

Nanocellulose: Extraction and application

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ARTICLE INFO

Article history:

Received 4 February 2018

Revised 18 April 2018

Accepted 24 May 2018

Available online xxx

Keywords:

Biomass

Cellulose

Nanocellulose fiber

Extraction

Application

Outlook

ABSTRACT

Recently, nanocellulose and its applications gain high attraction in both research and industrial areas due to its attractive properties such as excellent mechanical properties, high surface area, rich hydroxyl groups for modification, and natural properties with 100% environmental friendliness. In this review, the background of nanocellulose originated from lignocellulosic biomass and the typical extraction methods and general applications are summarized, in which the nanocellulose extraction methods related to ball milling are mainly introduced. Also, an outlook on its future is given. It is expected to provide guidance on the effective extraction of nanocellulose from biomass and its most possible applications in the future.

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1. Introduction

In the 21st century, when humans become aware of environmental conservation, applications of renewable resources become

more and more important for their daily life since they are friendly to nature. Nanocellulose is a natural nanomaterial which can be extracted from plant cell wall. With its nanometer size in diameter, nanocellulose consists of attractive properties such as high strength, excellent stiffness, and high surface area [1,2]. In addition, with its structure, nanocellulose contains a plentiful of hydroxyl groups which are accessible for surface modification. Nanocellulose can be used in various fields in our life, such as biomedical products, nanocomposite materials, textiles, and so on.

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<https://doi.org/10.1016/j.crcon.2018.05.004>

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Nowadays, nanocellulose gets high attraction from research and industries. The study of nanocellulose is not only about its extraction from biomass, but also the new applications in various fields. The aim of this review is to make a brief summary on the study of nanocellulose, including the typical extraction methods and the general and special applications. An outlook on its future is also given. It is expected to provide guidance on the effective extraction of nanocellulose from biomass and its most possible applications in the future.

2. Lignocellulosic biomass

Lignocellulosic biomass includes various natural organic matters which mostly refer to the plants or plant based materials, which is the largest amount of sustainable carbon material group and the most promising feedstock for the sustainable production of biochemical, bioethanol, and biofuels [3]. Especially, lignocellulosic biomass is a source of natural fiber which can substitute the petroleum-based polymers due to its outstanding environmentally friendly properties. Furthermore, the wastes from biomass such as agricultural wastes and forest residues have high potential for reuse as fuel or feedstock for production of high value-added materials without the competition with human and animal food chains.

Cell wall structure of lignocellulosic biomass mainly consists of three kinds of polymer, i.e. lignin, hemicellulose, and cellulose. However, the composition and the content of these three components are varied due to the difference in species, types, and sources of lignocellulosic biomass [4,5]. Lignin represents about 10–25% by weight of dry lignocellulosic biomass [6–8]. In plant cell walls, lignin serves as the binder which holds between and around cellulose and hemicellulose complex (Fig. 1). With its binding function, lignin provides the stiffness, compressive strength, resistant to decay, and water impermeability to plant cell wall. Lignin consists of the cross-linked amorphous copolymer synthesized from the random of three different phenylpropane monomers, i.e., p-coumaryl, coniferyl, and sinapyl alcohols which contains zero, one, and two of methoxyl groups, respectively [9–11]. The ratio of these three primary monomer units depends on the species and sources of lignocellulosic biomass. Recently, the isolation of lignin from lignocellulosic biomass and the depolymerization of lignin are mainly studied for the production of biofuels and chemicals from natural materials [10,12]. In addition, lignin-based carbon materials are also applied for catalysis, energy storage, and pollutant removal, which are attractively developed [11].

Hemicellulose represents about 20–35% in lignocellulosic biomass [6–8]. Hemicellulose is the heteropolymer which is composed by the short, linear, and branched chains of different kinds of monomers such as pentoses and hexoses [13,14]. The common types of hemicellulose are xylans and glucomannans. Xylans are abundantly composed in hardwood while glucomannans are mostly found in softwood [15,16]. Hemicellulose adheres to the cellulose fibrils through hydrogen bonds and Van der Waal's interactions (Fig. 1). In addition, it also cross-links with lignin [15]. The imbedding of hemicellulose with cellulose and lignin relates to the strength in structure of plant cell wall. Hemicellulose can be hydrolyzed by acid, alkali, or enzymes in mild conditions for pro-

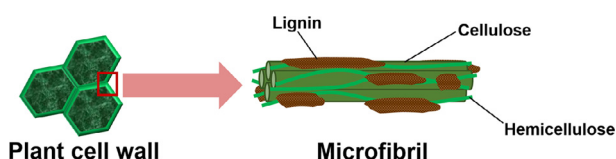


Fig. 1. Main structure of plant cell wall in lignocellulosic biomass which is consisted of lignin, hemicellulose, and cellulose.

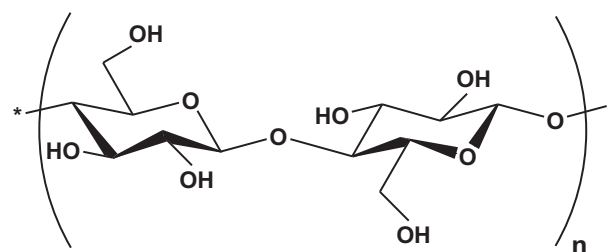


Fig. 2. Schematic of cellobiose.

duction of fuel ethanol and the valuable chemicals from its oligomers or monomers which can be used for food, cosmetic, mining industries and so on [15,16].

Cellulose is the major component in lignocellulosic biomass which is mainly localized in the plant cell wall at around 35–50% [6–8]. It is composed of the linear homopolysaccharide of β -1,4-linked anhydro-D-glucose units with the repeating unit of cellobiose (Fig. 2) [17]. The monomer of cellobiose, named anhydroglucose unit, consists of three hydroxyl groups which form strong hydrogen bond with the adjacent glucose unit in the same chain and with the different chains, called as intramolecular and intermolecular hydrogen bonding networks, respectively (Fig. 3) [17]. These hydrogen bonding networks are strong and tightly packed in the crystalline parts of cellulose fibrils which lead to the tough, strength, fibrous, insoluble in water, and high resistant to most organic solvents in plant cell wall [18–20]. The orientation of glucose molecules and hydrogen bonding networks in cellulose has wide orientation, resulting in different allomorphs of cellulose [17]. The variation of cellulose allomorphs depends on the source of lignocellulosic biomass and the treatment method. Generally, there are four types of cellulose allomorph namely cellulose types I, II, III, and IV [19,20]. Cellulose type I is the general allomorph of cellulose in nature or native cellulose which is the parallel packing of hydrogen-bond network. Cellulose type II comes from the chemical regeneration of cellulose type I by dissolving in a solvent or swelling in acid or alkaline solution. With these chemical regenerations, cellulose type II is composed by the different arrangements of antiparallel packing of hydrogen-bond network. Cellulose type III can be obtained from the ammonia treatment of cellulose I or II, while cellulose type IV is the modification of cellulose III by heating up to 260 °C in glycerol [19,20]. With its plentiful carbon, hydroxyl groups, monomers of glucose, cellulose is the most natural source for the production of carbon-based materials, valuable chemicals, textiles, papers, and so on [20,21].

3. Nanocellulose

With various hydroxyl groups and strong hydrogen bonding networks, cellulose fiber is composed of the outstanding physical and mechanical properties [1,2]. However, cellulose fibrils aggregate with the highly ordered regions (crystalline structure) and the disordered regions (amorphous structure) [17]. At the crystalline parts, the chain molecules are of orderly packing which promotes high stiffness and strength of cellulose. In other ways, the amorphous parts contribute to the flexibility of the bulk material [2]. Within the aggregation of ordered and disordered regions, cellulose fibers contain 3–100 μm of size in diameter with 1–4 mm in length for general lignocellulosic biomass [20].

Nanocellulose is the natural fiber which can be extracted from cellulose. The special attention is the size of nanocellulose fiber which generally contains less than 100 nm in diameter and several micrometers in length. Nanocellulose is a biodegradable nanofiber with light weight, low density (around 1.6 g/cm^3) and outstanding

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