Highly Anisotropic, Highly Transparent Wood Composites

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Wood is a widely used structural material that has excellent mechanical properties due to the unique structures from its natural growth.[1–3] Depending on their types and geographical differences, different woods display an extraordinary variety of mesostructures.[3] For example, softwoods typically have a more porous structure due to their fast growth. Hardwoods normally have a denser structure and a higher density compared to softwood. Although the large-scale structures in different woods can be dramatically different, the mesoporous structures of wood share amazing similarities in their hierarchical structures.[3] The most outstanding feature of woods is their structural anisotropy, where there exist many aligned vertical channels. Vertically aligned channels in wood are used to pump ions, water, and other ingredients through the wood trunk to meet the need for photosynthesis.[2,3] The cell walls consist of cellulose nanofibers of ≈3–5 nm in diameter, lignin, pectin, and others.[1,4–6] The hierarchical structure and the strong interactions among cellulose, hemicelluloses, and lignin lead to excellent mechanical properties in wood.[7] Recently, there is a great interest in abundant cellulose nanocrystals extracted from wood in electronics, energy, and a range of other types of applications due to their nanostructures, excellent mechanical, optical properties, etc.[8–14] For example, transparent substrates have been developed by mixing CNFs with index matching polymers.[13] While cellulose and hemicelluloses are optically colorless, lignin has an extremely complex structure with dark color. The mesoporous structure in wood also leads to large light scattering in the visible range. Therefore, wood always appears nontransparent with certain colors.

Advanced functional structures have been made by taking advantage of the unique microstructure in wood. Wood–polymer hybrids, wood–mineral hybrids (such as magnetic wood), and bioinspired structures have been demonstrated.[16] Wood can be made transparent through chemical bleaching followed by polymer inclusion, as demonstrated by Fink.[17] Transparent wood could be used for a wide range of applications from everyday uses such as wood furniture to more advanced applications such as structural materials in automobiles and optoelectronics. The anisotropic structure in almost all kinds of wood will still lead to anisotropic properties after being made transparent. For the first time, we investigated anisotropic transparent wood composites by removing colored lignin and filing index-matching polymers to achieve high optical transparency. We fabricated two types of transparent wood, where the original channels in wood align either perpendicularly to the wood plane or along the wood plane. We investigated the structure–process–properties relationship in wood and found that the fabrication processes need to be dramatically different due to the length differences in lignin removal and polymer filtration along the lumina. The resulting anisotropic wood composites keep the original wood micro- and nanostructures, including the aligned cell walls and the inside cellulose fibers. The composite displays extraordinary anisotropic optical and mechanical properties.

Figure 1a highlights the structure of Type 1 transparent wood, where the open through channels are perpendicular to the plane direction of a piece of wood. Type 1 wood is obtained by radially cutting the wood trunk, which is also called R-wood in this study. Lignin can be removed easily in R-wood while the cellulose backbone structure is preserved. After lignin is removed, the yellowish wood block becomes white due to the light scattering and the lack of light absorption by lignin. The lumina in the delignified wood now can allow fast infiltration of a refraction index-matching polymer to decrease the light scattering, thus leading to a highly transparent wood composite. A similar process can also be applied to fabricate Type 2 transparent wood, where the lumina are in the plane direction of a piece of wood. Figure 1b displays the structure of Type 2 transparent wood, where the lumina are in the plane direction of a piece of wood. Type 2 wood is obtained by longitudinally cutting the wood trunk, which is also called L-wood in this study. The processes for lignin removal and polymer infiltration are the same for Type 2 as for Type 1 but with a much longer mass transport length for Type 2. As shown in Figure 1b, thick transparent wood composites can be made through these simple processes, where literally the colored lignin nanoglue is replaced by colorless, index-matching polymer nanoglue, and the original wood structure is well preserved.

There are many straight channels in a wood trunk along the growth direction.[3] Wood slabs with dramatically different microstructures can be readily obtained by cutting in two different directions as shown in Figure 2a. The definitions of R-wood and L-wood are well illustrated in Figure 2b,c, respectively. R-wood has lumina perpendicular to the plane with a depth the same as the thickness of the wood; L-wood has the identical mesoporous lumina but the depth of the lumina is as long as the length of the wood block. The microstructural difference leads to different mass transfer behavior, where lignin can be extracted out much more easily in R-wood due to the lumina with a short depth (Figure 2b). It is expected to take a much longer time to extract lignin from L-wood (Figure 2c). Figure 2d,e displays the microstructures of R-wood and L-wood, respectively. Note that the lumina in wood are not uniform in...
diameter, ranging from 10 to 80 μm, which leads to the difficulty in removing lignin in L-wood.

In our experiment, a wood block with a dimension of 50 mm × 50 mm and a thickness of 3 mm was used. Traditional chemicals and processes used in paper pulping process were used in our experiment. Briefly, wood blocks were soaked in boiling solution containing NaOH and Na₂SO₃ (Process I, Figure 2f) to dissolve part of the lignin content referring to the chemicals and processes in kraft pulping[18]. Then the wood blocks were transferred into H₂O₂ solution to remove the remaining lignin in L-wood.

Figure 1. a) Schematic to display the mesoporous structures in wood where the cell walls are aligned vertically. After lignin is removed and the index-matching polymer is filled in, the thick (up to centimeter) piece of wood becomes a highly transparent structural material. b) Pictures to show that wood becomes highly transparent after the two steps.

Figure 2. a) Schematic to illustrate two types of wood blocks that can be cut from tree trunk, where the radially cut piece is named as “R” and the longitudinal one “L.” b) In R-wood, the lumina in wood are perpendicular to the plane. c) In L-wood, the lumina are along the plane direction. d) The SEM image of R-wood showing its numerous channels perpendicular to its surface. e) The SEM image of L-wood showing its long channels. f) A picture of lignin removal in the laboratory, where a few pieces of wood are heated in water with chemicals for lignin removal. g,h) Comparison of color changes of wood during lignin removal process I and II, respectively. i,j) Comparison of lignin content for wood during lignin removal Process I and II, respectively, where lignin removal is much faster for R-wood due to its open and short channels. The blue circles in (i) indicate the terminal time of process I for further treatment by process II.
lignin (Process II, Figure 2f). Since lignin is colored while cellulose is colorless, the color in the wood blocks indicates the amount of lignin present in the wood block surface. The color comparison for lignin removal in R-wood and L-wood is shown in Figure 2g,h. As expected, the color becomes lighter as lignin was removed. The process for R-wood is much faster than that for L-wood. Figure 2f also shows the experiment setup, which can be scaled up to process many wood blocks at the same time for mass manufacturing.

We also quantified the lignin removal in both types of woods (Figure 2i,j), where the y-axis is the lignin content of the wood blocks after a certain period of times for processes of I and II. In both types of wood treated by process I, the lignin was removed fast in the first hour, where the lignin loss for R-wood is higher, up to ≈25%. Figure 2i shows clear difference in lignin removal kinetics, where the process is much faster in R-wood. During the treatment of process II, the lignin in R-wood is also removed much faster (Figure 2j). These results agree with the fact that the channel length is much larger in L-wood than that in R-wood, which determines their different lignin loss kinetics.

The anisotropic lumina in wood blocks not only allow fast lignin removal but also lead to fast polymer infiltration to form transparent wood composite, especially for R-wood. Figure 3a shows the scanning electron microscope (SEM) image of a wood block after most lignin is removed. The wood block displays massive lumina along the wood growth direction. The lumen is surrounded by the cell wall, which is made of cellulose and hemicelluloses. Zoomed-in SEM also shows the smaller pits on the inner surface of the lumen (Figure 3b), which enables materials transport in the radial directions in the wood trunk. The inset of Figure 3b shows the picture of the delignified wood block after lignin removal. It is astounding that the microstructure with the well-defined channels is well preserved during the delignification process, which is critical for the fast infiltration of the polymer. A zoomed-in SEM image also shows the cellulose nanofibers on the cell walls, which are aligned and densely packed (Figure 3c).

Polymer is then infiltrated into the wood microstructures under vacuum assistance.[19] Transparent liquid epoxy resin precursor (the mixture of #300 resin and #21 nonblushing cycloaliphatic hardener) with relatively low velocity was used in the experiment. The lignin-removed white wood is then immersed in the polymer followed by repeated vacuum and devacuum process. A complete infiltration is achieved after about three times vacuum and devacuum cycles. SEM image in Figure 3d shows that the polymers can indeed fully fill the luma. The original delignified wood cell walls and the inner filled polymer can be distinguished clearly, as marked in the SEM image. All the channels and apertures are completely filled with the polymer, which was confirmed by breaking the wood–polymer composite in the middle followed by SEM imaging. Note that the polymer infiltration process does not destroy the framework of the natural wood microstructures. Strong interaction such as hydrogen bonding or van der Waals forces between the wood cellulose and infiltrated polymers is expected. After the polymer
infiltration, the white wood block (inset in Figure 3b) is optically clear (inset in Figure 3d).

The anisotropic structures in the two types of transparent wood potentially lead to a range of anisotropic properties. We have carefully investigated the anisotropic optical properties of R-wood and L-wood. Figure 4a,b illustrates the optical measurement for the two types of transparent wood composites. The thickness of both R-wood and L-wood is 2 mm for comparison purpose. A 532 nm single mode laser (Thorlabs Inc) was used as the incoming light source for the anisotropy measurement. The laser was collimated first with a spot size around 200 μm before perpendicularly illuminating the samples. The incoming light rapidly diverges due to the scattering in transparent wood composites. While the scattering effect is isotropic in the light propagation cross-section plane for R-wood (Figure 4c), the light scattering in L-wood is highly anisotropic (Figure 4d). A photodiode power sensor S130C from Thorlabs was used to record the scattered light intensity distribution in both the x and y directions (marked in Figure 4e,f) of the 2D plane perpendicular to the light propagation direction (z direction). After the polymer infiltration of the R-wood, the index mismatch between polymer and cellulose fibers facilitates angle-independent scattering of the single mode Gaussian laser beam. The resulting scattered light thus exhibits a Gaussian-like distribution with similar scattering angle in both the x and y directions. On the other hand, the wood fibers in the L-wood are aligned in the x direction, yielding a discrete index variation in the y direction (Figure 4f). A greatly traverse-expanded beam is observed in the y direction with an extremely large scattering angle, which resulted from the strong light diffraction by densely packed and aligned wood fiber cells with diameter ranging from 10 to 80 μm. In the x direction, there is little refractive index fluctuation and the incident light is scattered slightly, which resulted in a mild light space distribution. The strong anisotropic microstructures in L wood lead to its intense anisotropic optical properties.

The simultaneously high transmittance and high optical haze are likely due to the collective scattering throughout the transparent wood at the polymer–delignified wood interfaces. Figure S9 (Supporting Information) shows the total transmittance and optical haze for transparent wood with different thickness. The optical haze has a stronger dependence on the thickness. To show the difference between the scattering at the surface and scattering in the bulk, we designed a new laser scattering experiment. A bulk epoxy board with a roughened side surface is used for comparison with the transparent wood composite (Figure S10, Supporting Information). When a laser beam is illuminated from the side surface, light is mainly scattering at

![Figure 4. a,b) The transmittance measurement setup for transparent wood with two different anisotropic structures. c,d) The photo images of the scattered light spot for R-wood and L-wood, respectively. e,f) The intensity distributions in the x and y directions as shown in (c) and (d) for R-wood and L-wood, respectively. The L-wood shows obvious anisotropic behavior of optical transmittance. g,h) The R-wood is placed directly on the grids and 5 mm above the grids, respectively. i,j) The L-wood is placed directly on the grids and 5 mm above the grids, respectively. Vertical white lines are more visible than the parallel white lines due to the anisotropic scattering. k) Total transmittance for nature R-wood, nature L-wood, transparent R-wood, and transparent L-wood. l) Both R- and L-wood composites show high transmittance haze.](https://www.advancedsciencenews.com/doi/abs/10.1002/adma.201600427)
the roughened edge of the epoxy sample. Thus the surrounding side surface seems to be the brightest, shown in Figure S10a (Supporting Information). On the other hand, while the incident laser beam remains the same and illuminates on a transparent wood composite, the brightest point is inside the sample along the wood cell lumen growth direction. Apparently, the light is reflected/scattered by the wood composite along its whole pathway (bulk), in sharp contrast with the surface scattering of the epoxy board. Also, the light pathway can be clearly seen along the lumen direction (Figure S10b, Supporting Information), which indicates that the reflection/scattering are mainly at the interface between the cellulose and the polymer. We further prepared a wood composite sample using the polished and unpolished raw wood slices before delignification and polymer infiltration, and compared their optical properties (Figure S11, Supporting Information). The experimental results show that there are little changes for both total transmittance and haze when the surface roughness changes, which confirms that the observed optical properties are due to the scattering in the bulk not the surface.

The anisotropic transparent wood composites also exhibit unique imaging effects. We designed a grid with perpendicular and parallel lines to show the angle dependence in light scattering (Figure 4g–j). The grid lines can be clearly seen for both the R- and L-wood when touching the surface of grid lines (Figure 4g,i). However, the visual effect is dramatically different when the transparent wood composites are 5 mm above the lines. For R-wood, no lines can be observed due to the high transmittance haze. For L-wood, in sharp contrast, grid lines are turned to parallel lines and the lines parallel to the lumina diminish, which is in accordance with the anisotropic haze effect shown in Figure 4f.

In addition to the anisotropic behavior of the optical properties, we also investigated the total transmittance and optical transmittance haze of the transparent wood composite (Figure 4k,l). Integrated sphere was used to measure the optical transmittance and transmittance haze. Nature L- and R-wood shows almost negligible transmittance due to the strong lignin absorption. After lignin extraction and polymer infiltration, both types of transparent wood composites show dramatically high transmittance as illustrated in Figure 4k. The R-wood transmittance is up to 90%, higher than L-wood, which may be due to better filling of polymer because of the small depth for the lumina. Interestingly, both samples exhibit large haze covering the entire visible wavelength ranging from 400 to 800 nm, while R-wood shows a generally higher value than that of L-wood (Figure 4l). For the transparent wood composite where the interface between the microsized cellulose and the polymer has a roughness larger than the wavelength of the incoming light, the scattering intensity is almost independent of the wavelength. This broad range light management is often referred to as Mie scattering. The high optical haze as exhibited by both the R- and L-wood when touching the surface of grid lines (Figure 4g–j). The grid lines can be clearly seen for both the R- and L-wood when touching the surface of grid lines (Figure 4g,i). However, the visual effect is dramatically different when the transparent wood composites are 5 mm above the lines. For R-wood, no lines can be observed due to the high transmittance haze. For L-wood, in sharp contrast, grid lines are turned to parallel lines and the lines parallel to the lumina diminish, which is in accordance with the anisotropic haze effect shown in Figure 4f.

To carry out the experiment, transparent R-wood and transparent L-wood were fabricated with a shape shown in Figure 5a,b. The dimensions are about 50 mm long, 10 mm wide, and 3 mm thick for mechanical tests. A Tinius Olsen HSKT tester was used to carry out the stress–strain measurement for the samples. Nature woods cut into similar dimensions were also evaluated for comparison. Compared with nature R-wood, the transparent wood shows improved mechanical properties with a fracture strength and modulus up to 23.38 MPa and 1.22 GPa, respectively (Figure 5c and Table 1). Note that the fracture strength and modulus of the nature R-wood is only 4.46 MPa and 0.19 GPa, respectively. Lignin removal and polymer infiltration leads to transparent R-wood with improved strength (Figure 5c and Table 1). Note that the transparent wood possesses a similar strain to the nature wood, ~3.7%. The transparent L-wood has a fracture strength and modulus of 45.38 MPa and 2.37 GPa, respectively, about two times of the corresponding values for transparent R-wood (Figure 5d and Table 1). The transparent L-wood also has a higher ductility (toughness up to 1.20 MJ m⁻³; Table 1) than the transparent R-wood. Compared with the nature L-wood, transparent L-wood after polymer infiltration has a higher strength and ductility. The simultaneous increase of strength and ductility is abnormal but highly desired for applications. Note that in most materials the mechanical strength and ductility are mutually exclusive. Compared with the nature wood, the increase in both ductility and strength leads to a much higher toughness in transparent wood composites (Table 1), making the transparent wood developed in this study highly desirable for structural material applications.

We also carefully examined the cross section after the stress–strain test until the fracture occurred. The lumina in the nature wood are visible in the SEM (Figure 5e,f). Note that the force is perpendicular the lumina in R-wood, and parallel to the channels in L-wood. The SEM images show similar morphology after breaking, the macroscopic feature shown in the photographs after the fracture is highly different. The cross section of L-wood has a rough surface (inset of Figure 5f) where the breaking happens within the channels. Meanwhile, the R-wood shows a cross section more like a brittle material (small surface, inset of Figure 5e), due to the parallel stacking of the channels, where the breaking happens between the channels. Similar microscale and macroscale studies were also examined for transparent wood composites to investigate the failure mechanisms. In transparent R-wood and L-wood, the macroscopic structures of the cross section after mechanical fracture are similar, with a smooth interface. In transparent wood composites, the polymers become cross-linked with the cellulose backbone after the lignin removal, which forms a 3D network. The alignment structure observed in the SEM leads to higher mechanical strength in transparent L-wood than in transparent R-wood.

For the first time, we have demonstrated two types of anisotropic wood composites by taking advantage of the unique nature macrostructures in wood. In both R-wood and L-wood composites, two simple steps in sequence were used to fabricate anisotropic transparent wood composites: (1) lignin removal along the lumina and (2) polymer infiltration along the lumina. The well-defined, aligned channels largely facilitate the two processes. In both types of transparent wood, the nature cellulose
structures are well preserved, the color lignin is removed, and the porous structure is filled with a polymer, which leads to a high transmittance, up to 90%. The numerous polymer–cellulose interfaces cause more forward light scattering, which leads to a high optical haze at the same time. The two types of transparent wood composites also display dramatically different light scattering and mechanical properties. For example, the transparent wood with lumina in the plane is mechanically much stronger and tougher. The readily achieved transparent wood composites can find many applications as structural materials where mechanical strength and optical appearance are both important.

**Experimental Section**

**Materials and Chemicals**: Basswood from Walnut Hollow Company was used in this study. The chemicals used in removing lignin contents from wood were sodium hydroxide (>98%, Sigma-Aldrich), sodium

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<tr>
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<th>Strength [MPa]</th>
<th>Modulus [GPa]</th>
<th>Toughness [MJ m⁻³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nature R-wood</td>
<td>4.46</td>
<td>0.19</td>
<td>0.10</td>
</tr>
<tr>
<td>Transparent R-wood</td>
<td>23.38</td>
<td>1.22</td>
<td>0.59</td>
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<tr>
<td>Nature L-wood</td>
<td>42.72</td>
<td>5.78</td>
<td>0.33</td>
</tr>
<tr>
<td>Transparent L-wood</td>
<td>45.38</td>
<td>2.37</td>
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sulphite (>98%, Sigma-Aldrich), and hydrogen peroxide (30% solution, EMD Millipore Corporation). The polymer used for infiltration was epoxy resin (#300 resin and #21 nonblushing cycloaliphatic hardener, AeroMarine Products, Inc.). The solvents used were ethanol alcohol (190 proof, Pharmco-Aaper) and deionized (DI) water.

**Lignin Removal from Wood:** The lignin removal solution was prepared by dissolving NaOH (2.5 mol L\(^{-1}\)) and Na\(_2\)SO\(_3\) (0.4 mol L\(^{-1}\)) in DI water. The wood slices were immersed in the lignin removal solution and kept boiling for 12 h, followed by rinsing in hot distilled water three times to remove most of the chemicals. The wood blocks were then placed in the bleaching solution (H\(_2\)O\(_2\), 2.5 mol L\(^{-1}\) in DI water) and kept boiling without stirring. When the yellow color of the sample disappeared, the samples were removed and rinsed with cold water. The lignin-removed samples were preserved in ethanol.

**Polymer Infiltration:** Epoxy resin was prepared by mixing the two liquid components (#300 resin and #21 nonblushing cycloaliphatic hardener) at a ratio of 2 to 1. Then the lignin-removed wood was placed at the bottom of a dish and immersed in the liquid resin. The solution was then degased under 200 Pa to remove the gas and ethanol solvent in wood. Approximately 5 min later, the vacuum was released to let the resin filling into wood structure by atmosphere pressure. The process was repeated for three times. All the above processes were finished within 30 min to avoid the polymer solidification. Finally, the dish containing the wood sample and resin was kept static at 30 °C for 12 h. The resin-infiltrated wood sample was peeled off from the dish after the resin was completely solidified.

**Measurements and Characterizations:** The morphologies of wood were characterized by a scanning electron microscope (SEM, Hitachi SU-70). The transmittance spectrum and haze were measured with a UV–vis Spectrometer Lambda 35 (PerkinElmer, USA.). The lignin contents were measured by the standard methods for lignin determination (Technical Association of Pulp and Paper Industry Standard Method T 222-om-83). Briefly, dry wood (1 g, \(m_0\)), was measured and extracted with ethanol alcohol for 4 h, which was then treated with cold H\(_2\)SO\(_4\) (72%, 15 mL) and boiled for 4 h. After cooling down, they were filtered and washed with DI water. The insoluble materials were dried and weighed (\(m_1\)). The lignin content was calculated as: 

\[
\text{content}\text{ }= \text{ }\frac{m_0 - m_1}{m_0}\times100\%.
\]

A 532 nm single mode laser DJ532-10 (Thorlabs, Inc.) was used as the incoming light source with a stabilized output power. The laser was collimated first with a spot size of about 50 mm \(\times\) 10 mm \(\times\) 3 mm. A 532 nm single mode laser DJ532-10 (Thorlabs, Inc.) was used as the incoming light source with a stabilized output power. The laser was collimated first with a spot size of about 50 mm \(\times\) 10 mm \(\times\) 3 mm. A 532 nm single mode laser DJ532-10 (Thorlabs, Inc.) was used as the incoming light source with a stabilized output power.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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