

Lignin Nanoparticles and Their Nanocomposites

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Lignin nanomaterials have emerged as a promising alternative to fossil-based chemicals and products for some potential added-value applications, which benefits from their structural diversity and biodegradability. This review elucidates a perspective in recent research on nanolignins and their nanocomposites. It summarizes the different nanolignin preparation methods, emphasizing anti-solvent precipitation, self-assembly and interfacial crosslinking. Also described are the preparation of various nanocomposites by the chemical modification of nanolignin and compounds with inorganic materials or polymers. Additionally, advances in numerous potential high-value applications, such as use in food packaging, biomedical, chemical engineering and biorefineries, are described.

lignin nanoparticles

nanocomposites

preparation methods

biodegradability

non-toxicity

1. Introduction

With our continued in-depth understanding of the environmental pollution and resource crisis, the renewable and degradable properties of biomass materials are being increasingly valued ^{[1][2]}. As the second most abundant natural polymer material after cellulose, lignin has received extensive attention in recent years ^{[3][4]}. The development of bio-based products from lignin is an important part of any comprehensive biorefinery concept because of their biocompatibility and biodegradability ^[5]. They not only diversify the combination of products and markets, but also benefit waste recycling and economic sustainability ^{[6][7]}. Nevertheless, worldwide only 5% of the lignin is explored for high value development, therefore, there are still numerous challenges and opportunities for the in depth research and development of lignin applications ^[8].

The three-dimensional network structure of lignin is formed by three phenylpropane monomers (*para*-coumaryl alcohol, sinapyl alcohol and coniferyl alcohol, Figure 1) which connect to each other through ether bonds and carbon-carbon bonds ^{[9][10]}. It contains multiple active functional groups, such as aliphatic, aromatic, hydroxyl groups, etc. The isolation technology of cellulose, hemicellulose and lignin in biomass is directly related to the effective utilization of biomass. The complexity and diversity of lignin structures mainly depend on their different sources, types, extraction and purification methods ^[11]. Different extraction methods and pulping procedures will produce lignin with different structures and properties, which determine its subsequent development and applications ^[12].

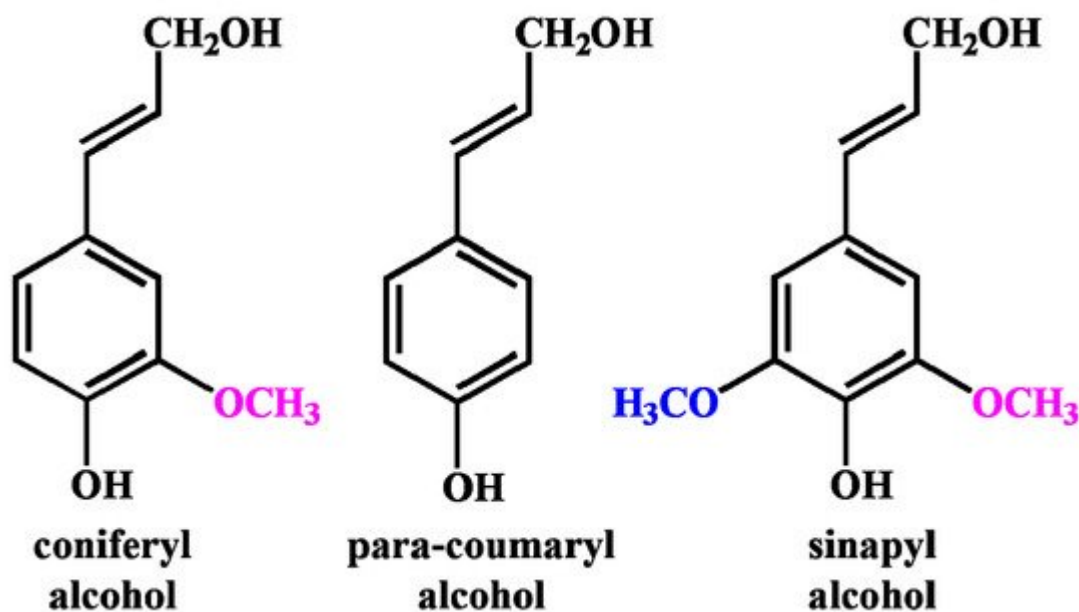


Figure 1. Three monomer structures of lignin.

The conventional separation and extraction methods for lignin mainly include grinding, acid/alkaline/thioacid hydrolysis, cellulose enzymolysis, organic solvent extraction and ionic liquid extraction [13][14]. Organic solvent pulping reduces the dependence on alkali or inorganic acids in the traditional pulping process [15]. Organic solvents such as alcohols, esters and amines can be used to dissolve the lignin in the raw materials to achieve the purpose of separation from cellulose [16].

In addition, biological enzymes are used to selectively degrade cellulose to achieve lignin separation. This biological treatment separates the lignin with less impact on its structure and chemical properties [17]. Therefore, it is particularly important to select suitable and efficient extraction methods for different raw materials without destroying the lignin structure. More importantly, the presence of different types of ions and the ionic strength of solutions is the foundation for the association and isolation of lignin [18]. The macromolecular and colloidal properties of lignin can be investigated in depth by studying the self-aggregation kinetics at some specific solution conditions [19]. The study of lignin solutions/colloidal behavior and the associative/dissociative processes also facilitates the understanding of its physicochemical properties [20].

Wide applications of lignin as an additive in composite materials and bio-based products from lignin deconstruction are being intensively developed [21][22]. However, it is not possible to completely achieve the high-value applications of lignin due to some unfavorable byproducts. The diversity of lignin sources and the complexity of the structures make the research on the potential applications of lignin have certain opportunities and challenges [23][24]. Therefore, the formation of lignin-based nanomaterials will open up a different perspective for expanding the high-value applications of lignin.

As for other materials and biopolymers, such as cellulose and chitosan, the rationale for the preparation of lignin nanomaterials is to gain new attractive properties occurring only when matter is organized on a nanoscale [25]. This

can be due to the so-called “quantum effect” bringing new tunable properties at the nanoscale or simply by the expanded surface to volume ratio of nanomaterials [26]. Compared with traditional composite materials, nanocomposites have obvious advantages, especially new materials from biorenewable and sustainable sources [27]. Due to the compatibility, degradability and environmental friendliness of bionanocomposites, their potential applications in the food packaging industry and pharmaceuticals are being exploited [28]. Polymer nanocomposites are being further used in additive manufacturing technology to produce more complex and diverse parts and components [29]. In addition, the application of multifunctional nanocomposite materials in the field of optics is also becoming increasingly prominent [30]. In the last few years, the research on multifunctional nanofibers is helpful for the development of potential applications in the field of medicine, biological tissue engineering, etc., especially chitosan electrospun nanofibers [31]. Electrospun nanofibers can be used to reinforce composite materials due to their specific molecular orientation and excellent mechanical properties [32].

As for lignin, with its aromatic and highly cross-linked network structure and chemical complexity, lignin contains plentiful of functional groups that are accessible for further surface modification [33]. This latent asset increases the potential activity of nanolignin to achieve high value-added applications of lignin [4]. In addition, the utilization of economical and environmentally friendly nanolignin as feedstock for the evolution of chemical industry conforms to green chemistry principles and sustainable development concepts [13].

Currently, the exploitation of nanolignin is the subject of a tremendous amount of research [34]. Lignin nanoparticles with different morphologies (smooth colloidal, hollow, spherical and quasi-spherical, Figure 2) have been successfully synthesized by controlling the reaction conditions of solvent/anti-solvent, the lignin concentration, the temperature and pH of solution, etc. [35][36]. Lignin nanoparticles have potential applications in antioxidants, thermal/light stabilizers, reinforced materials and nanomicrocarriers owing to their advantages of non-toxicity, environmental resistance, excellent thermal stability and biocompatibility [37].

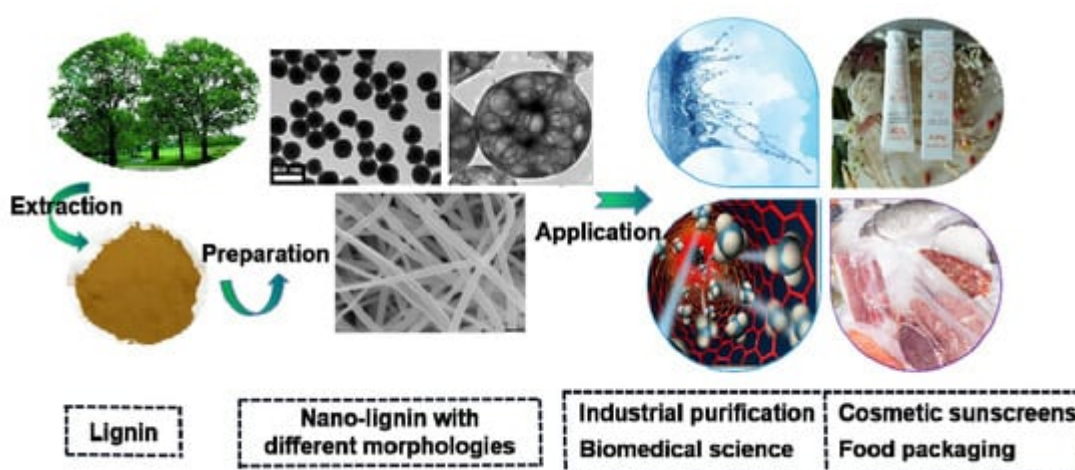


Figure 2. Nanolignins with different morphologies and their applications in different fields.

2. Synthesis Methods of Lignin Nanoparticles

The physical and chemical properties such as non-toxicity, corrosion and UV-resistance, antibacterial and anti-oxidation activity of lignin are attracting more and more attention [3][33]. Therefore, the use of low-cost and abundant lignin raw materials to prepare nanoparticles is an important aspect of expanding their high value-added utilization [38]. At the same time, finding simple, scientific and safe methods for preparing lignin nanoparticles is of great significance. The current preparation methods of nano-lignin mainly include anti-solvent precipitation, self-assembly, gradual addition and mechanical methods, etc [1][7][10]. Some emerging methods, such as ice segregation-induced self-assembly, aerosol-flow synthesis and electrospinning, are also being developed [35][39][40][41][42]. Figure 3 gives an overview of the synthesis and modification methods of nano-lignin. Lignin nanoparticles with different morphologies and sizes, which can be prepared through these different methods and conditions, will be of great value for their subsequent applications in different fields [43].



Figure 3. Overview of the synthesis and modification methods of nano-lignin.

3. The Value-Added Applications of Lignin Nanomaterials

In the process of exploring nanolignin materials, it was found that sometimes the ordinary nanolignin cannot satisfy the diverse requirements in different application fields. In addition to the basic thermal and mechanical properties of nanomaterials, some diverse nanostructures and specific performance such as metal adsorption are widely required [44][45]. Therefore, the ordinary nanolignin can be used to directly modify or compound with other nanomaterials, which can take advantage of nanolignin structure and further improve the performance of nanocomposite materials [46].

Lignin nanoparticles have attracted more and more attention because of their green, renewable and abundant source, antioxidant, antibacterial or ultraviolet absorption properties, biodegradability, biocompatibility, etc [47]. They are excellent substitutes for partially harmful nanomaterials, which are extensively used in the fields of drug release and control [48], food packaging, biomedicine, adsorbent materials, nanocarriers, environmental restoration and so on [49][50][51][52]. This not only solves the potential safety hazards of traditional nanomaterials from the source, but

also broadens the value-added applications of lignin nanomaterials, which conforms to the principles of green chemistry development [53].

4. Conclusions and Future Perspectives

Overall, this review summarizes the current status of the preparation of nano-lignin by sedimentation, mechanical, self-assembly and stepwise addition polymerization methods. In order to provide a reference for the chemical deep processing of biomass resources and the development of nano-lignin, the application characteristics of nano-lignin in UV protection and anti-bacteria, nano-fillers and biomass-based carriers are also outlined. Through the specific analysis of the preparation methods and application status of nano-lignin, it can promote the further research of nano-lignin and the development of novel nano-lignin-based products. This is of great significance to the utilization and sustainable development of lignin.

The multiple structures and the diverse properties of lignin make the prepared nano-lignin more complicated, which brings challenges to the research of the preparation and performance of nano-lignin. Meanwhile, it provides broader prospects and opportunities for the multi-functional and multi-field applications of nano-lignin. Nanometersized lignin with high specific surface area and activity is a novel approach to achieve high value-added utilization of lignin. Compared with the research of inorganic nanoparticles and renewable nanocellulose, the preparation and application of nano-lignin are still in their infancy. The scale and industrialization of nano-lignin-based products will become an important aspect of future lignin research.

In view of the problems of complex process and toxic organic solvents in the preparation of lignin nanoparticles, methods such as electrostatic spinning, self-assembly, ultrasonication and homogenization can be utilized. In terms of multi-functional applications of lignin-based nanomaterials, the range of use can be expanded by improving their strength, electrical conductivity, thermal stability, crystallization performance, etc.

The following points need attention in the application of nanolignin materials. First of all, achieving uniform dispersions of nanolignin in composite materials is a difficult problem to solve. Lignin nanoparticles are extremely prone to agglomeration because of the high surface energy and the large number of hydrogen bonds and Van der Waals forces between the molecules. Therefore, completely solving the problem of particle agglomeration and achieving the monodispersion of nano-lignin are the key to fully exerting the nano-effect. Furthermore, the diversified morphology and size of lignin nanoparticles are prerequisites for high value-added and multi-field applications of lignin. To solve the interface and dispersion problems of nano-lignin materials, it is essential to find chemical methods to modify nano-lignin and also supplement with effective physical dispersion methods, such as mechanical stirring, ultrasonication and high shear homogenization. In addition, the amount of nano-lignin added, the type of treatment agent and dispersing equipment are all key factors that affect agglomeration, which need to be controlled and improved during the preparation of lignin-based nanomaterials.

The structural and functional properties of lignin determine its extremely promising applications in the field of biochemicals. Lignin and its derivatives have a wide range of functionalities and can be used as dispersants,

adsorbents/desorbents, oil recovery aids, asphalt emulsifiers, etc. They can also be converted into aromatics, agrochemicals, polymers and high-performance materials. However, all these processes depend on improvements and innovations in the field of catalysis and product separation. Most importantly, to realize the full industrial potential of lignin, further refinement of biopulp technology is needed to achieve efficient separation of lignin and cellulose. It can be said that the contribution of lignin to sustainable human development lies in its ability to provide a stable and continuous source of organic matter. Thus it can truly guarantee sustainable green development and energy supply.

In addition, the antioxidant and anti-UV effects of lignin are its most prominent properties, so the application of lignin-based composites in food packaging and other fields has been increasingly developed. The lignin-based nanocomposites are also excellent carriers for a variety of metal ions and drug loading due to their unique nano-effects. They can be used as bio-nanocomposite catalysts and reducing agents for heavy metal ions, which are of great importance for environmental protection and wastewater treatment. Furthermore, the biocompatibility and non-toxicity of lignin are being intensively investigated.

Numerous scientific findings indicate that lignin-based nanocomposites have a very promising future in the biomedical field. Specific lignins have significant anti-lipid peroxidation and oxygen radical scavenging effects. Significant inhibitory effects of lignin on the central nervous system or on cancer cell proliferation can also be observed. Most importantly, lignin nanoparticles can be used as biological carriers for drug delivery and targeted drug release. The molecular expression, biocompatibility and cytotoxicity of lignin-based nanocomposites in cell lines have also been intensively studied. Conclusively, the development of novel biomass materials and products will be applied to the medical field and have a positive and effective impact on human life and health.

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