultant NCC may be chemically modified by sulfate groups on its surface [19–22]. In case of production of NCC from wood pulp, energy intensive mechanical means (refining, homogenization, cryo-grinding) of fibrillation are being followed wherein physical, chemical and/or biological pretreatments are employed to reduce energy consumption. As concerned to the published articles, 75% of them reported on the extraction of NCC with H2SO4. Other acidic medium also used as catalyst such as HCl

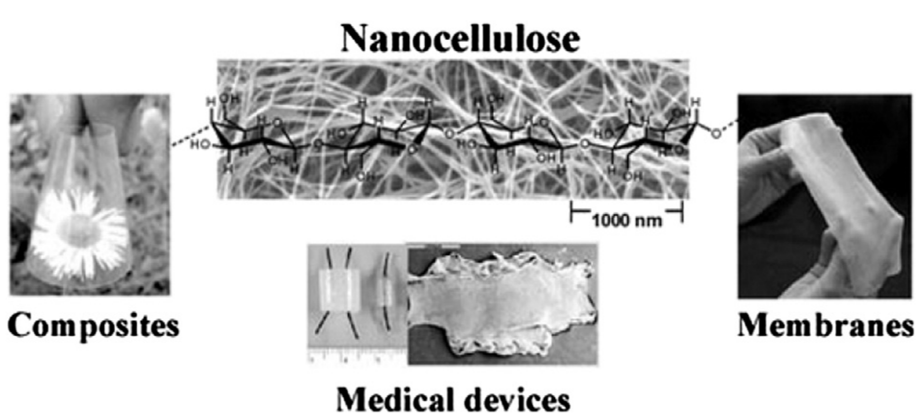


**Fig. 1.** General application of nanocellulose [8].