Nanocellulose: Types, Sythesis and Applications

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Abstract

Based on the current level of ecological awareness, it is difficult to ignore hazardous emissions from any industrial process or human activities because of its adverse impacts on the environment. The substitution of input materials with less- or non-toxic, eco-friendly or renewable raw materials, where possible, has been the concern of various researchers in recent times. Nanocellulose, a subset of nanomaterials obtained from cellulose which is one of the most abundant natural resources globally, has the potential to provide a sustainable, renewable and environmentally benign building blocks, with improved characteristics for diverse applications in the nanotechnology community for the benefit of mankind. In this paper, the three main categories of nanocellulose and synthesis approaches are presented. Its applications in catalysis, thermal insulation, fire retardation, sensing and biosensing, wastewater treatment, pharmaceuticals and medicine are highlighted.

Keywords: nanocellulose, sustainable, eco-friendly. top-down, miniaturization, bottom-up, hydrolysis, ionic liquids, diverse applications

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Introduction

The interdisciplinary field of nanotechnology has witnessed considerable attention from the scientific community in the last decade. This situation is not likely to decline any time soon because of the widely held opinion that nano-based products and devices have superior properties that can be tailored for human utilization in a smarter and more environmentally benign pattern (Bulota, Maasdam and Tiekstra, 2013; Allhoff, Lin and Moore, 2012; Drexler, 1986; Matteo, Candido, Vera and Francesca, 2012; Drexler and Minsky, 1990; Moran-Mirabal and Cranstan, 2015; Iguchi, Yamanaka and Budhiono, 2000). This stance is supported by the remarkable difference, in terms of physical, chemical and biological properties which substances exhibit in the nanoscale range (1-100nm) compared to its bulk state, as well as the wide range of adaptations and applications which nanoparticles offer; from medicine, pharmaceuticals, electronics and computers to catalysis, adsorption, heat transfer, oil and gas, perovskite supported solar panels and batteries, consumer goods and biomedical devices and consumables (Sireesha, Babu, Kiran, and Ramakrishna, 2018; Seyda, 2011; Singh, Manikandan and Kumaraguru, 2010; Ye, *et al.* 2015: Singh, Ahmed and Growcock 2010).

Therefore, nanotechnology refers to the scientific miniaturization and manipulation of natural and engineered materials at the nanoscale range for diverse applications (Allhoff, Lin and Moore, 2010; Drexler, 1986; Moran-Mirabal and Cranston, 2015; Hubbe, Rojas, Lucia and Sain, 2008). Whereas nanoparticles can be defined as ultrafine particles of matter having at least two spatial dimensions in the size range of a billionth of a metre (Horikoshi and Serpone, 2013; Roco, 2011, Drexler and Minsky, 1990; Feyman, 1961; Drexler, 1986). The properties which accounts for its prominence and versatility include: large surface area versus volume ratio, reduced degree of structural defects which enhances its mechanical strength, increased array of surface exposed atoms which enhances reactivity and functionality, increased quantum effects, improved thermal and electrical characteristics, as well as corrosion resistance profile, flexibility, ease of adaptation and plasmonic effects (Xia, 2014; Yang, Hoang and Dridi, 2015; Drexler, 1992).

However, a less restrictive but vital term for the building blocks of devices, systems and products of nanotechnology is **nanomaterials.** A comparative analysis of the numerous definitions of nanomaterials proposed by various standard organisations, industries and governments are available in the literature (Beverhof *et al.,* 2015). One of such definitions adopted by the European Commission states that a nanomaterial is "a natural, incidental or manufactured material containing particles, in an unbounded state or as aggregate or as a agglomerate, in which 50% or more of the particles size distribution have one or more external dimensions in the range of 1nm - 100nm" (Beverhof, *et al.* 2015). It must be noted that the term nanomaterials encompass **nanostructures (NSs), nanostructured materials (NSMs)** and **nanocomposites (NCMs).** Nanostructures are characterized by form and dimensionality whereas the nanostructured materials are characterized by form, dimensionality and composition while nanocomposites comprise two or more of these components.

Classification Of Nanomaterials

The pioneering effort in the classification of nanomaterials, which was done on the basis of the chemical composition and dimensionality was attributed to Gleiter (Tiwari, Tiwari and Kim, 2011). However, the classification scheme presented here is on the basis of the variations in spatial dimensions which is not in the nanorange as Postulated by Pokropivny and Skorokhod (Pokropivny, *et al.* 2007). These include:-
Zero-dimensional nanomaterials (0 D): Presently, this is the simplest building blocks that can be used for nanotechnology devices and products. It includes amorphous or crystalline materials in which all the dimensions (x, y, z) are measured within the nanometric range (d < 100nm). It may be composed of a single or multi-chemical and elements and can exist individually as an entity or incorporated in a matrix or composites. Typical examples of 0D nanomaterials are molecules, nanoparticles, quantum dots, fullerenes, nanocrystalline films, nanopowders, nanoclusters and nanorings.

One-dimensional nanomaterials (1D):- These are amorphous or crystalline needle-shaped materials with one dimension outside the nanoscale range. It may be composed of one or more chemical elements and can exist individually or embedded within another medium. Examples of 1D-nanomaterials are nanofibers, nanotubes, nanorods, nanowire, nanobelts, nanoribbons, nanofilaments, nanowhiskers and quantum wire.

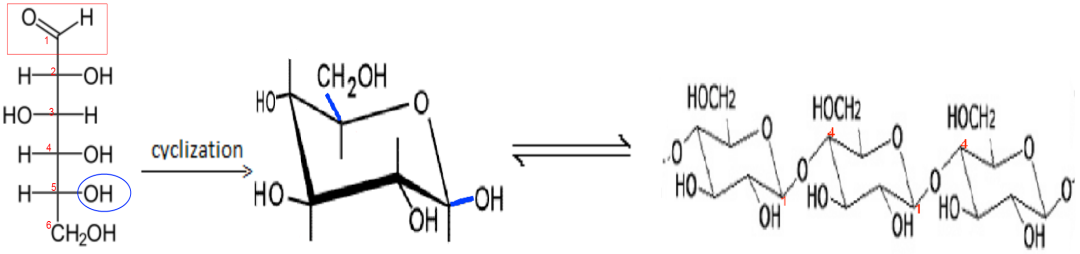
Two-dimensional nanomaterials (2D):- These set of nanomaterials are confined to the nanoscale in one dimension only. It can be amorphous or crystalline, single or multi-layered and consists various chemical components. Examples of 2-D nanomaterials include nanolayers, nanocoatings, nanoplates, nanoprisms, nanosheets, nanowalls, nanodisk, quantum well and graphene.
Three-dimensional nanomaterials (3D):- These are nanomaterials that are not confined to the nanoscale in any dimension. Typical examples are nanoballs, nanocoil, nanocones, nanopillars, multi-nanolayer, nanoflower, diamond, graphite and lonsdaleite.

Cellulose

In line with the growing demand for eco-friendly, sustainable, biodegradable and renewable raw materials for the production of equally eco-friendly goods and services, cellulose, the most universally abundant polymeric polysaccharide presents enormously viable prospects as a versatile biomaterial (Shrestha, 2010; Chirayil, Mathew and Thomas, 2014; Kiro 2015). It has been estimated that cellulose constitutes approximately 1 to 1.5×10^{12} tons of total biomass synthesized annually; including lignin and hemicellulose from the cell walls of woody plants (Klemm, Philip, Heinze and Wagenknecht, 1998; Youssef, Lucia and Rojas, 2010; Moran-Mirabel et al, 2015). Cellulose has crystalline structure, whereas hemicellulose has amorphous structure consisting of xylans, namans, β-glucans and xyloglucans. Lignin is a hydrophobic substance that can be removed by bleaching and chemical pulping (Gharenkhani, Sadeghinezhad, Kazi *et al.,* 2014). Besides, higher plants cellulose is also found in the cell walls of several marine animals, algae, bacteria, protozoa, and some invertebrates (Youssef, *et al.* 2010). Regardless of its source, cellulose consists of a long chain repeating dimers of D-glucose called pyranose, or cellobiose linked by single oxygen atoms with respect to its neighbours between C1 of the pyranose ring and C4 of the next ring. Thus, these linkages are referred to as D-1-4 linkages. Each D-1-4-glucopyranose bears three hydroxyl groups (OH^-) and can form intra- and intermolecular hydrogen bonds which plays a major role in determining the physical properties of the cellulose (Kim, Yun and Ounaies, 2006; John and Thomas, 2008; Chandrahasa, Rajamane and Jeyalakshmi, 2014; Moran, Alvarez, Cyras and Vasquez, 2008, Maleki, Mohammadi and Ji, 2016). Essentially, one of the D-glucose molecule involved flips at 180º angle to allow for the alignment of the hydroxyl groups (OH^-) alongside each other in order to combine to form the linking glucosidic bonds by condensation. The molecular formula of glucose can be represented as $(C_6H_{10}O_5)_n$; where n can assume values between 3000 and 15000 as natural polymer depending on the source (Keshk, 2014; Wang, 2009). Fig. 1 shows the different molecular structures involved in the conversion of D-glucose units to cellulose.

Many properties of cellulose depend on its degree of polymerization or chain length and degree of crystallinity, which in turn varies with source. The higher the degree of polymerization, the greater the resistance to tensile forces. High crystallinity index indicates preference in industrial utilization of the product.

Fig. 1



(a) (b) (c)

(a) D-glucose (b) D-anhydroglucopyranose (c) cellulose

This parameter can be determined using any of the following methods; density measurements, x-ray diffraction, deuterium exchange kinetics, hygroscopicity measurements, hydrolysis, periodate oxidation, substitution, spectroscopic methods – nuclear magnetic resonance (NMR), fouriers transform infrared (FTIR) and Raman vibrational spectroscopies. The response of cellulosic materials varies with different measurement techniques and the accompanying interpretations (Qingqing, 2012).

Cellulose is typically hydrophilic due to the large amount of OH^- groups it possess and can absorb or lose water with corresponding swelling or shrinkage but it is neither soluble in water nor organic solvents. As a raw material, cellulose is widely known for its application in pulp and paper, textile, foods, personal hygiene items, pharmaceuticals and biofuel processing industries (Wang, 2009).

Types Of Cellulose

Several analytical investigations have revealed that there are four polymorphic forms of cellulose, namely: CI, CII, CIII and CIV (Van der Hart and Atalla, 1984; Baker, Helbert, Sugiyama, Chanzy and Langan, 2003; Isogai, Usuda, Kato *et al.*, 1989). Based on the source, cellulose microfibrils consist of two regions; the neatly ordered crystalline region and the disordered amorphous or para-crystalline region, in a variety of shades. The CI allomorph, referred to as native cellulose comprises two distinct crystalline forms Iα and Iβ (Dufresene, 2012; Gardner and Blackwell, 1974; Van der Hart *et al*, 1984; Ciolacu and Popa, 2011; Wang, Yang, Kubicki and Hong, 2016). Cellulose Iα and Iβ can coexist in varying proportions depending on the source of cellulose. Cellulose Iα is the predominant form in algae and microbes that emit cellulose e.g. gluconacetobacter xylinum bacteria, *halicystis* (algae), *cladophora*, *sarcina ventriculi* and *valonia.* Cellulose Iβ is the predominant form in higher plants (wood, cotton, flax) and tunicates (Saxena and Brown Jr. 2001; Van der Hart et al, 1984; Keshk, 2014; Jonas, Farah and Luiz, 1998). The difference between the two varieties of native cellulose include dissimilar molecular shape, hydrogen bonding type and crystal packing type as well as the difference in the pattern of resonance around 106ppm, which is singlet for Iα but doublet for Iβ. In terms of the crystal packing, the unit cell of cellulose Iβ is monoclinic while that for Iα is triclinic crystals (Horii, Yamamoto and Hirai, 1997). Furthermore, cellulose I can be converted to other polymorphic forms via different transformation processes by contacting with certain reagents at elevated temperatures (Moon, Martini, Nairn, Simonsen, Youngblood, 2011; Tort-Agell, 2016).

Nanocellulose

Nanocellulose is a generic term used to describe cellulose-based nanomaterials. It is an emerging and sustainable raw material for the nanotechnology community (Klemm, *et al*. 2011; Charreau, Foresti and Vasquez, 2013; Milanez, Amaral, Faria and Gregolin, 2013; Araujo, Mohajan, Kerr da Silva *et al.,* 2012).

Besides being in the nanoscale range, nanocellulose exhibit potentially versatile characteristics which is viewed by various researchers as the aggregation of advantages over the inorganic counterparts, namely (Klemm, Heublein, Fink and Bohn, 2005; Liu, Deng, Ma and Brian, 2015; Abdul-Khalil, Davoudpour, Nazuruyl *et al.,* 2014; Bulota, Krieitsmann, Hughes and Paltakar, 2012; Saito, Kuramae, Wohlert *et al.,* 2013; Tanpichai, Quero, Nogi and Yano, 2012)
(i) Renewability and biodegradability,
(ii) Wide range of options globally,
(iii) Potential of engaging local farmers,
(iv) Ease of production,
(v) High capacity to interact with neighboring molecules,
(VI) low cost of production,
(vii) Low energy demand,
(viii) Low density,
(ix) Improved mechanical properties (e.g. young modulus, magnetic properties, stiffness, high aspect ratio),
(x) Improved thermal capacities and
(xi) Improved reactive surface

Presently, three categories of nanocellulose had been synthesized, namely: cellulose nanofibers or nanofibrillated cellulose (NFC), cellulose nanocrystals or nanowhiskers or nanocrystalline cellulose (NCC) and bacterial nanocellulose (BNC) (Klemm et al., 2011; Lavoine, Desloges, Dufresne and Bras, 2012; Quero, Nogi, Yano *et al.*, 2012; Goncalves, Cruz, Sales *et al.,* 2016; Vora and Shah, 2015).

NFC: The major industrial source of fibrillated nanocellulose is wood fiber. It can be described as a long, thin and flexible nano-cellulosic particle composed of alternate crystalline and amorphous regions having dimensions in the range of 20-50nm in width and 500-2000nm in length (Moon, Martini, Nairn *et al.,* 2011; Kangas, Lahtinen, Sneck *et al.,* 2014; Kargarzadeh, Ioelovich, Ahmad *et al.,* 2017).

NCC: Nanocrystalline cellulose are highly crystalline (90%) and elongated rod-like particles with limited flexibility. It can be obtained from a wider variety of sources than NFC including plant, tunicate- algae- and bacterial-based cellulose as well as commercial micro-crystalline cellulose. The dimensions of the particle sizes can be in the range of 5-50nm in diameter and 100-500nm in length. However the dimensions and degree of crystallinity depends on the source of the cellulose and extraction conditions (Habibi, Lucia, and Rojan, 2010; Abdul-khalil, Davoudpour, Nazuruyl *et al.,* 2014; Abitol, Rivkin, Cao *et al.* 2016).

Its high crystallinity renders it nearly defect free structurally, which confers on it superior mechanical properties suitable for its usage as reinforcement nanofibres. For example, the young modulus of elasticity for cotton and tunicate derived nanocrystalline cellulose had been reported as 105 GPa and 143 GPa respectively, while the theoretical value is estimated to be 167.5 GPa (Kangardeh, Ioelovich, Ahmad *et al.,* 2017; Chauhan and Chakrabarti, 2012; Panaitescu, Frone, Ghiurea *et al.,* 2011).

The tensile strength, modulus of elasticity and density of nanocrystalline cellulose and other materials are shown in Table 1.

Table 1: Properties of nanocrystalline cellulose relative to other materials (Chauhan and Chakrabarti, 2012)

Material	Tensile strength (GPa)	Elastic modulus (GPa)	Density (kg/m^3)
NCC	7.5	120 - 143	1500
Glass Fiber	8.4	86	2500
Steel Wire	4.1	207	7850
Graphite Whisker	0.021	410	1800
Nanotube	0.011 - 0.063	270 - 970	1330
Kevlar	0.005	124	1400

It must be mentioned that though both NFC and NCC differ in the degree of crystallinity, strong acid, alkali or some other solvent is required to break down the vegetal matrix of pectin, lignin and hemicellulose which makes up the skeletal framework of the cellulose in both cases.

BNC: Bacterial nanocellulose derives its identity from the methods of production, which can be described as an extracellular, non-photosynthetic fermentation process. This process enhances the biocompatibility as well as supports the economical and eco-friendly profile of BNC (Jozala, Lencastre-Novaes and Lopez, 2016; Keshk, 2014; Siquera, Bras, and Dufresne, 2010; Iguchi, Yamanaka, and Budhiono, 2000; Bae and Shoda, 2005).

BNC particle is an organized network of extremely fine, pure and dimensionally uniform ribbon-like structure. It has the same chemical composition as plant cellulose but without the carboxyl or carbonyl groups which are usually introduced to the wood or plant derived cellulose during the purification process (Stevanic, *et al.* 2011).

It had been reported to assume average dimensions in the range of 20-100 nm in width, density of 1600kg/m^3 and modulus of elasticity of 28 GPa (Kamel, 2007; Abitol et al, 2016).

The properties which differentiate BNC from NFC and NCC are its biosynthetic origin, stable nanofibers network, moldability during biosynthesis, non-cytotoxicity and non-genotoxicty, high purity, high resistance to degradation, high polymerization degree and excellent mechanical strength while flexible in the wet state. These properties inspire its novel applications as wound-dressing materials, artificial blood vessels, artificial skin, fuel cell membranes, films for electronic appliances, ,biosensors, electrochemical lithium ion battery, purification of drinking water, air cleaning, contact lenses, cornea replacement, drug delivery and scaffolds for tissue engineering (Qingqing, 2012; Moniri, *et al.* 2017).

Synthesis

There are two broad categories of preparing nanocellulose, namely: top-down and bottom-down approaches (Moon, Martini Nairn *et al.,* 2011). The top down approach which obtains nanocelluloses by extracting cellulose particles from different sources at nanoscale, can be subdivided into three subcategories: mechanical, chemical and mechanical-chemical methods. The bottom-up approach assembles cellulose nanostructures either from the solution state of the cellulose molecules or from biosynthesis process (Klemm, *et al.* 2011). Through either "extraction" or "assembly", nanocelluloses are relatively uniform particles with enormously expanded surface area, which brings in many of the favourable properties that enhances its diverse and novel applications.

Top-down approach

The top-down approach starts with a raw material like woodchips, cotton litters, etc. From these sources, mechanical, chemical or mechanical-chemical methods are used to liberate cellulose microfibrils and nanocelluloses from the native cellulose structures. For high purity raw materials like cotton litters, this means to release individual microfibrils from the large fiber bundles whereas for the raw materials existing in natural composite form e.g. wood chip, the top-down approach means to separate cellulose from its lignin-hemicellulose matrix to derive nanocelluloses particles (Moon, *et al*. 2011).

Mechanical Methods

These processes mainly result in the production of NFC.
High pressure homogenization process: This process utilizes a high pressure homogenizer (50 - 2000MPa) to convert different types of pulp to net-like nanostructures ranging from 25 - 100 nm in the dry state by several passes. The major challenge with this process is its large energy consumption which could be as high as 70,000 kWh/t (Klemm *et al*., 2011; Spence, Venditti, Rojas *et al.,* 2011; Lavoine, Desloges, Dufresne and Bras, 2012). To overcome this problem, the pulp can be subjected to prior pre-treatment with acid hydrolysis, enzymatic hydrolysis or oxidation which can result in the reduction of energy consumption to about 2,000 kWh/t.

Grinding: A typical grinding equipment for cellulose fiber fibrillation as developed by Masuko (Tokyo, Japan) consists of two grinding stones with countersense rotation capabilities. The cellulose slurry is passed between a static grinding stone and a rotating grinding stone revolving at about 1500rpm, severally until the desired dimensions in the nano-range is obtained and further size reduction can no longer be achieved. The basic principle involves the breakdown of cell wall owing to the shearing force generated by the grinding stones (Kargarzadeh, Ioelovich, Ahmad *et al*., 2017; Missoum, Belgacem and Bras, 2013; Lavoine *et al*., 2012). Wet grinding is preferred because it prevents agglomeration and promotes effective dispersion of the created nano-cellulose particles. It also prevents the inhalation of respirable particles.

Sonocation: Sonocator utilizes ultrasound power to induce the formation of nanofibrils from cellulosic fibers. A typical sonocation system is made up of three major components; generator, converter and horn/probe. It is equipped with bottons to facilitate the control of the sonocation parameters. The generator transform alternating current to high frequency electrical energy at high voltage pulses (≈1200W) with a frequency of 20 KHz to drive the piezoelectric converter. The converter transforms electric energy to mechanical vibrations which is amplified down the length of the probe. There are two types of sonocation methods namely; direct and indirect sonocation. The amplified vibration energy can either be transmitted directly into the sample with high intensity during direct sonocation process or the ultrasonic energy can be transmitted from the probe through water medium into the sample vessel or multiple sample tubes during the indirect sonocation process. In this case, actual contact between the probe and the sample is eliminated. Any of these processes can induce the formation of nanofibrillated cellulose (Dufresne, 2012).

Cryo-crushing: Cryo-crushing refers to the process of crushing cellulosic fibers which had been frozen with liquid nitrogen to liberate the fibrillated cellulosic fibers. A typical cryo-crusher is equipped with two grinding stones, a stator and a rotor capable of revolving at 1500rpm. The dimensions of the derived fibrillated cellulose fibers depends on the source of the native cellulose but usually in the nano-range of 5-100 nm in diameter. The major drawback of this technique is the high energy requirement

(Chirayil, Matthew and Thomas, 2013; Missoum, Belgacem and Bras, 2013; Kumari, Sreenivasalu and Reddy, 2016).

Refining: Pulp refining is a widely practiced technique in the pulp and paper industries to improve pulp quality by changing the fiber characteristics. The most commonly used laboratory refiner is the PFI mill. In this device the pulp is refined between a stainless steel roll with bars and a rotating disk with a smooth bed where the pulp is distributed evenly over the disk wall. Both elements rotate in the same direction but at different speed (Gharehkhani, *et al*. 2014; Kerekes, 2005).

Chemical Methods

The cardinal procedure in the chemical treatment methods is the acid hydrolysis, which leads to the synthesis of mainly nanocyrstalline cellulose (NCC). It is usually preceeded by pre-treatment processes e.g. purification of the raw cellulosic material, treatment with alkali to increase surface area and render the fibers more prone to hydrolysis as well as disrupt lignin structures and/or treatment with a bleaching agent e.g. H_2O_2, O_2, O_3, Cl_2, $NaClO_2$ or ClO_2 to remove lignin and other impurities in order to obtain cellulose. Subsequently, the acid hydrolysis step is usually succeeded by appropriate mechanical treatment for proper dispersion of the derived cellulose (Dufresne, 2012).

Acid hydrolysis

Acid hydrolysis is the process in which a protic acid is used to catalyse the cleavage of a chemical bond via nucleophilic substitution reaction, accompanied by the addition of water molecules. Specifically, when a certain strong mineral acid (6-8M) under controlled temperature, time, agitation and acid/cellulose ratio conditions, is contacted with cellulose, the long chain of **β**-1,4 - glucosidic bonds becomes fragmented into shorter chain lengths with the addition of water molecules. The various types of acid which had been used for this purpose include sulphuric acid (often the preferred choice), hydrochloric, nitric, phosphoric, hydrobromic, hydroflouric, maleic, formic and oxalic acids (Kargarzadeh, Ioelovich, Ahmed *et al.,* 2017; Brinchi *et al*., 2013). The acids predominantly hydrolyse the disordered amorphous region leaving the stable crystalline region which can be recovered as rod-like crystalline particles. The study of the effects of higher concentrations, longer reaction times and higher temperatures reveal that nanocrystalline cellulose so derived will have lower yield, decrease crystallinity and degree of polymerization (DP) but higher surface charge and narrower sizes (Kargarzadeh *et al.,* 2017; Ioelovich, 2012). However, the drawback to acid hydrolytic processes are corrosion of reactors and equipment, poor catalyst recyclability, product separation and hazardous effluent treatment and high cost of production. It has been well documented in the literature that various solid acids can be used to minimize some of the problems encountered with this approach. Some examples of solid acids used for the hydrolysis of cellulose are phosphor-tungsten acid ($H_3PW_{12}O_{14}$), sulphonated carbonaceous based acids, polymer based acids and magnetic solid acids (Huang and Fu, 2013; Kargarzadeh *et al.,* 2017). Alternatively, several time consuming and environmentally harmful steps associated with mineral acid hydrolysis can be avoided by using certain gaseous acids e.g. gaseous nitric, hydrochloric or triflouroacetic acids. For effectiveness, moist cellulose is required. This will minimize the large amount of water usually needed for the purification of products, eliminate the dialysis step encountered with mineral acids and acid recycling becomes easy (Kargarzadeh *et al.,* 2017).

Enzymatic hydrolysis

Enzymatic hydrolysis is the process in which enzymes are used to facilitate the cleavage of bonds in organic molecules, accompanied with the addition of water molecules. In the case of cellulose, these sort of enzymes are called cellulase and are of fungal origin. Enzymatic hydrolysis is an important pretreatment step if significant reduction in energy consumption is desired since it is nature inspired. Microfibrillated cellulose (MFC) obtained enzymatically from pretreated wood fibers had been reported to show more favourable structure in terms of length and aspect ratio than MFC obtained from strong acid hydrolysis (Islam, Alam, Patrucco *et al.,* 2014; Mossoum, Belgacem and Bras, 2013; Janardhanan and Sain, 2006).

TEMPO-mediated oxidation

TEMPO-mediated oxidation is one of the most promising methods of obtaining cellulose nanofibrils. Essentially, it entails the oxidation of cellulose fibers by adding $NaClO_2$ or NaClO (oxidant) to aqueous cellulose suspensions in the presence of a nitroxyl radical such as 2, 2, 6, 6 - tetramethylpyperidine-1-oxyl as catalyst and halogen salt (e.g. NaBr) in alkaline medium. Subsequently, the aggregating nanofibers can be disintegrated by mechanical agitation with the aid of a waring blender. the TEMPO-mediated oxidation based nanocrystalline cellulose possesses higher viscosity, higher shear stress, higher carboxylic groups, improved transmittance and smaller sizes of oxidized NCC particles compared to conventional hydrolysis based NCC (Qian, Tang and Chen, 2011; Tang, *et al.* 2017; Missoum Belgacem and Bras, 2013).

Carboxymethylation Process

The procedure aims at introducing functional groups to the cellulose backbone. It can be affected by the reaction of monochloroacetic acid or its sodium salt (sodium monochloroacetate) under alkaline condition, in the presence of an organic solvent (isopropanol). Therefore, carboxymethylation of cellulose fibers promote the individualization of nanofibrils as wells as increase the number of anionic carboxyl groups on the fibrillated celluloses, thereby increasing its capacity to bond to cationic materials (Mohkani and Talaeipour, 2011; Asi, Mousavi and Labbafi, 2017).

Acetylation Process

Acetylation of cellulose fibers is another surface modification technique carried out to improve its dispersability and compatibility in other polymeric matrices as reinforcing materials. The principle behind this process is to react the hydroxyl groups (OH-) of the fiber constituents with a coupling agent having acetyl groups (CH_3CO-) e.g. acetic anhydride the reaction may be sped up by a suitable catalyst (Bledzki, Mamum, Lucka-Gabor and Gutowski, 2008; Islam, Alam, Zoccola, 2013; Beztout, Boukerrou, Djidjelli *et al.,* 2015).

Chemical-Mechanical Approach

The chemical-mechanical approach refers to the amalgamation of one or more chemical pretreatment methods with mechanical disintegration techniques. Figure 4 is the flow diagram of a typical chemical-mechanical nanocellulose preparation procedure (Dufresne, 2012).

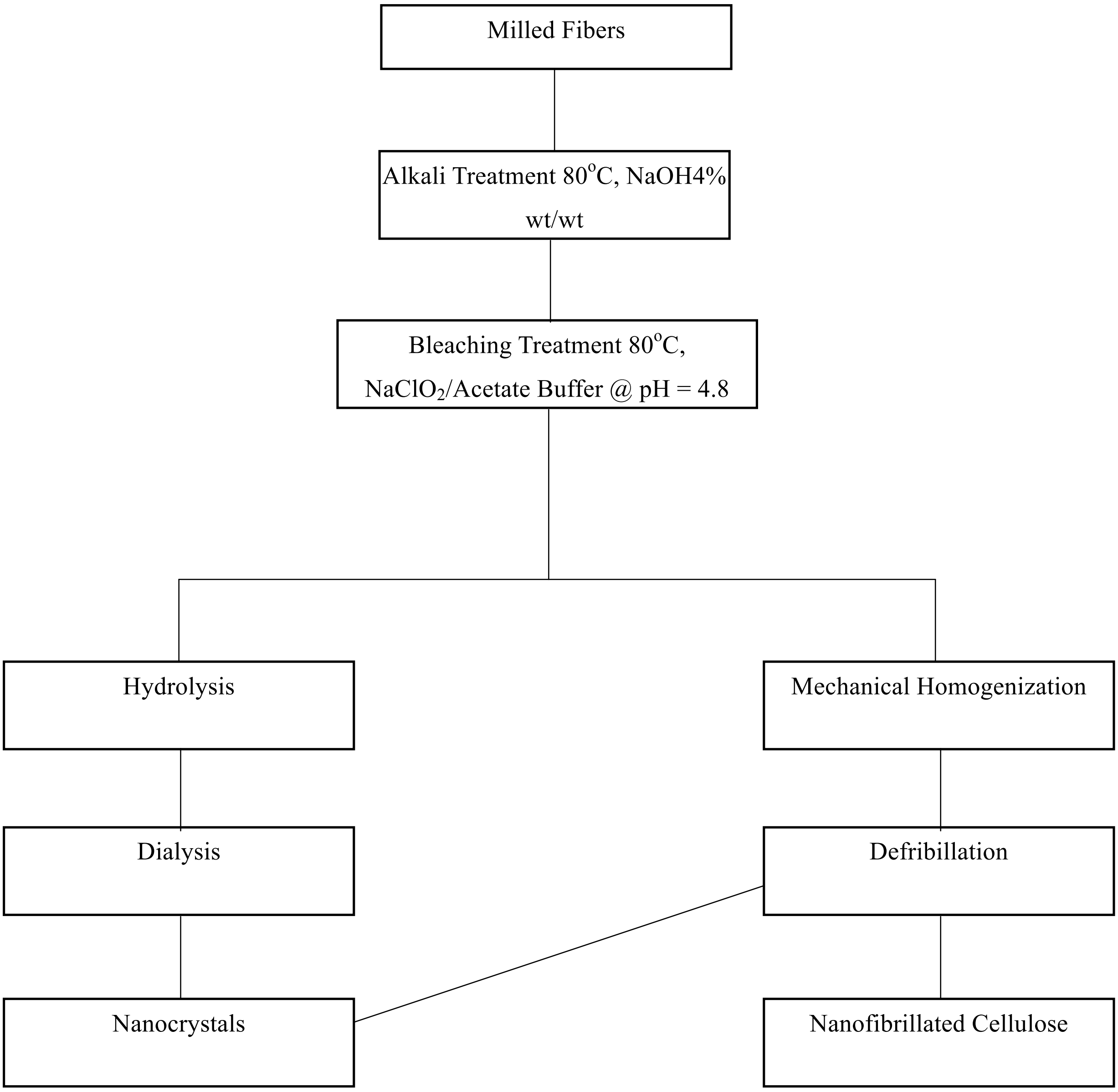


Figure 4: Typical chemical-mechanical procedure for the synthesis of cellulose (Dufresne, 2012).

Bottom-Up Approach

The Bottom-Up Approach can generally be viewed as the assemblage techniques where substances at atomic and molecular scales are stacked on each other to yield relatively uniform and rather consistent nanofibers. Typical examples of the bottom-up methods for nanocellulose synthesis are electrospining and bacterial biosynthesis

(Dufresne. 2012).

Electrospinning

A typical electrospinning equipment consists of a metering syringe pump equipped with a spinneret, a pippete and complimentated with a high voltage DC power supply and a collector screen (target) for the propagation of nanocellulose fibrils. During the process, a sufficiently high voltage (30KV) is imposed on a droplet of polymer solution held by surface tension at the end of the capillary, which stretches the droplet to a crititical point where it tapers to a conical shape called Taylor cone. At this point, the electrostatic force overcomes the surface tension of the droplet and a stream of liquid erupts from the surface. The solvent evaporates while the jet is on flight leaving the ultrafine polymeric fibers measuring 10-100nm in diameter on the target. Dissolution of cellulose can be achieved with the acid of the derivatizing solvents or non-derivatizing solvents. The dissolved cellulose or polymer solution becomes the raw material for the electro-spinning process. Derivatizing solvents induces covalent modification on the cellulose backbone while non-derivatizing solvents separate the individual cellulose chain from each other without chemical modification. Some examples of the widely used solvents are: - dimethylacetamide or DMAC/LiCl, NaOH/Urea/Water; n-methylmorpholine oxide (NMMO)/Water or ionic liquid. The morphological features of the electrospun nanofibers depends on the effect of various process parameters including electric field strength, tip-to-collector distance, polymer solution feed rate and composition (Rebouillat and Pla, 2013; Kargarzadeh, 2017).

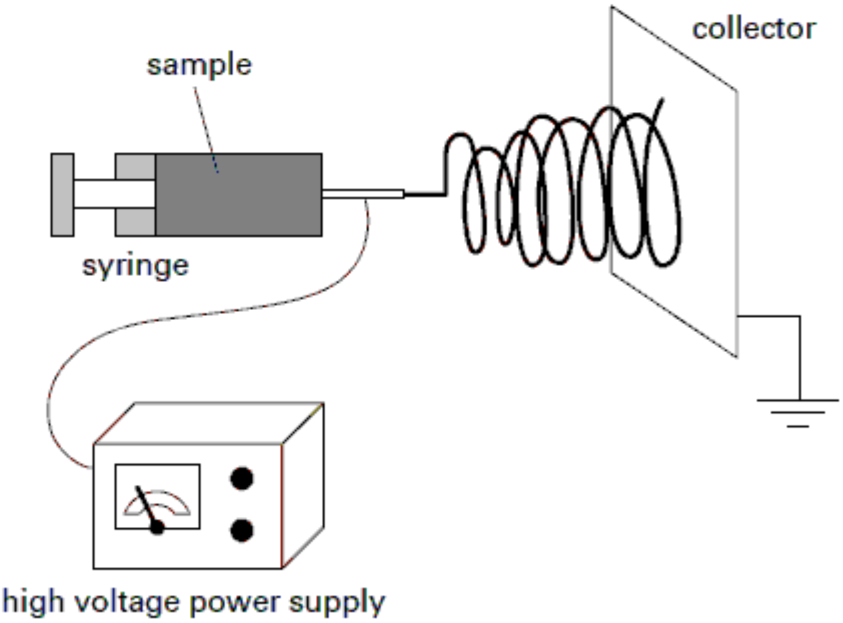


Figure: An electrospinning set-up (Alain Dufresne, 2012)

Bacteria Synthesis: The metabolic processes of certain aerobic bacteria (e.g. gluconacetobacter xylinus) can convert low molecular weight sugars and alcohols to cellulose molecules free from lignin and hemicellulose components found in plant cellulose. This simple purification process can remove all impurities leaving pure nanocellulose fibers. BNC has the same chemical composition as plant cellulose, but without the carboxyl or carbonyl group which are usually introduced to wood or plant derived cellulose during the purification process (Stevanic *et al.* 2011; Dfresne, 2012;

Ashajaran Yazdanshenas, Rashidi *et al.,* 2013)

Applications Of Nanocellulose

Paper, Absorbent Products and Cosmetics

Paper and paperboard industries are the traditional users of cellulose and nanocelluloses. Particularly, nanocellulose offer strong reinforcement and barrier effects on paper materials. Its capacity to absorb water makes it a suitable candidate for the manufacturing of various absorbents. It can also be used as composite coating agent in cosmetics, for example hair, eyelashes, eyebrows and nails (Eriksen, Syverud, Gregersen, 2008).

Waste Water Treatment

Usually industrial effluents contain various kinds of contaminants depending on the processes and operations applicable. Such impurities include metal ions, humic acids, inorganic and organic particles, fine suspended solids, dissolved solid and other impurities. The development of various nanocellulose adsorbents for the removals of such toxic pollutants are well documented in literature.(Fu and Wang, 2011; Gupta, Tyagi, Salegh *et al.,* 2015; Charpentier, Neville, Lanigan *et al.,* 2016; Viosin *et al.,* 2017).

Jebali *et al.* (2015) reported on the adsorption of humic acid with the aid of amine-modified nanocellulose. Bagheri *et al*., (2017) separated water and ethanol with the aid of the membrane derived from bacterial cellulose.

Catalysis: the quest for greener and cleaner environment requires thorough chemical processes that are devoid of hazardous waste generation. Conventional catalysts are often non-biodegradable, non-toxic and non-renewable. Green catalysis is a subset of catalysis concerned with the philosophy, design, synthesis and application of eco-friendly catalysts (Atabay and Ersoz, 2016; Lu and Ozcan, 2015).

The superior attributes of nanocellulose, namely; high surface area, thermal stability, abundant hydroxyl and sulphate ester groups, capability of forming stable suspension in water, biodegradability, non-toxicity and sustainability potential make it quite suitable in catalyst systems (Kaushik and Moores, 2016). Nanocellulose usually serve as a catalyst support, in order to hinder aggregation of nanoparticles either as metal or metal oxides. Examples include precious metal (Au, Ag, Pt and Pd) - nanoparticles/nanocellulose composite (Wei, Rodriguez, Rennecker and Vikesland, 2014). The advantage of highly dispersed inorganic nanoparticles is to ensure efficient contacting between reacting species, resulting in increased rate of reaction. (Bagheri, Julkapli and Mansouri, 2017).

Energy and electronics

It had been reported by Wei *et al.* (2014) that:

(i) Nanocellulose can be used as a raw material for rechargeable energy storage devices in Lithium-ion batteries.

(ii) Pd-NP/BC nanocomposite can be used as membrane electrode assembly (MEA) in fuel cell, and

(iii) Transparent nanocellulose-paper based solar cell which showed significant power conversion efficiency had been designed.

Bacterial nanocellulose membrane are used to manufacture paper diaphragms for loud speakers and headset of electronic devices (Sukara and Meliawati, 2014).

Nanocellulose Concrete

Nanocellulose can be used as an effective and eco-friendly replacement for hazardous asbestos fibers and glass fibers as concrete composite reinforcement because of its improved mechanical and physical properties (Bagheri *et al*., 2017).

Thermal Insulation

The thermal conductivity of native cellulose based insulating material is 40mW/mK while a thermal conductivity of less than 25mW/mK had been reported for nanocellulose derivatives which qualifies them as super-insulating materials. (Lavoine and Bergstrom, 2017).

Fire Retardation

The limiting oxygen index of most fire retardants is in the range of 22-25 LOI, while nanocellulose foam laced with inorganic fillers (clay or graphene) with a limiting oxygen index of 34 provides a better option (Lavoine and Bergstrom, 2017).

Nanofluids: nanofluids refer to fluid suspension of nanomaterials. The evaluation of the application of nanocellulose fluids as well as its chemically modified counterparts as a 'green' flooding agent in enhanced oil recovery is well documented in literature (Qinzhi, Bing, Yan *et al.,* 2016; Wei *et al.,* 2016; Xiaofei, Yanyu, Guangpeng and Zhiyong, 2017).

Sensing and Biosensing

Nanocellulose based technology has become an emerging platform for the fabrication of efficient, simple, cost-effective and disposable optical/electrical devices for several sensing applications ranging from environmental monitoring, health care diagnostics, food quality control and forensic analysis. (Golmohammadi, Morales-Narvaes, Naghadi and Merkoci, 2017; Weishaupt *et al.* 2016).

Biomedical Applications

Bandages obtained from BNC is used for wound dressing, skin grafting and treatment of various other injury sites (Meftahi, Khajavi, Rashidi, *et al*. 2009). It is also applied in several other tissue engineering treatment such as bone and cartilage grafts, contact lenses, cornea replacement, cardiovascular, trachea, artificial blood vessel and many other tissue scaffolds, reconstruction or regeneration treatment in humans (Czaja, Young, Kawecki, Brown, 2007; Moniri, *et al*. 2017).

In the pharmaceutical industry, nanocellulose is used as excipients for drug delivery (Ul-Islam, Khattak, Khan *et al*.,2015).

Conclusion And Future Prospects

The present day mantra for the advancement of science and technology in the phase of growing ecological and social awareness fueled by the precarious impacts of the exploration, exploitation and the uncertainties bordering the pricing of fossil fuel, is the adoption of “green and clean technological approaches to goods and services”. This has in turn inspired research in the direction of “green” raw materials for diverse applications. Nanocellulose comprising nanofibrillatd cellulose, nanocrystalline cellulose and bacterial nanocellulose are important integral of the aggregating ideas as emerging and sustainable raw materials for the nanotechnology community. The relevance of the candidacy of nanocelluloses is attributable to its sustainability, biocompatibility, biodegradability, high aspect ratio, transparency, hydrophilicity and non-toxicity.

Due to the interdisciplinarity of nanoscience, effectively coordinated synergy is necessary for the transformation of bench-scale researches to rewarding investments commerce, devoid of safety, health and environmental (SHE) concerns.

In a nutshell, it is safe to opine that the world is currently awaiting nanocellulose-enabled body parts of automobiles, aircrafts, flexible electronic displays, light weight military armour, artificial organs and many more.

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