Overview of cellulose nanocrystals: extraction, physicochemical properties and applications

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Abstract. The development of cellulose nanocrystal (CNC) has attracted significant attention over the past few decades owing to its unique and superior properties. To date, acid hydrolysis process is still the most frequently used method to treat cellulosic material for the production of CNC. The main reason being that acid hydrolysis method is highly effective in removing the amorphous regions within the cellulose microfibrils while retaining the crystalline domains, thereby yielding CNC. CNC exhibits various outstanding characteristics such as large specific surface area, high aspect ratio, good thermal and mechanical properties, lightweight, high stiffness and high tensile strength. Owing to this, CNC has been subjected into a wide array of research, including implementation as reinforcing agent in nanocomposites and sustainable bio-materials to be utilized in various potential areas of industrial application. Overall, this review summarizes the current knowledge on the isolation, physicochemical properties and applications of CNC.

1. Nanocellulose

Nanocellulose refers to cellulose in the nanometer scale, also known as cellulose nanomaterial which commonly derived from disintegration of the naturally occurring biopolymer or produced by bacteria [1]. Nanocellulose can be divided into three main types; cellulose nanocrystal (CNC), cellulose nanofibril (CNF) and bacterial cellulose (BC). Although all these three types are relatively similar in chemical composition, but somehow different in morphological structure, particle size, crystallinity and physicochemical properties due to the varied sources and extraction methods [2]. The elementary fibrils in cellulose fiber generally consist of highly ordered regions (crystalline structure) and disordered regions (amorphous structure) which can be segregated through mechanical, chemical and enzymatic methods in order to produce either CNF or CNC. In general, Nanocellulose exhibits excellent physical and mechanical properties due to the presence of hydroxyl groups and strong hydrogen bonding network [3].

1.1. Cellulose Nanocrystal (CNC)

Cellulose nanocrystal with other terminologies also known as nanocrystalline cellulose (NCC), cellulose nanowhisker (CNW) or rod-like cellulose microcrystals. Individual cellulose molecules are linked together to form elementary fibrils. Each elementary fibril contains nano-sized and highly...
crystalline rod shaped fragments, commonly referred as CNC [2]. Each CNC rod generally has a width about 2-30 nm and length of few hundred nanometers. However, the physical dimensions of CNC rod are vary depending on several factors, including the source of the cellulose, hydrolysis conditions and the ionic strength of acid. CNCs have high distribution in length due to the diffusion-controlled nature of the acid hydrolysis process [4]. CNCs can be extracted from many different cellulosic resources such as cellulose enriched pulp, microcrystalline cellulose and cotton via acid hydrolysis method [5].

2. Extraction of CNC

The initial concept of isolating CNC using acid hydrolysis method was introduced by Nickerson and Habrole [6]. In the 1950s, a stable colloidal suspension of CNC was first obtained by Råbhy through a controlled sulfuric acid-catalyzed degradation of cellulose fibers [7]. During the controlled acid hydrolysis process, amorphous regions of elementary nanofibril are preferentially hydrolyzed when the hydronium ions infiltrate the cellulose chains in amorphous domains, triggering hydrolytic cleavage of the glycosidic bonds by releasing individual crystallites while leaving the crystalline domains intact [4].

There are many different types of strong inorganic acids such as sulphuric acid (H₂SO₄), hydrochloric acid (HCl), phosphoric acid (H₃PO₄), hydrobromic acid (HBr), phosphotungstic acid (PTA) and nitric acid (HNO₃) have been successfully used for the production of CNCs [8]. All these strong inorganic acids are diluted to the desired concentration before treating with cellulosic fiber under strictly controlled conditions of temperature, agitation speed and reaction time. Among all the inorganic acids, H₂SO₄ and HCl are the most common inorganic acids used for CNC preparation. Many studies have reported that 55-65 wt. % of H₂SO₄ or 25-30 wt. % of HCl at moderate temperature (40-60 °C) were applied in acid hydrolysis along with subsequent mechanical and ultrasound disintegration of the hydrolyzed cellulose in aqueous suspension [9].

However, there are many alternative methods in extracting and improving the yield of CNC have been introduced since the beginning of twenty-first century such as cation-exchange resin-catalyzed hydrolysis [10], ultrasonic-assisted sulphuric acid hydrolysis [11], two-stage mildly acidic ionic liquid-mediated hydrolysis [12] and acidic deep eutectic solvents (DESs) treatment [13]. Owing to the emergence of DES, choline chloride (ChCl) has been successfully combined with organic acids such as oxalic acid, p-toluensulfonic acid monohydrate and levulinic acid to produce acidic DES which used in acid hydrolysis of cellulosic fibers. In addition, Sirviö reported that these acidic DESs could provide a green alternative pathway for CNC production [13].

3. Physicochemical properties of CNC

3.1. Specific surface area

Specific surface area (SSA) can be defined as the total surface area of a material per unit of mass. The SSA of a non-porous material increases as the size of a particle decreases. For nanocellulose, the SSA can be measured from the average geometrical dimensions of the particles, assuming that each CNC rod-like geometry with a density of 1.5 or 1.6 g/cm³ [4]. Moreover, the SSA can be also determined by Brunauer-Emmet-Teller (BET) surface area analysis from nitrogen gas adsorption isotherms at 77k using a surface area or porosity analyzer [14]. However, the determination of SSA using nitrogen gas adsorption isotherm is often inaccurate due to the irreversible aggregation of the CNC upon oven drying [4]. Spray dried CNC, freeze dried CNC and spray-freeze dried CNC extracted from bleached kraft pulp with SSA of 0.5 m²/g, 17.2 m²/g and 56.4 m²/g, respectively were reported by Abdallah and Kamal [15]. Therefore, the CNC with high specific surface area is potentially useful in various nano-applications, especially applied as porous template for the preparation of aerogel [4].

3.2. Thermal stability

Thermal stability is one of the important physical property which plays an essential role in preparation of the CNC reinforced nanocomposites. The thermal stability of CNC can be determined using thermogravimetric analysis (TGA). For CNC, the thermal stability is varied depending on the types of surface chemistry [16]. For instance, the introduction of negatively charged sulphate half ester groups
on the CNC surface obtained via dilute acid hydrolysis using sulphuric acid significantly affect the thermal stability of CNC. During the acid hydrolysis, partial esterification of hydroxyl groups of cellulose along with substitution by sulphonic acid groups (-SO$_3$H) occur, significantly reduces the thermal stability of CNC. Morais reported that the pure cellulosic fiber obtained from cotton linter decomposes with a maximum rate at 340 °C while the isolated CNC degrades at 288 °C [17]. Moreover, the increasing of sulfonic acid groups content in CNC also leads to lower thermal stability [18]. However, the thermal stability of CNCs isolated via HCl and H$_3$PO$_4$ acid hydrolysis tend to be higher in which decompose at 325 °C and 350 °C respectively. Therefore, CNC with lower thermal stability may limit its use as reinforcing filler to produce bio-nanocomposites at high temperature in manufacturing process [16].

3.3. Aspect ratio
Aspect ratio is defined as the ratio of the length to the width. It is an important parameter to determine the anisotropic phase formation and reinforcing properties. In general, the aspect ratio of CNCs which isolated from cellulosic materials such as cotton, sisal, flax and jute via acid hydrolysis ranging between 16 and 50 [2]. Some literature reported that the CNC prepared from the rare marine creatures, also known as tunicates has higher aspect ratio (70-100) [19]. In fact, CNC with higher aspect ratio has greater reinforcement capacity when added into the nanocomposite materials. Consequently, this can improve the mechanical properties of the nanocomposite such as tensile modulus due to the alignment of high aspect ratio filler particles which increases the surface area of the fillers [20]. Owing to this, CNC with higher aspect ratio has great potential in filter and composite membrane applications for air and water purification [4].

4. Application of CNC
CNC has been used in various applications owing to its availability and remarkable physical properties. For instance, CNC exhibits high thermal conductivity and low coefficient of thermal expansion which may suitable for the use in applications such as electronic devices and packaging. Moreover, CNC often chosen as the nano-sized filler that act as reinforcement to improve the mechanical and barrier properties of the matrix in bio-nanocomposite material. This is due to the CNC generally has a high aspect ratio and large specific surface area that could provide better reinforcing effects [21].

CNC has also been applied in the production of hydrogels and aerogels owing to its light weight and toughness. The hydrophilic surfaces of CNC serve as building blocks to form the gels, which enables crosslinking with other different metals, organic materials and polymers via hydrogen bonding, covalent bond or ionic interactions [22]. In coating industry, the durability of water soluble paints can be improved by incorporating CNC. The reason being that CNC acts as the thickening and stabilizing agent that enhances the mechanical properties, scratch resistance and UV-shielding property [23]. CNC is also serving as an important cosmetic ingredient that improves the sensation and nourishment in facial and body applications. This is owing to the CNC having high dispersion stability in water and water holding capability for a long period of time [4]. Furthermore, CNC can form a very dense and resistant mats because of its strength to weight ratio which is eight times stronger than stainless steel. This feature allows the CNC to be applied in manufacturing of bullet-proof vests and body armor.

In medical application, CNC is widely utilized due to its excellent physical properties such as extended surface area, surface functionality, biocompatibility, biodegradability and low toxicity. This allow the CNC to be used in drug delivery, enzyme or protein immobilization, tissue skeleton for cell culture and macroscopic biomaterials [24]. Moreover, CNC has been added into composite membrane and adsorbtant materials for the removal of contaminants. This is attributed to its high aspect ratio and specific surface area, large retention capacity and environmental inertness. Consequently, the pollutants such as heavy metal ions are binding to the active sites, thereby enhancing the filtration efficiency [25].
5. Conclusion

In conclusion, CNC is a rod-like nanoparticle that can be isolated from cellulosic sources through acid hydrolysis process. CNC generally has many outstanding physical properties, including low density, high aspect ratio and specific surface area, good thermal and mechanical properties that plays a vital role as an intermediate in sustainable biomaterials and nanocomposites. Therefore, the transformation of cellulose into CNC is perceived as a milestone in the field of materials science and engineering. This is proven by the global attention in which CNC have been utilized in various applications such as electronic devices, packaging, bio-nanocomposites, medical, filter, membranes and etc.

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References

[1] Shak K P Y, Pang Y L and Mah S K 2018 Beilstein J Nanotechnol 9 2479-2498.
[2] Moon R J, Martini A, Nairn J, Simonsen J and Youngblood J 2011 Chem Soc Rev 40 3941-3994.
[3] Tayeb A, Amini E, Ghasemi S and Tajvidi M 2018 Molecules 23 2684.
[4] Dufresne A 2019 Curr Forest Report 5 76-89.
[5] Beck-Candanedo S, Roman M and Gray D G 2005 Biomacromolecules 6 1048-1054.
[6] Nickerson R F and Habrle J A 1947 Ind Eng Chem 39 1507-1512.
[7] Rånby B G 1951 Discuss Faraday Soc 11 158-164.
[8] Habibi Y, Lucia L A and Rojas O J 2010 Chem Rev 110 3479-3500.
[9] Hubbe M A, Rojas O J, Lucia L A and Sain M 2008 Bioresources 3 929-980.
[10] Tang L, Huang B, Ou W, Chen X and Chen Y 2011 Bioresource Technol 102 10973-10977.
[11] Tang Y, Yang S, Zhang N and Zhang J 2014 Cellulose 21 335-346.
[12] Mao J, Heck B, Reiter G and Laborie M P 2015 Carbohydr Polym 117 443-451.
[13] Sirviö J A, Visanko M and Liimatainen H 2016 Biomacromolecules 17 3025-3032.
[14] Rouquerol J, Avnir D, Fairbridge C W, Everett D H, Haynes J M, Pernicone N, Ramsay J D F, Sing K S W and Unger K K 1994 Pure Appl Chem 66 1739-1758.
[15] Abdallah W and Kamal M R 2018 Cellulose 25 5711-5730.
[16] Camarero Espinosa S, Kuhnt T, Foster E J and Weder C 2013 Biomacromolecules 14 1223-1230.
[17] Morais J P S, Rosa M de F, de Souza Filho M de sã M, Nascimento L D, de Nascimento D M and Cassales A R 2013 Carbohydr Polym 91 229-235.
[18] Lin N and Dufresne A 2014 Nanoscale 6 5384-5393.
[19] Amiralian N, Annamalai P K, Garvey C J, Jiang E, Memmott P and Martin D J 2017 Cellulose 24 3753-3766.
[20] Landry V, Alemdar A and Blanchet P 2011 Forest Prod J 61 104-112.
[21] Azizi Samir M A S, Alloin F and Dufresne A 2005 Biomacromolecules 6 612-626.
[22] Lavoine N and Bergström L 2017 J Mater Chem A 5 16105-16117.
[23] Mascheroni E, Rampazzo R, Ortenzi M A, Piva G, Bonetti S and Piergiovanni L 2016 Cellulose 23 779-793.
[24] Du H, Liu W, Zhang M, Si C, Zhang X and Li B 2019 Carbohydr Polym 209 130-144.
[25] Abouzeid R E, Khiari R, El-Wakil N and Dufresne A 2019 Biomacromolecules 20 573-597.