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Article

In Situ Wood Delignification toward Sustainable Applications

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CONSPECTUS: As one of the most abundant and versatile natural materials on Earth, recently wood has attracted tremendous attention from scientists and engineers due to its outstanding advantages, including hierarchically porous microstructure, high mechanical strength, environmental friendliness, renewability, and biodegradability. Wood's hierarchically porous structure and chemical components (e.g., cellulose, hemicelluloses, and lignin) enable its mechanical, ionic, optical, and thermal properties to be tuned via physical, chemical, and/or thermal modifications. Among these various approaches, the chemical delignification of bulk wood is the most fascinating, in which the majority of lignin and hemicelluloses is removed while leaving the cellulose intact, maintaining wood's physical integrity and hierarchical structure. This delignified structure is unique, composed of hollow, aligned channels made up of cellulose microfibrils, and particularly attractive given its origin from a sustainable and renewable resource. As a result, delignified wood has attracted increasing attention for applications that go far beyond traditional wood utilization, such as lightweight yet strong structural materials, energy storage and conversion, environmental remediation, flexible electronics, and bioengineering.

This Account reviews recent developments in bulk wood delignification strategies toward the achievement of such advanced wood technologies for sustainable applications, with a focus on the research in our group. Similar to chemical pulping and bleaching, wood delignification involves a series of nucleophilic reactions based on alkaline Na_2SO_3 or Na_2S systems (i.e., chemical pulping) or electrophilic, radical, and oxidation reactions based on H_2O_2, ClO_2, or $NaClO$ systems (i.e., chemical bleaching) to deconstruct, fragment, and promote the hydrophilicity of lignin macromolecules, which finally make lignin easier to be removed. We discuss the structure and properties of partially and near-completely delignified wood, with a focus on process-structure–property relationships. The resulting delignified wood materials, with tunable structure and properties, demonstrate various advanced functions, in a wide range of advanced applications, such as building and construction, green energy, and electronics. Finally, the potential challenges and appealing perspectives of in situ wood delignification are discussed. In situ wood delignification, as a powerful modification strategy, has speeded up the development of advanced wood technologies and wood-based functional materials and products.
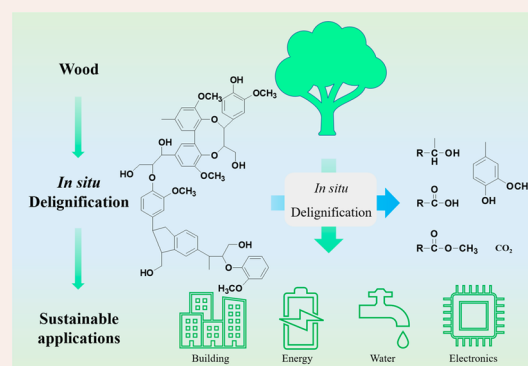
1. INTRODUCTION

The ongoing use of fossil-fuel related chemicals and materials has created both resource scarcity and significant environmental challenges that must be addressed. One alternative to petroleum-based materials is wood, which has been ubiquitously utilized in buildings and tools[1,2] as well as a fuel source[3] since ancient times. Given its renewability and biodegradability, wood is also attractive for a wide range of products and functions beyond its traditional use.[1–4] For these reasons and aided by advances in synthesis and characterization technologies, researchers have engineered wood toward emerging applications, such as structural materials,[1] optical devices,[5] medicine and bioscience,[6,7] energy storage and conversion,[8,9] environmental remediation,[10] electronics,[11,12] and advanced manufacturing.[13] For example, the Hu group developed the superstrong yet low-density structural material from wood (the so-called "Super wood"),[1] the Burgert group constructed the interpenetrating phase composite of wood toward the high-stiffness

sustainable material,[4] the Hu[3] and Berglund[5] groups made progress on transparent wood for energy-efficient buildings and optical devices, the Yu group designed the conductive smart isotropic wood with excellent electromagnetic shielding performance,[12] and the Söderberg group used the wood material to prepare the bioactive scaffold.[7]

What makes wood so versatile is its anisotropic, hierarchically porous structure that consists of several chemical components, including cellulose, hemicelluloses, lignin, and various extractives.[3,14] These unique structural and chemical characteristics enable wood to transport water and bear significant loads but
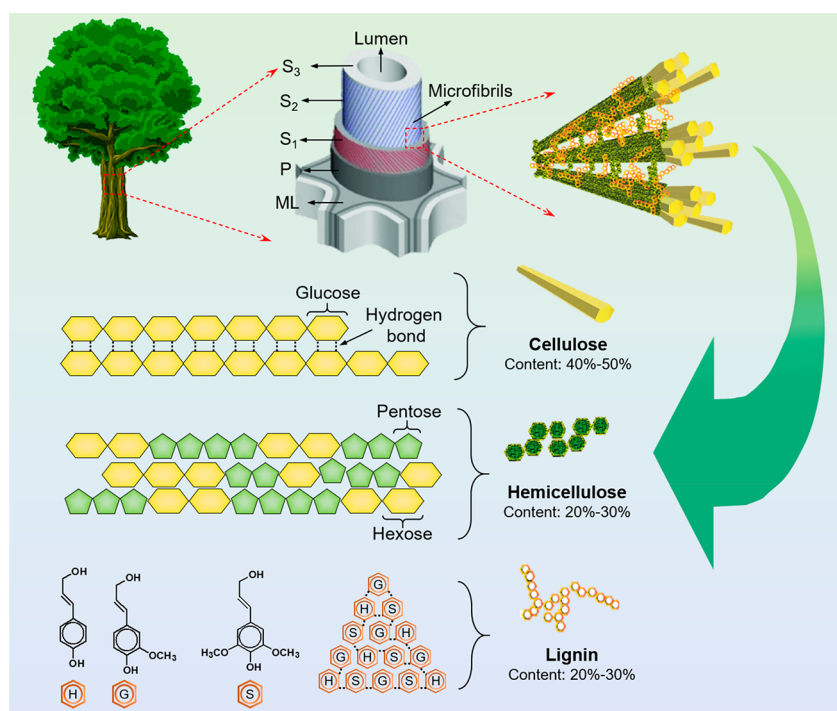
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Figure 1. Schematic illustration of the unique structure and chemical components of wood. The cell wall of wood features a multilayered structure, including the middle lamella (ML), primary layer (P layer), and secondary layer (S_1, S_2, and S_3 layers), which surround a hollow lumen space. The wood cell is made up of three main components, including cellulose (with a basic unit of glucose), hemicellulose (hexose and pentose units), and lignin (phenylpropane units of H, G, and S types), as well as trace ash and extractives. The tree image is reproduced with permission from ref 6. Copyright 2017 American Chemical Society. The cell wall structure is reproduced with permission from ref 25. Copyright 2018 Elsevier B.V.. The chemical compositional distinction is reproduced with permission from ref 28. Copyright 2015 Springer-Verlag Berlin Heidelberg.

also make it possible to modulate the material's mechanical, ionic, optical, and thermal properties toward sustainable applications.[3,15] Early wood modification technologies mainly focused on physical engineering to improve wood's stability and mechanical performance. Specifically, due to its hygroscopic character, the dimensions of wood tend to vary in wet or open-weather environments, which also impacts the material's strength.[16,17] To address these problems, thermal treatment technology[17] has been commercially used to improve the stability and durability of wood. Another traditional modification example is the joint engineering of wood,[18] in which wood pieces or blocks are jointed into large-scale, complex structures using adhesives/glues, fasteners (e.g., nails and screws), and wood elements (e.g., pinned mortise and tenon structures).

More recently, chemical engineering, particularly in situ delignification,[1] has been further investigated as a powerful wood modification strategy. Lignin was demonstrated in wood structure first by Anselme Payen and later named by Schulze,[19] which considerably covers cellulose to construct the whole wood cells. In situ delignification of wood effectively removes and modifies lignin of the wood cell walls, including in the middle lamella and secondary layers. Such removal and modification allow the multiscale structure and properties of wood to be tuned, yet still maintaining the material's originally aligned, anisotropic cellular structure, which is very different from the commercial wood pulping that completely deconstruct wood cell walls and therefore wood structure for producing wood fibers. In addition, in situ delignification also significantly improves cellulose microfibers and fibrils accessibility to other functional materials/chemicals and facilitates functionalized modifications for producing advanced biobased, multifunc-

tional, sustainable composites. Of note, this Account focuses on the wood delignification chemistries and their relationships with wood structures, properties and functions. More comprehensive discussions on the material and structural perspectives on how wood can be redesigned via structural engineering, chemical and/or thermal modification to alter its properties and functions are referred to previous review article.[3]

In this Account, we review in situ delignification as the functionalization strategy toward advanced wood products for various sustainable applications. Of note, herein, in situ delignification functions as a top-down approach, focusing on the bulk wood material. We discuss delignification chemistry, involving the partial or near-complete removal of lignin from natural wood, serving as effective strategies for multiscale engineering of wood's structure and chemical compositions. Additionally, this review explores the relationship between the delignification chemistry, wood structure, and properties toward various emerging applications, such as lightweight structural materials, thermal and light management, energy storage, and flexible electronics. We also show how in situ delignification can be extended to other nonwood biomass, such as bamboo. Finally, the Account ends with possible challenges and prospects of delignification in terms of developing future wood-based sustainable materials.

2. WOOD'S PHYSICAL STRUCTURE AND CHEMICAL COMPONENTS

Trees have evolved a hierarchical structure at different scales, in which the macroscale trunk/stem is composed of cells (i.e., vessels, fiber cells and tracheids), which are themselves made up of cellulose fibrils, hemicelluloses, and lignin.[20−24] This
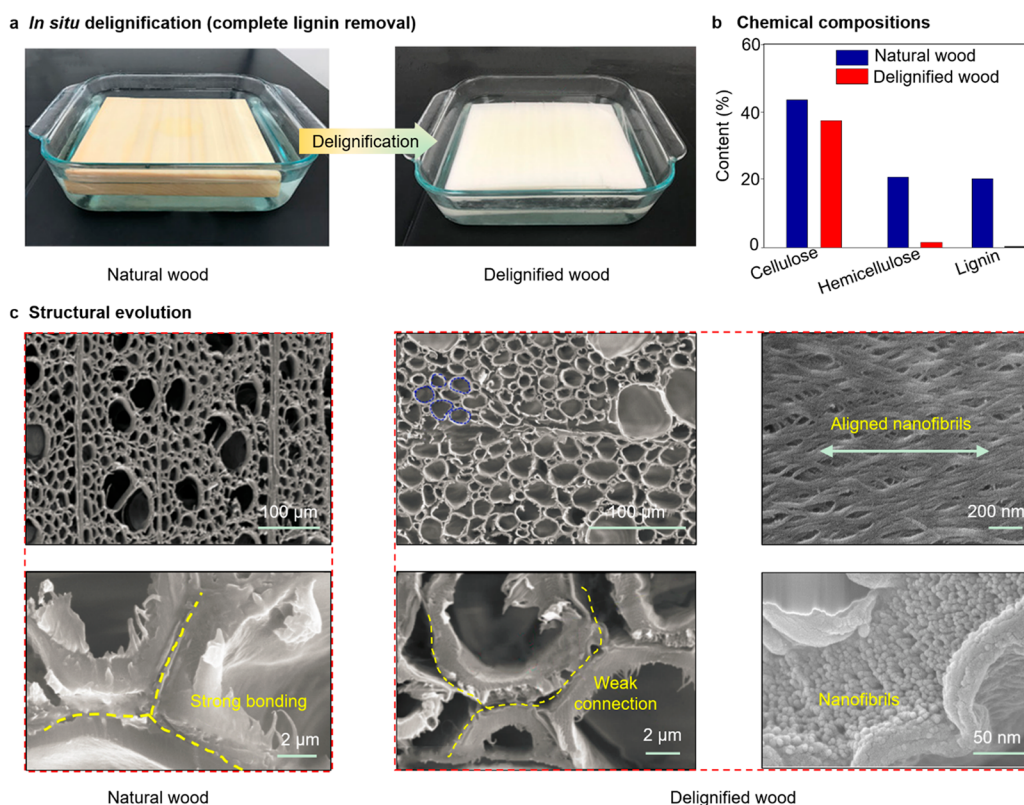
Figure 2. In situ delignification (near-complete lignin removal) for controllably modulating the structure and chemical compositions of wood. (a) Appearance changes of wood appearance during the delignification treatment. Reproduced with permission from ref 34. Copyright 2021 Wiley-VCH. (b) Compositional change of wood (cellulose, hemicelluloses, and lignin) before and after delignification treatment. (c) Structural evolution of wood via delignification, such as separation of the adjacent cells, exposing of fibrils, and formation of nanopores. (b, c) Reproduced with permission from ref 35. Copyright 2018 The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. Distributed under a Creative Commons Attribution NonCommercial License 4.0 (CC BY-NC) http://creativecommons.org/licenses/by-nc/4.0/.

structure varies depending on wood species, which are divided into two categories, softwoods and hardwoods.[3,23] Softwoods feature a large volume of tracheids (~90−95%), which provide multiple functions, such as transporting water and nutrients mainly by thin-walled tracheids, as well as providing mechanical strength mainly by thick-walled tracheids. In contrast, hardwoods are mainly made up of vessels and fiber cells, which respectively realize these two functions.[3] Tracheids, vessels, and fiber cells possess a typical wall-around-lumen structure (Figure 1), in which the wall features a multilayered structure, generally composed of a primary layer (P layer) and secondary layer (S_1, S_2, and S_3 layer), as well as a middle lamella (ML) located between two adjacent cells/tracheids.[25] Of note, the S_2 layer is 5−10 μm thick, i.e., 70−90% of the total cell volume,[26] causing it to play a critical role in controlling the properties of the tracheids, vessels, and fiber cells. Furthermore, abundant microfibrils at various angles compose the wall structure,[27] including 50−70° microfibrils in the S_1 layer, 10−20° microfibrils in the S_2 layer, and 60−90° microfibrils in the S_3 layer, as well as the randomly orientated microfibrils in the P layer.

In terms of biochemistry, wood is composed of three major components, including cellulose, hemicellulose, and lignin,[28,29] as well as other trace constituents, such as ash and various extractives. Cellulose makes up ~40−50 wt % of wood's content and is composed of numerous D-glucose units joined together by covalent and hydrogen bonds, which results in a linear and stiff macromolecular structure.[28,30] This unique structure imparts cellulose with a load-bearing function in trees. Hemicellulose is

another carbohydrate polymer in wood and has a lower content of ~20−30 wt %, with a complex chemical structure composed of hexose (glucose, mannose, and galactose) and pentose (xylose and arabinose).[31,32] Finally, lignin, different from the carbohydrate polymers of cellulose and hemicellulose, displays a complex structure constructed from the basic units of phenylpropane (C3−C6 structure), which have three types of ρ-coumaryl alcohol (H), coniferyl alcohol (G), and sinapyl alcohol (S).[28,33] Of note, lignin of hardwood is mainly composed of G and S units, whereas the softwood lignin is primarily G units with low amount of H units. These lignin basic units connect with each other via carbon−carbon and ether bonds, forming various functional groups (e.g., phenolic and aliphatic hydroxyls, methoxy, and carbonyl) in the 3D-network structure of lignin.[13]

Softwoods and hardwoods show different wood structures and chemical compositions at some degree. Certain hardwoods, such as fast grown poplar, feature relatively low density and loose wood structure constructed by the large-diameter fiber cells than softwoods. Such structural distinction makes certain hardwoods highly reactive and accessible to chemicals for modifications. In addition, most hardwoods have a lower content of lignin. Despite the above structural and compositional distinctions between softwoods and hardwoods, they share common structural and compositional features (i.e., hierarchically porous structure and consisting of cellulose, hemicellulose and lignin).
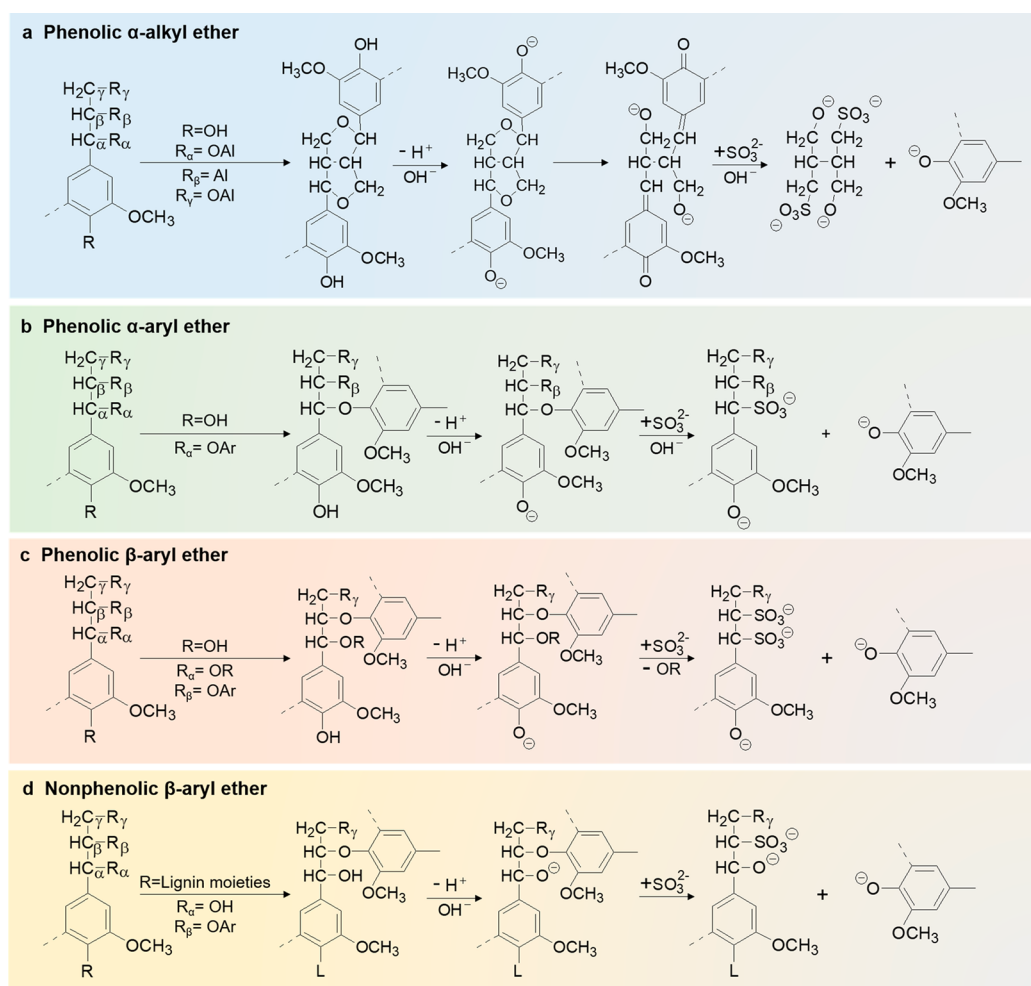
Figure 3. In situ delignification chemistry of the alkaline Na_2SO_3 system for partially removing lignin of wood. Al and Ar indicate the alkyl and aryl structures. (a) Phenolic α-alkyl ether structure. (b) Phenolic α-aryl ether structure. (c) Phenolic β-aryl ether structure. (d) Nonphenolic β-aryl ether structure.

3. IN SITU DELIGNIFICATION CHEMISTRY OF WOOD

3.1. Overview of Wood Delignification

In natural wood, lignin, as an important filler and adhesive, bonds to hemicelluloses at the molecular scale and in physical contact with fibers at the nano and microscales, owing to its abundant functional groups and amorphous network structure. The chemical removal and/or modification of lignin from wood is able to alter the structure and chemical compositions of wood, serving as a powerful engineering strategy. For example, near-complete chemical removal of lignin from wood cell walls (Figure 2a,b) results in the separation of the cellulose fibers from the middle lamella (Figure 2c), which has the highest concentration of lignin in all of cell wall layers of wood.[34,35] Delignification also leads to more exposure of cellulose fibrils, which are originally embedded in the lignin and hemicellulose matrixes. The resulting near-completely delignified wood maintains the anisotropic, hierarchically porous structure of natural wood but with more nanopores within the cell walls.[35,36] Meanwhile, in situ delignification also changes the color of wood depending on the extent of delignification and lignin condensation.

Of note, in addition to the near-complete removal of lignin, "delignification" also implies partial delignification and lignin modification, similar to the term "lignin engineering" (hereafter

we use "delignification" as a common term). In this regard, in situ delignification as a powerful approach has been widely used to modify wood structure and properties, producing various wood-based functional materials that are not limited to delignified wood (also called "white wood" or "nanowood") for a wide range of sustainable applications.[3]

3.2. Delignification Chemistry

3.2.1. Partial Delignification. The alkaline wood pulping approaches including sulfite $(NaOH + Na_2SO_3)$, kraft $(NaOH + Na_2S)$, and soda $(NaOH$ alone), have been used for delignification in the pulp and paper industry for decades. During the delignification process, the alkali treatment causes the fragmentation, degradation, and hydrophilic modification of lignin via a sequence of complex chemical reactions. These chemical reactions vary following different molecular structures of lignin, mainly including phenolic α-alkyl ether, phenolic α-aryl ether, phenolic β-aryl ether, and nonphenolic β-aryl ether.[37−39]

In the phenolic structure of lignin, the phenolic hydroxyl group features lone-pair electrons at the oxygen atom, being capable of overlapping with the π-electron system of aromatic ring. Under alkaline condition, phenolic hydroxyl group facilely ionizes to form the anionic phenol type, serving as a strong electron donor (Figure 3a). Given the inductive effect of anionic
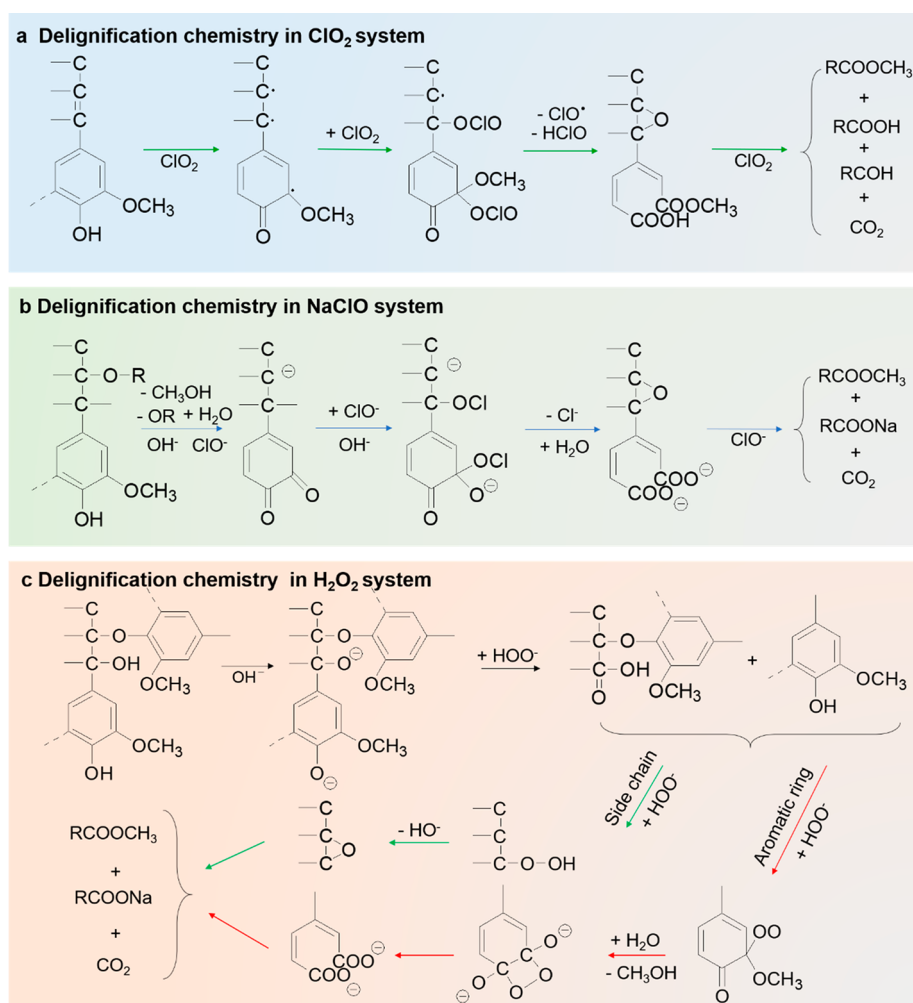
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Figure 4. In situ delignification chemistry for near-complete removing lignin of wood. (a) ClO_2 attacks the unsaturation structure of lignin, involving the aromatic ring moieties and olefinic side chains. (b) NaClO deconstructs the quinone type of lignin, as well as decomposing the aliphatic side chain. (c) The H_2O_2 system breaks the ether linkage of lignin structure, forming the aromatic moieties and side chains, which are further oxidized into carbonyl and carboxyl compounds.

phenol for the α-carbon atom, the cleavage reaction of α-alkyl ether bonding takes place, leading to the quinone methide structure. The α-carbon atom of the quinone methide structure is further attacked by the sulfite ions, which degrades the original phenylpropane structure into the aryl and alkyl fragments.[37] In addition to the phenolic α-alkyl ether structure, the phenolic α-aryl ether unit can also be converted into quinone methide intermediates via the cleavage of α-aryl ether bond, followed by the introduction of sulfite ions to the α-carbon atom (Figure 3b). The chemical reaction of β-aryl ether unit plays another crucial role in the delignification of wood (Figure 3c,d), as it is the most abundant and reactive units in the lignin molecule. In the phenolic β-aryl ether unit, the α-ether bonds are first cleaved due to the alkaline condition yielding a quinine methide which subsequently reacts with sulfite ions, which further induces the rupture of β-aryl ether bonds, yielding the lignosulfonate.[38] Of note, the cleavage of phenolic α-and β-aryl, and nonphenolic β-aryl ether bonds generates new lignin moieties with the phenolic structure, which would undergo the same fragmentation reactions as described above. In addition, because of the strong nucleophilic feature, the sulfide ions also facilitate the cleavage of methyl-aryl ether bonds to some extent. The fragmentation via cleaving chemical bonds and the sulfonation by introducing

sulfite ions to the lignin structure, promote the solubility and hydrophilicity of lignin moieties, thus removal of lignin from the wood structure.

In addition to the alkaline Na_2SO_3 system, the alkaline Na_2S engineering strategy also functions as an effective approach for the partial delignification of wood.[40,41] In the alkaline Na_2S system, the ionized OH^- and S^{2-} can break the lignin macromolecules via the similar nucleophilic reactions that occurred in the alkaline Na_2SO_3 approach. For example, the hydroxyl and sulfite ions can destroy the α-ether bonds in the phenolic β-aryl ether unit to yield the thiol structure. Such mercaptide anion can attack the β carbon forming the thiirane complex and eliminate the β-aryloxy group.[37,38] This reaction is often referred to as a neighboring group participation reaction. In addition, element sulfur in the thiirane complex can further dissociate, which leads to the degradation of side chain of lignin molecules. Such reactions for the cleavage of phenolic β-aryl ether linkages can take place rapidly and easily, which functions as a key step on determining the rate of the overall reaction. The β-aryl ether linkages in the nonphenolic lignin structures having a hydroxyl group at the α position can also react in the alkaline Na_2S system, while featuring a low reaction rate. In such lignin structure, the hydroxyl group ionizes due to the strong alkaline

conditions, which can form an alkoxide anion, inducing the cleavage of the β-aryl ether linkages and elimination of the β-aryl substituent.

The alkaline system for in situ delignification also induces the depolymerization of cellulose molecules, comprising the peeling reactions starting from the reducing end group and hydrolysis reactions happening at the randomly glycosidic linkage. The alkaline aqueous environment induces an equilibrium between the hemiacetal and aldehyde types, and a further equilibrium between the aldehyde and keto forms on the reducing end group of cellulose molecule chains. Once forming the keto structure, a subsequent β-alkoxy elimination reaction takes place even at mild temperature, more specifically, the glycosidic bond at the 4-carbon atom is cleaved, which results in the liberated glucose unit and new reducing end unit of cellulose chains. The dissociative glucose further forms an isosaccharinic acid via the benzilic acid rearrangement reaction. Simultaneously, the formed reducing end units of cellulose chains continuously undergo the same cleavage reaction, thus constructing the peeling reaction of cellulose molecule. On the other hand, a dehydration reaction occurs in the aldehyde types of cellulose molecule, leading to a stable metasaccharinic acid structure and finally stopping the degradation reaction of cellulose chain. At fairly high temperatures, a hydrolysis reaction of glycosidic linkage occurs to some extent, more specifically, the rection starts by the ionization of C-2 hydroxyl group, which attracts the C-1 carbon atom and finally leads to the exfoliation of attached glucose unit from the cellulose chain. Of note, both peeling and hydrolysis reactions affect the properties of cellulose, via depolymerizing cellulose chain and decreasing its molecular weight.

3.2.2. Near-Complete Delignification through Bleaching.

As highlighted above, in the pulping of wood, at some point the rates of delignification decrease and cellulose depolymerization occurs to such an extent that pulping needs to be halted and the remaining lignin needs to be removed via oxidative bleaching systems. Depending on the oxidative agent, these reactions involve nucleophilic reactions, the electrophilic, radical, and oxidation reactions also function as the effective pathways toward in situ delignification of wood.[38,42,43] Owing to the variable valence states, the chloride-based chemicals,[44] such as ClO_2, $NaClO_2$, and $NaClO$, show strong competitiveness. Among them, ClO_2 and $NaClO_2$ attract more attention owing to their outstanding selectivity in degrading lignin yet maintaining most cellulose and generating significantly reduced amounts of chlorinated compounds.

As a natural radial, the ClO_2 attacks preferentially the unsaturation structure of lignin, such as the aromatic ring moieties and olefinic side chains (Figure 4a). For the former, the reaction starts initially by one-electron transfer of phenolic hydroxyl group, leading to a phenoxy radical followed by introducing one-molecule chlorine dioxide at radical carbon atom to form the hypochlorous esters. Subsequently, the hydrolysis reaction takes place at the aromatic ring moieties, accompanied by the liberation of hypochlorous acid, which generates a muconic acid structure. The C—C double bond of olefinic side chains is cleaved to form the epoxide units, via the introduction of chlorine dioxide and subsequent elimination of monochloro monoxide. The final oxidation reaction occurs on both the muconic acid structure of aromatic ring moieties and the epoxide structure of side chains, leading to the lignin degradation and conversion into small molecular products. The nonphenolic structures can undergo the analogous reactions of

the phenolic structures with ClO_2, however, with an extremely low rate. In addition, ClO_2 can disrupt the bonds between aromatic rings and side chains in the benzylalcohol structures, forming lignin fragmentations.

The $NaClO$ is an alternative toward in situ delignification of wood in the alkaline media (Figure 4b). Lignin with the anionic phenol and cleaved β-ether bonds owing to the existing $NaOH$ in the system, is attacked by the hypochlorite ions, leading to the hydrochloride ester structure of lignin. Via the liberation of hypochlorite ions, lignin is oxidized, hydrolyzed, and further convert into the carboxyl- and carbonyl-based fragmentations, as well as CO_2. During the process of $NaClO$-based delignification, the chemical reactions of cellulose also take place, mainly involving the conversion of functional groups from hydroxyl into carbonyl and further carboxyl types, and the degradation of polysaccharides into oligosaccharides, and related saccharic and organic acids.

Hydrogen peroxide (H_2O_2) has been recognized as an environmentally friendly chemical toward effective delignification,[5,43] because the decomposition products of hydrogen peroxide are oxygen and water. In the H_2O_2 system, some active anions and radicals easily form from the H_2O_2 molecules, such as hydroperoxide (HOO^-) ions, superoxide ($O_2^{-\bullet}$), and hydroxide ($HO^\bullet$) radicals. Among these anions and radicals, HOO^- ions, function as the predominate groups to react with lignin by cleaving the bonds between aromatic rings and side chains (Figure 4c).

HOO^- ions further disrupts the unsaturation bonds in the side chains of lignin molecules, such as carbonyl groups and olefine aldehyde structures, which gives rise to the formation and subsequent deconstruction of oxirane intermediates into the small molecular aliphatic compounds. Simultaneously, the aromatic moieties are also attacked by HOO^- ions to form the epoxide intermediates, which are finally oxidatively decomposed into the end products mainly composed of the carbonyl and carboxyl compounds. In analogy to HOO^- ions, the HO^- ions, $HO^\bullet$ and $O_2^{-\bullet}$ radials, in addition, also contribute to the oxidation, hydrolysis, and degradation of lignin toward the delignification target of wood. The fragmentation of lignin macromolecules and deconstruction of lignin conjugated types suggest these chemistries are powerful in in situ delignification to tune the structure of wood at the micro- and nanoscale.

It should be mentioned that transition metal ions induce the decomposition of H_2O_2 to form O_2, which negatively affects the total rate of delignification. Commonly, the chelating agents (e.g., ethylenediaminetetraacetic acid and diethylenetriaminepentaacetic acid), are introduced to the H_2O_2 delignification system to prevent the metal catalyzed decomposition of H_2O_2. On the other hand, the earth-metal-based chemicals, for example, $MgSO_4$ and Na_2SiO_3, can serve as stabilizers to suppress the H_2O_2 decomposition and finally enhance the rate and efficiency of delignification.

Consequently, via the fragmentation and hydrophilic modification of lignin molecules, in situ partial delignification controllably removes the lignin from wood (the content of residual lignin is commonly higher than 10 wt %),[1,6,9,20,22,45] to result in a more porous, softer structure of a partially delignified wood, with a well preserved original hierarchical wood structure. In situ near-complete delignification refers to control lignin content of less than 2 wt %.[46−50] Such delignification leads to cellulose more accessible yet still maintaining the hierarchical structure of wood. Both partial and near-complete delignifica-

tion endow wood with more opportunities for functionalized modifications toward advanced, sustainable applications.

4. ADVANCED WOOD NANOTECHNOLOGIES

The engineering of wood structure and compositions is able to tune the mechanical, ionic, fluidic, optical, and thermal properties of wood, imparting wood with more advanced functions toward various sustainable applications, such as lightweight structural materials, thermal and light management, green energy, and electronics. Besides, during the process of engineering wood structure and compositions (i.e., delignification), the lignin of wood is significantly removed. As the byproduct of wood delignification, the recovery, modification and utilization of the removed lignin are important toward sustainable wood utilization. The details of lignin valorization will be discussed in the next section.

4.1. Partial Delignified Wood for Lightweight Structural Materials and Soft Materials

Wood has been widely used as a structural material for buildings and construction since ancient times.[1,51,52] The relatively low mechanical strength of natural wood (20 to 120 MP depending on wood species), however, fails to satisfy the performance requirements of advanced engineering fields, such as high-rise buildings, lightweight vehicles, airplanes, and so on. Recently, various strategies have been developed to strengthen and toughen wood toward such requirements, including mechanical densification, polymer impregnation, chemical modification (e.g., in situ delignification) or they combined.[1,3,53,54] One of the most recent developments is from the Hu group, where a novel two-step process (i.e., partial delignification and hot pressing) was invented to make wood 10 times stronger and tougher (namely, super wood in Figure 5a).[1] The partial delignification played a critical role by effectively softening the structure of the rigid fibrils and increasing the porosity of the wood structure, which is further densified (80% reduction in thickness) with ease via the subsequent compression treatment at 100 °C. Although wood was substantially densified, the density of the obtained super wood remains at a low value of 1.3 g·cm^{-1}. Such a low density and high mechanical tensile strength contribute to a superior specific strength of 422 MPa·cm^{-3}·g^{-1}, surpassing most structural metals and alloys.

Through in situ delignification, wood can not only be made stronger and harder, but also made softer and more flexible (or compressible). For example, Chen and co-workers developed a partial delignification strategy to make wood highly compressible like rubber.[45] In this process, the cell walls were softened, at the same time, an interconnected cellulose fibril network inside the individual wood channel was formed, both of which contribute to the excellent compressibility of the obtained elastic wood (Figure 5b). The elastic wood was able to sustain a large compression (up to 70% reduction of thickness) and a substantially repeated compression (up to 10,000 compressing/releasing cycles at a compressive strain of around 40%) with negligible deformation of its structure, which surpasses most cellulose-based and noncellulose-based hydrogels made by a bottom-up approach.

Alternatively, wood can also be made flexible through in situ delignification, as demonstrated in a recent work by Song and co-workers.[6] Balsa wood membrane was first chemically treated to remove partial lignin and soften the cell walls. The treated wood was then dried in air to create a unique crumpled cell lumina structure comprising closely packed cellulose nanofibers
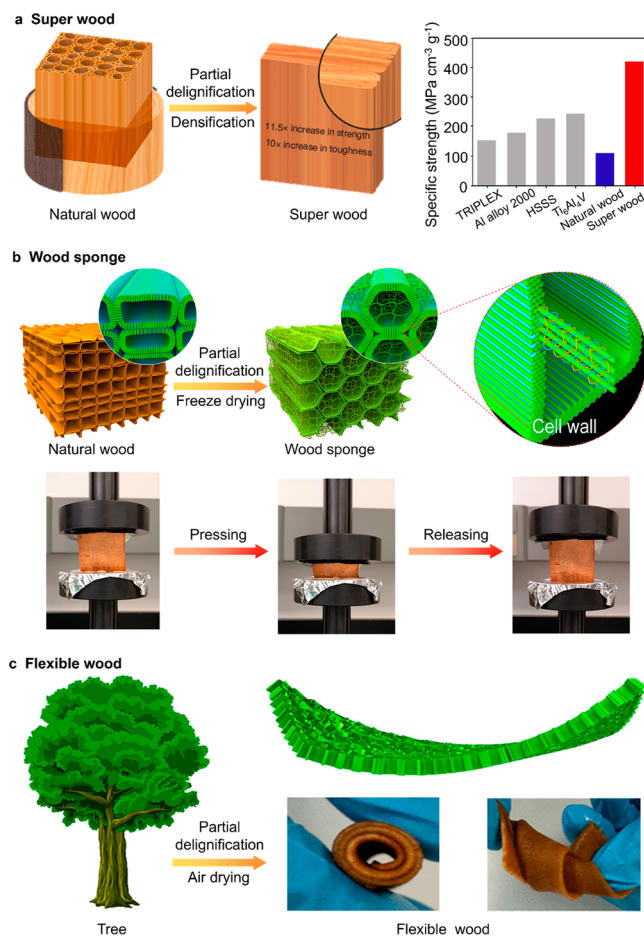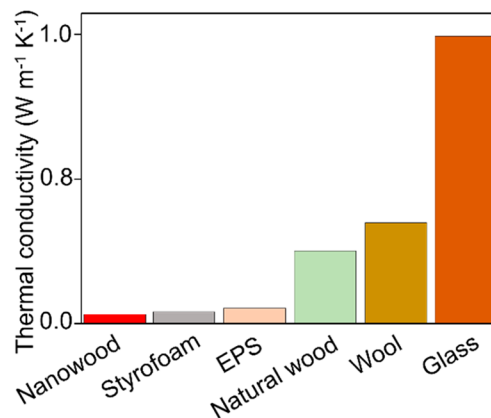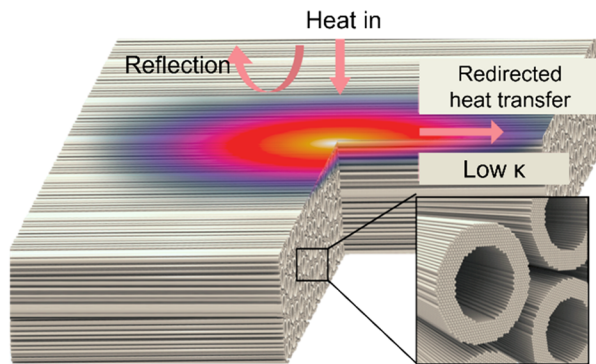

Figure 5. Partial delignification of wood toward lightweight structural materials and soft materials. (a) A two-step manufacturing process involving partial delignification and hot pressing to strengthen wood. The super wood exhibits a specific strength of 422 MPa·cm^{-3}·g^{-1}, which is higher than those of typical structural materials, including Fe—Al—Mn—C alloy (TRIPLEX) and high-specific-strength steel (HSSS), and even lightweight titanium alloy (Ti$_6$Al$_4$V). Reproduced with permission from ref 1. Copyright 2018 Spring Nature. (b) Partial delignification, freeze-drying, and hydrated technologies manufacture the wood sponge showing high compressibility with desirable structural stability. Reproduced with permission from ref 45. Copyright 2020 American Chemical Society. (c) Partial delignification and air-drying technologies construct the flexible wood enduring the bending, folding, and twisting treatments. Reproduced with permission from ref 6. Copyright 2017 American Chemical Society.

due to the severe shrinkage of cell walls. The distinct wavy, 3D porous structure endows a super softness and flexibility to the engineered wood (namely, flexible wood in Figure 5c), which is demonstrated by the complete recovery of its original shape upon severe bending, folding, and twisting. The appealing soft-structure materials of wood sponge and flexible wood can be potentially used in a variety of applications, e.g., scaffolds and carriers, energy storage, water purification, soft robotics, and ionic conductors.

Although great success has been achieved, continuous efforts are still needed to integrate the mechanical properties, fire, water, and chemical resistance for wood structural materials serving in the construction, civil engineering, transportation, and aerospace applications.
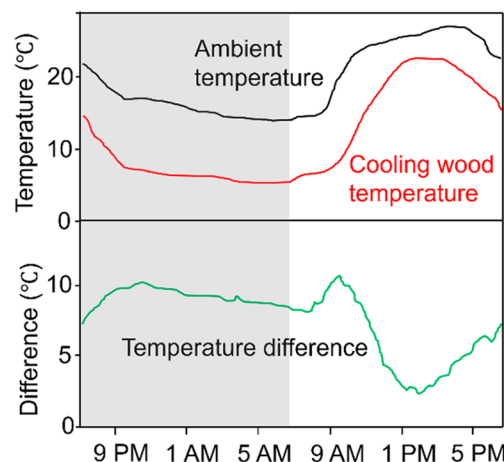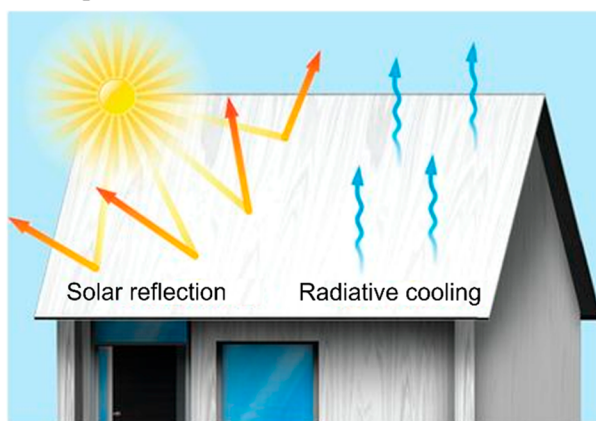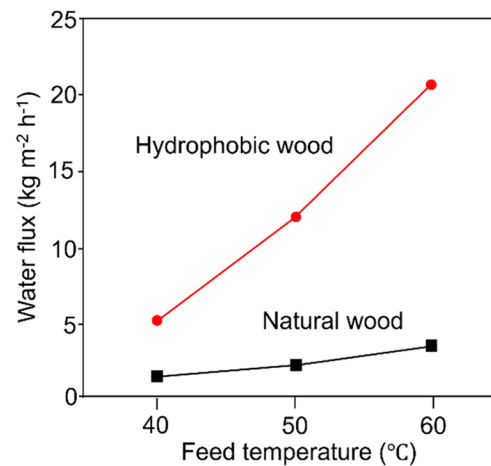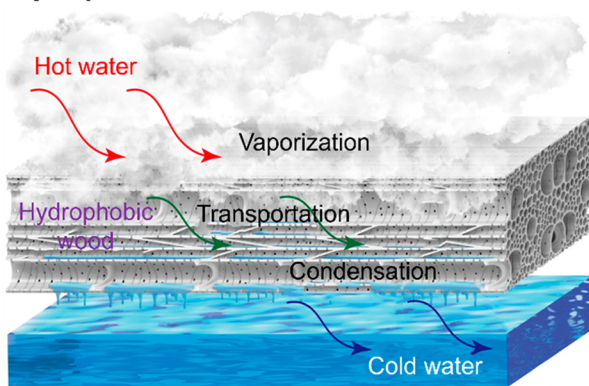
Figure 6. Delignification of wood toward thermal-management material. (a) Near-complete delignification reduces the thermal conductivity of wood by removing high thermal-conductivity lignin and creating more nanopores. Near-complete delignification endows the nanowood with a thermal conductivity of ∼0.03 W·m^{-1}·K^{-1}, which is lower than those of thermally insulating materials, such as such as Styrofoam, expanded polystyrene (EPS), wool, and grass. Reproduced with permission from ref 35. Copyright 2018 The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. Distributed under a Creative Commons Attribution NonCommercial License 4.0 (CC BY-NC) http://creativecommons.org/licenses/by-nc/4.0/. (b) Near-complete delignification and compression result in the cooling wood with a temperature lower than ambient temperature, in which the temperature reduces >9 °C during the night and >4 °C between 11 am and 2 pm due to the coverage of the cooling wood. Reproduced with permission from ref 48. Copyright 2019 The American Association for the Advancement of Science. (c) Near-complete delignification and hydrophobic modification prepare the hydrophobic wood enabling thermal-efficient distillation with a high flux of water. Reproduced with permission from ref 36. Copyright 2019 The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. Distributed under a Creative Commons Attribution NonCommercial License 4.0 (CC BY-NC) http://creativecommons.org/licenses/by-nc/4.0/.
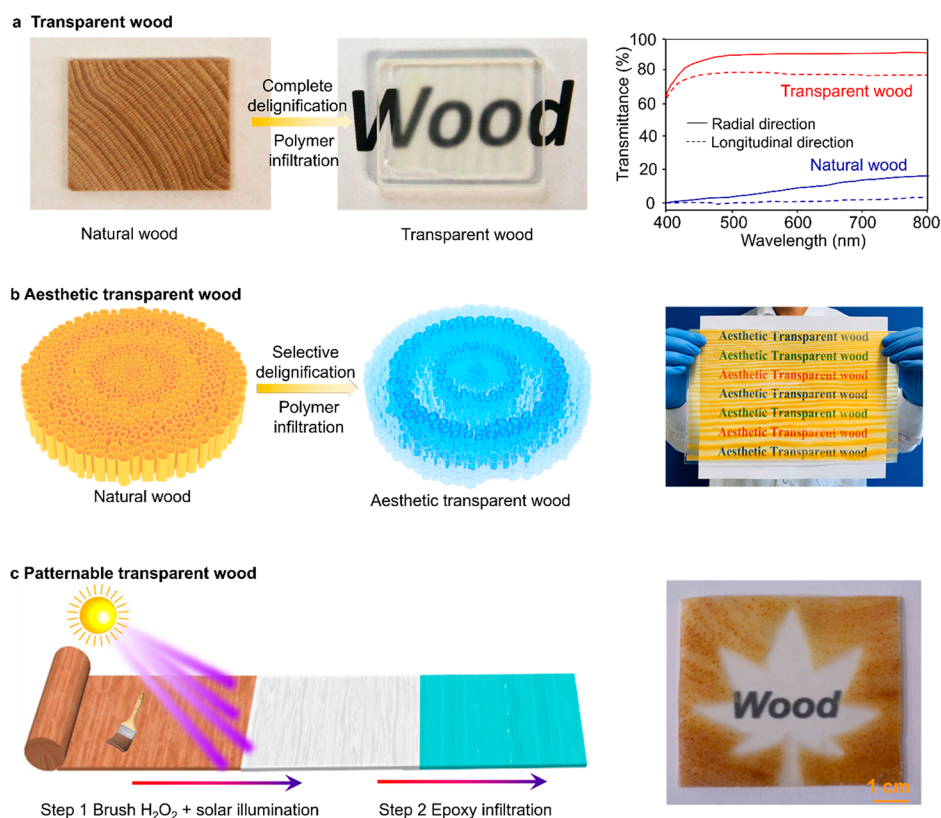
Figure 7. Delignified wood−polymer composites toward light-management materials. (a) Delignification and polymer infiltration modulate the optical performance of wood via making wood transparent. The transparent wood features a transparency of 90% in the radial direction and almost 80% in the longitudinal direction, both of which are much higher than the natural wood. Reproduced with permission from ref 49. Copyright 2016 Wiley-VCH. (b) Spatial-selective delignification and polymer infiltration enables a high transparency and aesthetic patterns of wood, thus constructing an aesthetic transparent wood. Reproduced with permission from ref 46. Copyright 2020 The Authors, some rights reserved; exclusive licensee Spring Nature. Distributed under a Creative Commons Attribution NonCommercial License 4.0 (CC BY-NC) http://creativecommons.org/licenses/by-nc/4.0/. (c) Solar-assisted chemical brushing strategy for manufacture the patternable transparent wood. The most lignin of wood is reservation and just light-absorbing chromophores of lignin are removed, which endows the patternable transparent wood with high strength and flexibility, as well as reducing the consumption of energy and chemicals. Reproduced with permission from ref 56. Copyright 2021 The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. Distributed under a Creative Commons Attributionsh NonCommercial License 4.0 (CC BY-NC) http://creativecommons.org/licenses/by-nc/4.0/.

4.2. Delignified Wood for Thermal Management

The exploitation of high-performance, thermally insulating materials is crucial toward energy-saving applications, such as energy-efficient buildings and solar evaporation. Wood has exhibited thermal insulation when used in buildings, which obstructs the heat transfer from warm indoor environment to cool outdoors in the winter, and vice versa in the summer. The thermal-management capacity of wood can be further promoted substantially by various strategies. A promising example is the super insulating nanowood developed recently by the Hu group through a simple delignification process.[35] During the delignification process, the removal of almost all lignin effectively liberates the cellulose fibrils, and creates numerous newly, nanoscale pores in the wood structure (Figure 6a). The abundant nanopores disrupt the phonon transport in wood structure, thus enabling the extremely low thermal conductivity of nanowood ($\sim$0.03 W·m^{-1}·K^{-1} in the transverse direction and $\sim$0.06 W·m^{-1}·K^{-1} in the longitudinal direction). Given the orientation of cellulose fibrils in wood, the nanowood features an anisotropic thermal conductivity, where the heat preferentially spreads along the direction of nanofibril alignment (i.e., the longitudinal direction of wood). Such uniquely anisotropic thermal conduction is supportive for preventing the accumu-

lation of thermal energy and local failure of heat in wood structure, thereby achieving the promoted thermal insulation performance of nanowood.

In addition to directly modulating thermal transport, the delignification followed by a mechanical compression technology enables the regulation of optical-induced thermal transport in wood structure, resulting in a passive radiative-cooling material (called "Cooling wood" in Figure 6b).[48] Such engineering technology imparts the cooling wood with partially isolated, multiscale fibers and channels, serving as the randomized and disordered scattering elements for intense reflection of all visible wavelengths, which is supported by the bright whiteness of the cooling wood. The strong vibration and stretching of cellulose molecules in cooling wood effectively emit Solar's rays in the infrared wavelengths. The reflection of solar radiation ranged from visible to infrared wavelengths surpasses the solar-irradiance adsorption of cooling wood, inducing the passive subambient radiative cooling, where the cooling wood generates a lowered temperature of >9 °C during the night and >4 °C between 11 am and 2 pm, in comparison with the ambient temperature. In addition, the mechanical compression also promotes the strength and toughness, as well as the thermal conductivity of the cooling wood. The integrated

merits, including passive cooling, high strength yet low density, sustainable and scalable production, offer opportunities for cooling wood toward applications in the building and aerospace sectors.

Given a number of exposed cellulose due to the delignification strategy, the nanowood is capable of chemical modification toward advanced functions, such as the hydrophobic modification via fluoroalkylsilane treatment (Figure 6c).[36] The hydrophobic nanowood inherits the high porosity and hierarchical pore structure composed of micropores amid the crystalline cellulose fibrils, mesopores of pits, and macro-channels of vessels and lumina. Together, these characters endow the hydrophobic nanowood with a lowered transfer resistance of water vapor and promoted water flux, as well as excellent thermal insulation property, all of which contributes to a high vapor permeability $(1.44 \pm 0.09 \text{ kg·m}^{-1}\text{·K}^{-1}\text{·s}^{-1}\text{·Pa}^{-1})$ and thermal efficiency ($\sim$70% at 60 °C).

4.3. Delignified Wood−Polymer Composite for Light Management

The optical properties of wood can be modulated by in situ delignification combined with other modifications (e.g., polymer infiltration to the delignified wood scaffold to make wood transparent). Transparent wood is one of the most exciting examples that demonstrate the potential of wood in optical management. In 2016, Zhu et al.[49] developed a high-performance transparent wood via the delignification and infiltrating polymer strategies (Figure 7a). The delignification leads to new nanopores owing to the removal of almost all the lignin and part of the hemicellulose, yet preserving the hierarchically porous structure of wood. The numerous pores enable the polymer infiltration into the delignified wood with ease, forming the wood−polymer composite. Once the infiltrated polymer features a similar refractive index to cellulose ($\sim$1.53), the resulting composite would become transparent (named as transparent wood). The transparent wood demonstrates outstanding optical transparency of up to 90% in the radial direction and nearly 80% in the longitudinal direction. Based on the transparent wood, the Berglund group further constructed a transparency and haze tunable smart window vis laminating the electrochromic polymer on such transparent substrate,[55] which can effectively modulate the light scattering vis adjusting the power supply, showing great potential in the promising energy-efficient construction.

Most recently, the Hu group developed an aesthetic transparent wood, featuring both a high transparency and aesthetic patterns inherited from natural wood (i.e., growth rings).[46] The unique aesthetics of wood is attributed to the annual-growth ring patterns of wood, in which earlywood possesses low-content lignin, low density and larger-diameter cells, where latewood shows the contrary properties (Figure 7b). Given such distinctions between earlywood and latewood, the delignification leads to the almost complete removal of lignin in earlywood area, yet the preservation of partial lignin in latewood area, which enables the inheritance of aesthetic pattern of natural wood to delignified wood. Via the further infiltration of polymer, the aesthetic transparent wood is interestingly developed, which exhibits a high transmittance of $\sim$80%. Of note, the residual lignin contributes to an excellent UV-blocking function of the aesthetic transparent wood.

Traditional technologies for preparing the transparent wood usually involves the near-complete removal of lignin from wood, which are relatively energy and chemical intensive and take a

long processing time. Xia et al.[56] exploits a solar-assisted chemical brushing strategy to manufacture the transparent wood with a patternable structure (Figure 7c).The strategy effectively removes the light-absorbing chromophores of lignin, rather than the entire lignin macromolecule (occurring in the traditional processes), via the ultraviolet-assisted H_2O_2 modification of lignin structure.[57] Owing to the reservation of lignin, the lignin-modified wood demonstrates a high tensile strength of 20.6 MPa under the wet conditions, being $\sim$50 times higher than the lignin-removed wood (0.4 MPa), which finally endows the excellent strength and flexibility to the prepared transparent wood. In addition, the transparent wood is patternable when designing the brushing location of H_2O_2 on the wood.

Wood−polymer composites with high transparency have enjoyed success for optical management toward energy-efficient buildings. Despite obvious progress of transparent wood, the challenges remain to be addressed. One crucial example is that the production of thick transparent wood is fairly challenging, where the increase of wood thickness can disrupt the infiltration of polymer to the delignified wood, leading to the nonuniform distribution of polymer and weakening its optical performance. Another challenge is the achievement of both high optical transparency and low haze in transparent wood with a desired thickness. Jia et al.[58] demonstrated that severer delignification to remove almost all lignin and hemicellulose while simultaneously defibrillating the cellulose fibrils within the cell wall could further mitigate the light scattering thus achieving a low haze of $\sim$10%, pointing out a promising direction toward clear wood with a high optical transparency and low haze.

4.4. Conductive Delignified Wood for Energy Storage and Electronics

In situ delignification confers the engineered wood with a more hierarchically porous structure, composed of nanosized pores, microscale pits, and macrochannels, which serves as the pathway of multiphase transport in wood, such as electrons, ions, and gases. With regard to electron transport, the conductive modification of wood is of necessity for building the electron-transport pathways in wood structure, which generally involves the introduction of conductive materials,[9,47] or direct carbon-ization of wood.[59]

For example, carbon nanotubes (CNTs) as a conductive component can be coated in the external and internal surfaces of delignified wood structure to form an interconnected and continuous network for electron transport (Figure 8a).[9] The resulting CNT-coated delignified wood (named as conductive wood) is used as a conductive membrane framework for the construction of current-collector-free cathode for Li−O$_2$ cells, where ions and oxygen can transport through abundant nanopores in cell walls and unperturbed wood lumina separately, in addition to electrons transporting through the CNT network. Such a unique structure enables a non-competitive, tripathway transport of electrons, Li$^+$ ions, and O$_2$ molecules in the conductive delignified wood-based Li−O$_2$ cell. The tripathway structure leads to a low overpotential of 0.85 V at 100 mA·g^{-1}, high areal capacity of 67.2 mAh·cm^{-2}, and long cycling life of 220 cycles. The capacity decreased dramatically if the hierarchical pores are eliminated by densification or blooded by extra electrolyte, highlighting the important role of the tripathway structure (Figure 8b). It should be noted that owing to the removal of lignin, the ultrathick wood-based electrode endows the robust flexibility to the wood-based battery, representing a promising strategy to address the long-standing
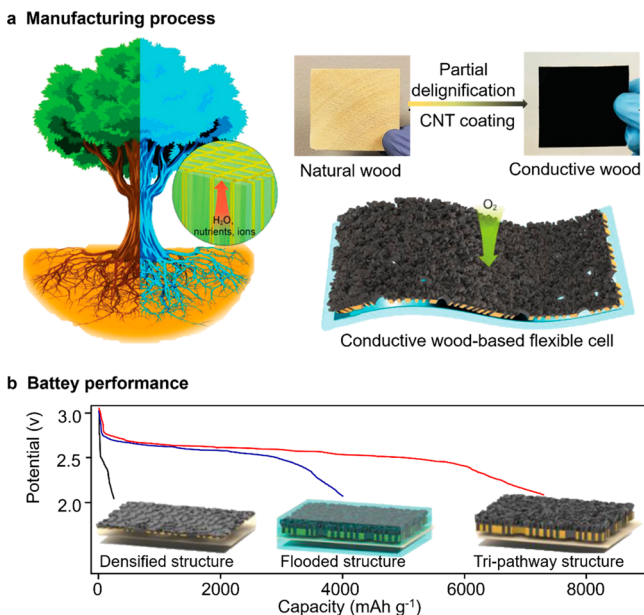
a Manufacturing process

b Battery performance

Figure 8. Conductive delignified wood for battery application. (a) The carbon nanotube (CNT) coating makes wood conductive to construct a flexible battery featuring a tree-inspired tripathway structure. (b) The conductive wood-based Li−O$_2$ cell with tripathway structure enables a high discharge capacity, surpassing the flooded structure and densified structure. Reproduced with permission from ref 9. Copyright 2019 Wiley-VCH.

challenge of balancing the thickness and flexibility of the electrode. Zhu et al.[60] transferred the graphite flakes with the electrolyte of PEO/LiClO$_4$ to the delignified wood (called isotropic paper) to construct a flexible transistor device. Such device shows the source-drain current changes as a function of the gate voltage, suggesting a typical bipolar transistor behavior. In addition, the delignified wood-based electronic device is slowly destroyed when being placed in soil, demonstrating its biodegradability, which further strengthens the competitiveness of delignified wood with other common substrates of flexible electronic devices, such as the silicon wafer.

Via transforming the lignocellulosic materials into the amorphous carbon, the carbonization strategy also imparts the delignified wood material with high conductivity, as well as maintaining the originally super compressibility and fatigue resistance of the delignified wood material with a lamellar structure (the so-called "wood sponge" or "wood aerogel").[11,50] The highly compressive and conductive wood features an excellent pressure sensibility, demonstrating a high-performance strain sensor for monitoring human motion and health. In addition to the electron transport in delignified wood toward the conductive wood, the ionic transport can also make the wood conductive. Li et al.[61] designed an ion-conducting wood via in situ delignification of wood followed by the densification and oxidation modification. The wood densification tunes the spacing of nanofibers of delignified wood from ∼20 to ∼2 nm, and the chemical modification of oxidation improves the surface charge density of the delignified wood, both of which lead to the fast ionic transport and imparts the delignified wood with a high
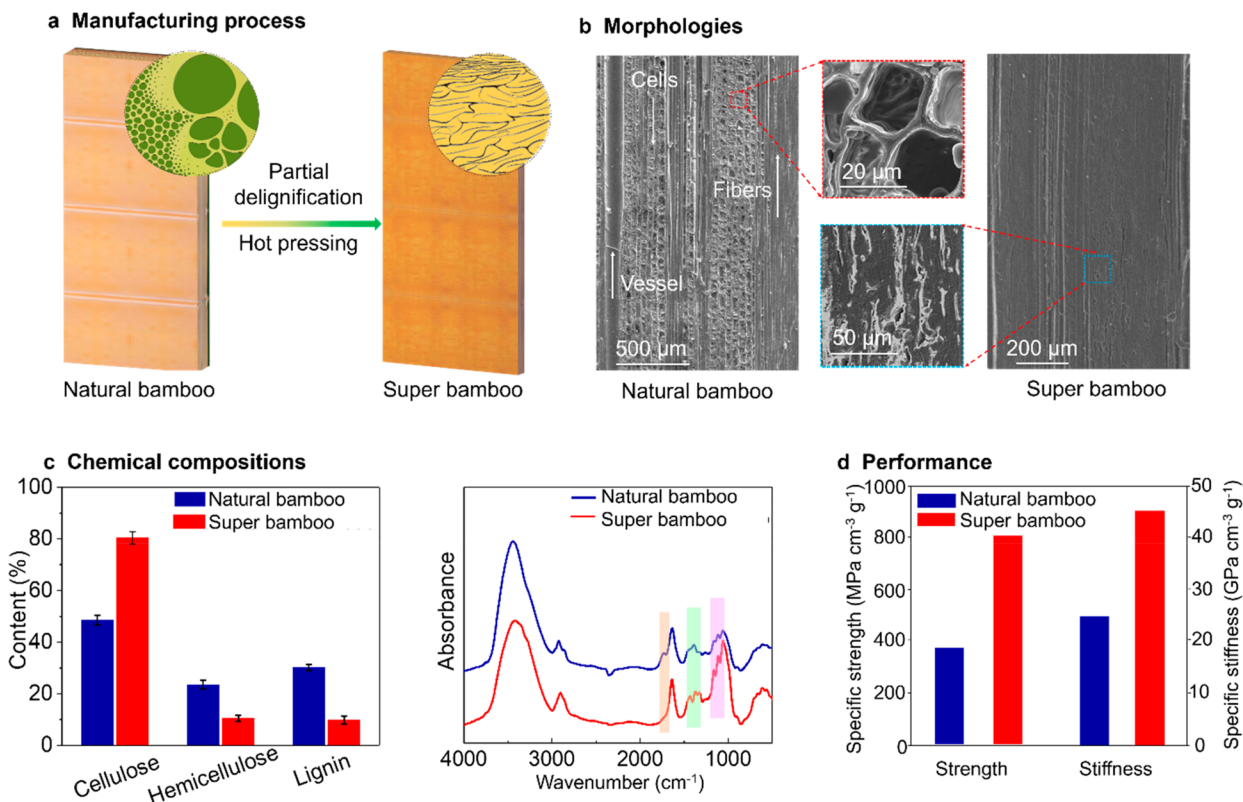
Figure 9. Delignification of bamboo toward strong structural material. (a) Partial delignification and hot pressing enable the softening and densification of bamboo to manufacture the super bamboo. (b) Super bamboo features a dense structure, because of the collapsing of pores, voids, and channels. (c) Compositional change of bamboo due to partial delignification. (d) Super bamboo shows a high specific strength and stiffness. (a−d) Reproduced with permission from ref 62. Copyright 2020 Wiley-VCH.

ionic conductivity of 2 mS cm^{-1}. Such modified wood material features the ionic rectification capacity, which is successfully used to construct a foldable transistor device. Although the delignified wood emerges unique advantages toward energy-related technologies, further studies are still needed to address the challenges for its practical applications. Advanced technologies focusing on the precise modification of conductive wood structure should be developed, for effectively modulating the transport of electrons and ions at multiple scales.

5. FROM WOOD TO OTHER BIOMASS

Given the similar structure and chemical compositions, in situ delignification technology can be extended from wood to nonwood biomass, such as bamboo. In addition to sustainability and worldwide availability, bamboo is one of the fastest-growing plants with a peak growth rate of up to 100 cm per day, making it attractive in value-added biomass utilization.[62,63] Similar to wood, bamboo can also be delignified in situ. For example, recently, Li et al.[62] developed a delignification technology of bamboo toward high-strength, lightweight structural materials, in which the partial delignification and hot-pressing treatments impart engineered bamboo with a dense structure, thus constructing a lightweight yet strong bulk structural material (namely, super bamboo in Figure 9a−c). The super bamboo features superior mechanical performance, where the record high tensile strength of ≈1 GPa and toughness of 9.74 MJ·m^{-3} are demonstrated. More importantly, the low density of lignocellulose in the super bamboo leads to a specific strength of 777 MPa·cm^{-3} g^{-1} (Figure 9d), which is significantly greater than most structural materials (e.g., natural polymers, plastics, steels, and alloys).

6. LIGNIN VALORIZATION

Lignin, as a ubiquitous and inexhaustible biomaterial, can be extracted and harvested during the delignification process.[39,64] Due to the abundant chemical groups (e.g., alcohol and phenol hydroxyl groups, and carbonyl groups) in lignin molecular structure, lignin can be functionalized modified toward advanced applications, such as platform chemicals and biofuels,[39] biobinders,[65] advanced manufacturing,[13] and so on (Figure 10).

A recent study by Hu et al.[65] demonstrated that lignin can serve as an excellent biobinder to strengthen cellulose paper, which is inspired by the reinforcement mechanism of lignin and cellulose in natural wood. Via a facile infiltration followed by hot-pressing treatment, lignin polymer effectively intertwines and bonds the cellulose fibers in paper scaffold, leading to a 200 MPa dried strength and 50 MPa wet strength for the modified paper. Lignin also endows the paper with improved thermostability and UV-blocking performance, as well as the maintained biodegradability, which enables the distinct competitiveness compared to the petroleum-based plastic products.

Although various products of lignin have been exploited, the low purity, nonuniform molecular weight, as well as sophisticated chemical structure still hinder further development of lignin functionalized products and advanced applications. The different engineering strategies for the delignification of wood further enhance the variability of properties of harvested lignin. The purification treatment can be an appealing strategy for tailoring the lignin properties toward advanced applications.
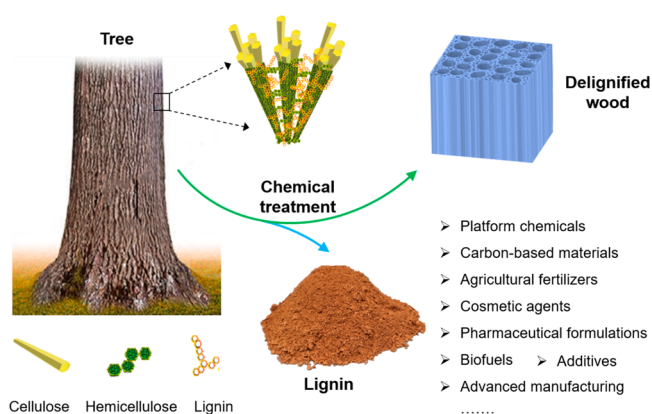

Figure 10. Functionalization and utilization of the extracted lignin in the delignification treatment. In situ chemical treatment enables the removal of lignin from wood, in which lignin can be recovered and further modified toward advanced lignin valorization. The tree image is reproduced with permission from ref 34. Copyright 2021 Wiley-VCH. The chemical compositional distinction is reproduced with permission from ref 28. Copyright 2015 Springer-Verlag Berlin Heidelberg. The delignified wood image is reproduced permission from ref 15. Copyright 2020 Wiley-VCH.

7. CONCLUSIONS AND PERSPECTIVE

In this Account, we investigated the in situ delignification of wood toward various sustainable applications. In situ chemical delignification involves the deconstruction and increased hydrophilicity of lignin molecules via a series of nucleophilic, electrophilic, radical, and oxidation reactions, enabling it to be removed effectively. This in situ chemical delignification strategy combined with other technologies (e.g., densification, polymer infiltration, chemical modifications, carbonization, and introducing conductive materials) enables the manipulation of wood's mechanical, ionic, optical, and thermal properties toward various advanced applications, such as lightweight structural materials, thermal and light management, energy storage, and flexible electronics.

Although great progress has been made in designing advanced, multifunctional wood-based materials, further efforts are needed to address technical challenges, as well as the environmental concerns of in situ wood delignification. Most recent technologies for delignification and functionalization of wood have been developed at the laboratory scale, where small-sized wood pieces, such as veneers with low thickness, are used as the raw material. However, as commercialized production uses large-sized (e.g., with length and width over 10 cm) wood blocks, we must consider the potential problem of the slow and nonuniform diffusion of the treatment chemicals into wood's structure, particularly given the material's anisotropic, hierarchical morphology, which can result in uneven distribution of the chemical modification. Enhanced pressure and elevated temperature can promote the transport of chemicals in the wood structure for more uniform reaction, which can be an effective strategy for manufacturing functionalized materials from industrial-scale pieces of wood.

Another challenge is that the compositional and structural properties of wood can depend on its growth environment and species. Such variability may negatively impact the precision and universality of various wood engineering and functionalization technologies. As a result, the process parameters may need to be adjusted, which can be costly and time-consuming if conducted in a trial-and-error approach. Artificial intelligence (AI) could

help in this process, as it is extremely effective at storing, analyzing, and mining data. For these reasons, we anticipate that AI could enable the real-time, in situ adjustment of manufacturing parameters for the continuous, large-scale, and high-quality production of wood-based functional materials.

Despite kraft pulping, chemical recovery has long been in commercial practice. Near complete removal of bulk wood lignin is difficult to achieve and often requires bleaching operations that can increase chemical oxygen demand (COD) in process streams. Water usage for washing the delignified wood can also be an environmental concern. Designing green chemicals is a promising direction for not only realizing the chemical engineering of wood but also decreasing environmental impacts. Despite these challenges and concerns, in situ delignification is a promising direction toward various functionalization and advanced applications of wood materials that could benefit a more sustainable future.

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Author Contributions

L. Hu, J. Li, and C. Chen conceived the concept and wrote the manuscript. J. Y. Zhu and A. J. Ragauskas revised the delignification chemistry part. All authors commented on the final manuscript.

Notes

The authors declare no competing financial interest.

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