Fire-retardant coatings have been proven effective at reducing the heat release rate (HRR) of structural materials during burning; yet effective methods for increasing the ignition temperature and delay time prior to burning are rarely reported. Herein, a strong, fire-resistant wood structural material is developed by combining a densification treatment with an anisotropic thermally conductive flame-retardant coating of hexagonal boron nitride (h-BN) nanosheets to produce BN-densified wood. The thermal management properties created by the BN coating provide fast, in-plane thermal diffusion, slowing the conduction of heat through the densified wood, which improves the material's ignition properties. Compared with densified wood without the BN coating, a 41 °C enhancement in ignition temperature ($T_{ig}$), a twofold increase in ignition delay time ($t_{ig}$), and a 25% decrease in the maximum HRR of BN-densified wood can be achieved. As a proof of concept for scalability, the pieces of the BN-densified wood are fabricated with a length larger than 25 cm, width greater than 15 cm, and thickness more than 7 mm. The improved thermal management, fire resistance, mechanical strength, and scalable production of BN-densified wood position it as a promising structural material for safe and energy-efficient buildings.

1. Introduction

Wood has been used to build structures such as bridges, house, towers, and furniture from ancient times to present day.[1–5]

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conductivity perpendicular to the plane, reducing the peak wood temperature and thus improving the ignition performance.

Herein, we present a simple and scalable method for improving the fire resistance of wood material by combining a densification treatment with a nano-laminated hexagonal boron nitride (h-BN) coating, 30 µm thick, to form what we call BN-densified wood (Figure 1). Densification has been proven to be effective in enhancing the fire-retardant performance of wood by self-forming a wood char layer upon exposure to a flame, which serves as an effective thermal and oxygen barrier.[32] In addition, unlike other inorganic flame retardant nanomaterials,[20–22] the 2D h-BN sheets are known to form a layered structure with anisotropic thermal properties (i.e., high in-plane and low through-plane thermal conductivities), as well as display good dimensional stability, desirable corrosion resistance, and antioxidant behavior,[25,33–40] which are attractive in fire protection of wood,[41] not only for reducing the HRR, but also for enhancing the ignition properties. As reported in the literature,[42] the thermal conductivities of h-BN in the in-plane and through-plane directions are 390 and 2 W m\(^{-1}\) K\(^{-1}\), respectively. Benefiting from the anisotropic thermal conductivity of h-BN, the BN-densified wood can effectively transfer the incoming heat along the wood surface and withstand the heat conduction in the vertical direction (Figure 1a). Simultaneously, the nano-laminated h-BN coating serves as a physical barrier to oxygen and volatiles, thus slowing exothermic reactions. As a result, the burning rates of BN-densified wood are significantly reduced. Furthermore, the coating method is simple and scalable, which can create a sandwich structure for BN-densified wood with a length larger than 25 cm and width greater than 15 cm (Figure 1b). Compared with other fire-retardant wood materials reported in the literature, BN-densified wood shows the longest ignition delay time and one of the highest tensile strengths (Figure 1c). The fire-retardant BN-densified wood meets the requirements of large-scale production, high mechanical performance, and good fire safety, representing an attractive candidate for structural applications.

2. Results and Discussion

Figure 2a shows photographs of the brown densified wood prepared by chemical delignification and hot-pressing. It also shows the subsequently formed white BN-densified wood after coating (see the Experimental Section for fabrication details). The color change demonstrates how the h-BN effectively covers the densified wood surface. The densified wood structure features totally collapsed cell walls, as shown by scanning electron microscopy (SEM) in Figure 2b. The BN-densified wood with a thickness of 7 mm was cut perpendicularly to the growth direction (Figure 2c), and the densified and intertwined wood structure was well-preserved after the BN coating (Figure 2d). The BN-densified wood exhibits a sandwich-like structure, with the densified wood entirely coated by a thin h-BN layer (≈30 µm, with a mass content of 4.7 wt%, see Figures S1 and S2, Supporting Information) with the adherence strength of 1B level (Figure S3, Supporting Information) on the outer surface (Figure 2e, g). The potential issues of low adhesion strength between the coating layer and densified-wood matrix for practical engineering application can be potentially solved by adding...
fire-retardant adhesives or 3D bulk coating both on surface and inside the wood lumens. High-resolution cross-sectional SEM imaging further reveals the layered structure of the h-BN sheets (Figure 2f). Furthermore, most of the h-BN sheets with the layer-by-layer structure are well coated on the densified wood surface, which is important for achieving effective thermal management in the wood substrate (Figure 2g). Aside from the functional groups belonging to components in natural wood (e.g., cellulose, hemicellulose, and lignin), two new peaks at 1360 and 780 cm\(^{-1}\) can be found in the Fourier transform infrared (FTIR) spectrum after BN coating, which correspond to the in-plane B–N stretching and bending vibrations, respectively (Figure S4, Supporting Information).\(^{[43,44]}\) Transmission electron microscopy (TEM) further shows that the h-BN sheets are hexagonal (Figure 2h). The selected area electron diffraction pattern also displays two characteristic diffraction rings (002) and (100) of the h-BN nanosheets (inset in Figure 2h).\(^{[45]}\)

We explored the fire-resistant properties of the densified wood and BN-densified wood samples by exposing them to a propane flame for 30 s and monitoring the flame propagation. The densified wood ignited within 5 s with a dramatic flame spread over the next 8 s. At 31 s, the densified wood remained burning even after the propane torch was removed (Figure 3a). Note that the densified wood showed improvement compared to natural wood which ignited within 3 s (Figure S5, Supporting Information). Figure 3b shows the schematic of the densified wood exposed to the flame. The completely collapsed wood cells expand after burning for 30 s and eventually form a wood char layer on the material’s surface (Figure 3c,d).

In contrast, the BN-densified wood can withstand exposure to the same flame until 8 s and exhibits self-quenching after the flame is removed at 31 s (Figure 3e). The observed resistance to ignition and self-quenching are correlated with the anisotropic thermal properties and oxygen insulating ability of the h-BN coating layer (Figure 3f). We conducted SEM measurements to better understand the protective effects of the h-BN layers. Compared with densified wood without BN coating, although some tiny cracks were observed in the cross-sectional surface of the BN-densified wood, most of the wood cell walls remained tightly closed even after burning for 30 s, suggesting the continued protective effects of the h-BN layers. The anisotropic thermal conductivity of the h-BN coating. Furthermore, the well-maintained h-BN layer slows the transport of oxygen and pyrolysate, thus helping to protect the wood from burning.

We further studied the combustion behavior of the BN-densified wood using a cone calorimeter. The experiment was performed in accordance with ASTM E1354 (2017).\(^{[46]}\) We applied external heat fluxes (\(q_{\text{ext}}\)) of 20, 30, and 40 kW m\(^{-2}\) to the

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**Figure 2.** Morphology and microstructure of the densified wood and BN-densified wood. a) Photographs of the densified wood and BN-densified wood. The densified wood surface changed from brown to white due to the h-BN coating. b) An SEM image of the densified wood demonstrates the highly compressed structure and totally collapsed wood cell walls, which are highlighted in the inset image. c) The BN-densified wood was cut perpendicular to the growth direction to show that the h-BN only coats the densified wood surface, while the inner densified wood structure is maintained. d) The SEM image shows the compact wood structure of the BN-densified wood. e) Cross-sectional SEM image of the BN-densified wood shows the thickness of the h-BN layer is 30 µm. f) Cross-sectional SEM image shows the layered structure of the h-BN coating. g) A top-view SEM image of the BN-densified wood shows the distribution of h-BN sheets on the densified wood surface. h) The TEM image and SAED pattern of h-BN sheets on BN-densified wood surface.
BN-densified wood and measured the corresponding HRR, which are plotted in Figures S6–S8 in the Supporting Information, respectively. Cone calorimeter results for the densified wood with the same $q_{ex}$ were conducted and reported previously.[32] The corresponding ignition delay times ($t_{ig}$) are plotted and compared in Figures 4a,b. For all the $q_{ex}$, the $t_{ig}$ for the BN-densified wood was at least twice as long as that of the densified wood (Figures S6–S8, Supporting Information). The ignition delay time can be fitted as Equation (1)[47]

$$t_{ig} = -\frac{b}{q_{crit} - q_{ex}}$$

in which $b$ is a fitted constant and $q_{crit}$ is the critical heat flux, which is the minimum heat flux for ignition. The results of $b$ and $q_{crit}$ are 3.37 s·MW m$^{-2}$ and 15.3 kW m$^{-2}$ for the BN-densified wood, and 1.79 s·MW m$^{-2}$ and 12.6 kW m$^{-2}$ for the densified wood, respectively. The greatly improved $q_{crit}$ of BN-densified wood demonstrates the enhanced fire resistance imparted by the BN coating. The thermal response parameter (TRP) is an indicator of ignition delay time, which can be calculated by Equation (2):

$$t_{ig} = \left( \frac{\text{TRP}}{q_{ex}} \right)^2$$

in which is the slope of the fitted line in Figure 4b. We determined the TRP of the BN-densified wood was 480 ± 57 s$^{0.5}$·kW m$^{-2}$, which is much higher than that of the densified wood (308 ± 9 s$^{0.5}$·kW m$^{-2}$). Compared with the densified wood, the BN-densified wood, with its longer $t_{ig}$ and higher $q_{crit}$ and TRP, presents substantially improved flame resistance.

Equation (1) predicts a $t_{ig}$ of 92 s for the BN-densified wood at an external heat flux of 50 kW m$^{-2}$. This is at least 2.3 times as long as most reported fire-resistant wood samples at that heat flux (Figure 4c).[17–24] Figure 4d compares the ignition properties of the densified wood and BN-densified wood. Ignition temperature ($T_{ig}$) is calculated by Equation (3):

$$T_{ig} = \text{a constant}$$

Figure 3. Flammability tests of the densified wood and BN-densified wood. a) The burning behavior of the densified wood under the propane flame for 30 s. The scale bar, 2 cm. b) The schematic shows the morphology change of the densified wood after burning. c, d) SEM images of the densified wood after combustion: c) Cross-sectional view and d) top view. e) The burning behavior of the BN-densified wood under the propane flame for 30 s. The scale bar, 2 cm. f) The schematic shows the morphology change of the BN-densified wood after burning. g, h) SEM images of the BN-densified wood after combustion: g) Cross-sectional view and h) top view.
\[ q_{\text{ext}} = h_c (T_{ig} - T_\infty) + \sigma (T_{ig}^4 - T_\infty^4) \]  

in which \( h_c \) is the convective heat transfer coefficient (15 W m\(^{-2}\) K); \( T_\infty \) is the ambient temperature (298 K), and \( \sigma \) is the Stefan–Boltzmann constant \((5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4})\). The ignition temperature \( T_{ig} \) of the BN-densified wood is 381 \( \pm \) 74 °C, which is 41 °C higher than that of densified wood.\(^{[32]}\)

Figure S9 in the Supporting Information shows the final residues of the wood samples after combustion. The densified wood is cracked into several pieces, while the BN-densified wood remains in one piece with few cracks and holes on the surface. The non-flammable h-BN layer on the wood surface serves as an insulating barrier that inhibits the release of pyrolysates (e.g., H\(_2\) and light hydrocarbons). The limited gas leakage through the cracks and holes on the h-BN coating layer significantly reduces the average and peak HRRs (HRR\(_{\text{ave}}\) and HRR\(_{\text{peak}}\)). The HRR\(_{\text{ave}}\), HRR\(_{\text{peak}}\), average mass loss rate (\( m_\text{ave} \)), burning time (\( t_{\text{burn}} \)), and the heat of combustion (\( \Delta h_c \)) of the BN-densified wood are 111 \( \pm \) 38 kW m\(^{-2}\), 146 \( \pm \) 28 kW m\(^{-2}\), 92.3 \( \pm \) 24 mg s\(^{-1}\), 507 \( \pm \) 197 s, and 12.1 \( \pm \) 1.1 kJ g\(^{-1}\), respectively (Table 1). All of these values are smaller than that of the densified wood,\(^{[32]}\) indicating the h-BN coating layer provides a better flame resistance for the BN-densified wood.

The significant improvement of the ignition temperature and delay time of the BN-densified wood emphasizes the crucial role of the thermal management properties imparted by the anisotropic thermal conductivity of the h-BN coating. Benefiting from the high in-plane and low through-plane thermal conductivity of the h-BN coating layer, we performed heat-transfer tests to show that the h-BN coating layer can achieve both thermal dissipation and insulation of the densified wood surface. First we used an incident laser beam with a diameter of 1 mm to provide a continuous and stable heat input on the top section of the densified wood (parallel to the wood growth direction, Figure 5a). The resulting temperature distributions of the top and cross-section of the densified wood surface were monitored and recorded by an infrared (IR) camera. Figure 5b shows the Table 1. Measurements of HRR\(_{\text{ave}}\), HRR\(_{\text{peak}}\), \( m_\text{ave} \), \( t_{\text{burn}} \), and \( \Delta h_c \) of the densified and BN-densified wood. 95% confidence intervals are shown.

<table>
<thead>
<tr>
<th>Materials</th>
<th>HRR(_{\text{ave}}) [kW m(^{-2})]</th>
<th>HRR(_{\text{peak}}) [kW m(^{-2})]</th>
<th>( m_\text{ave} ) [mg s(^{-1})]</th>
<th>( t_{\text{burn}} ) [s]</th>
<th>( \Delta h_c ) [kJ g(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Densified wood(^{[27]})</td>
<td>121 ( \pm ) 31</td>
<td>194 ( \pm ) 12</td>
<td>99.8 ( \pm ) 30</td>
<td>522 ( \pm ) 82</td>
<td>13.0 ( \pm ) 2.8</td>
</tr>
<tr>
<td>BN-densified wood</td>
<td>111 ( \pm ) 38</td>
<td>146 ( \pm ) 28</td>
<td>92.3 ( \pm ) 24</td>
<td>507 ( \pm ) 197</td>
<td>12.1 ( \pm ) 1.1</td>
</tr>
</tbody>
</table>
temperature contour of the top surface, which features a maximum value of 74 °C in the densified wood after exposure to the laser for 5 min, suggesting obvious heat concentration in densified wood surface caused by the poor thermal conductivity of the wood material.\cite{48,49} Due to the rapid heat accumulation on the surface, the densified wood with a relative low ignition temperature will easily ignite. In the cross-section, the temperature distribution is semicircular, which verifies that heat transfers isotropically into the densified wood, which can increase the flammability (Figure 5c).

Interestingly, the BN-densified wood displays a completely different heat transfer behavior. When the top section of the BN-densified wood is exposed to the constant heat source, we anticipated the heat conduction would occur in the wood growth direction, following the lateral path of the h-BN coating, while the cross-section of the BN-densified wood would display better thermal insulation behavior (Figure 5d). Because of the high thermal conductivity of h-BN in the planar direction, the heat uniformly disperses, leading to a circular temperature contour on the top surface of BN-densified wood (Figure 5e). The temperature of the top surface reaches a maximum of 48 °C, which is 30 °C lower than that of the uncoated densified wood with the same laser power input, demonstrating the large amount of inputted heat that is dissipated along the BN-densified wood surface. Meanwhile, as verified in Figure 5f, heat insulation occurs in the cross direction due to the poor cross-plane thermal conductivity of h-BN. The temperature contour for the cross-section of the BN-densified wood shows a horizontal ellipse shape, indicating that heat transport paths from the top surface to the interior of the densified wood has been blocked. As a result, the underlying densified wood can maintain a low temperature, allowing increased ignition delay times and increased ignition temperature of the BN-densified wood.

To directly display the heat concentration and heat diffusion, we provided the temperature distribution of the wood specimens on the top and the cross-section under the radiative heat source, and the defined axes are shown in Figure 5g. As shown in Figure 5h, the maximum temperature on the top surface of the BN-densified wood is 48 °C with a full width at half maximum (FWHM) of 5.06 mm, compared with 78 °C on the densified wood with an FWHM of 3.86 mm, suggesting the better heat dissipation of the BN-densified wood on the top surface. Meanwhile, the BN-densified wood with a lower temperature distribution shows a slowly decreased profile in cross-section, demonstrating the good insulating performance imparted by the low through-plane thermal conductivity of the h-BN coating.
(Figure S1i). Moreover, the thermal conductivity of BN-densified wood in the through- and in-plane directions is 0.56 ± 0.13 and 1.63 ± 0.25 W m⁻¹ K⁻¹, respectively, indicating the anisotropic thermal properties (Figure S10, Supporting Information). The anisotropic thermal conductivities of the BN-densified wood provide a mathematical backing to the heat transfer behaviors observed. These results demonstrate that the inputted heat can be easily conducted along the top surface (parallel to h-BN plane) and effectively impeded in the cross-section (perpendicular to h-BN plane), which contributes to the material’s excellent fire-retardant performance, particularly its long ignition delay time that surpasses most previously reported wood composites.

Besides its enhanced thermal management and fire resistance, the BN-densified wood can also meaningfully compete with steel or concrete in the construction industry due to its superb mechanical properties. The maximum tensile strength of the BN-densified wood along the longitudinal direction approaches 471.5 MPa, which is almost 8.7-times stronger than that of natural wood. Meanwhile, the tensile strength of BN-densified wood along the radial direction is 38.7 MPa, which is approximately 11 times higher than that of natural wood (Figure S11, Supporting Information). Taking the density into account, the specific tensile strength of the BN-densified wood is also much higher than that of commercial construction materials (concrete, Al alloy, high-specific-strength steel, and natural wood; Figures S12 and S13, Supporting Information), revealing the lightweight alternative to these traditional structural materials. The newly developed BN-densified wood with its excellent thermal management, enhanced fire resistance, super strong, lightweight, scalable, and environmentally friendly character make it an attractive structural material for modern building applications.

3. Conclusion

In summary, we demonstrate a super strong and fire-resistant BN-densified wood through a simple but effective coating method. The h-BN coating is homogeneous and horizontally stacked on the surface of the 7-mm-thick densified wood, which provides an excellent protective barrier for inhibiting oxygen diffusion and flammable volatiles released when exposed to heat. Benefiting from the anisotropic thermal conductivity of h-BN, the BN-densified wood exhibits excellent heat diffusivity along the in-plane direction and effective heat blocking in the through-plane direction. Compared with the uncoated densified wood, the BN-densified wood displays a 41 °C enhancement in ignition temperature ($T_{90}$), a twofold increase in ignition delay time ($t_{90}$), and a 25% decrease in the maximum HRR, suggesting an overall improvement of the fire resistance. Meanwhile, the BN-densified wood also demonstrates excellent mechanical properties with a high tensile strength of up to 471.5 MPa and a special tensile strength of 362 MPa cm² g⁻¹, indicating the super strong and lightweight alternative to these traditional structural materials. This work demonstrates that the anisotropic thermally conductive h-BN fire-retardant coating not only enhances the fire resistance of wood but also maintains the high strength imparted to the material by densification, representing a promising direction for developing high-performance structural materials that can fulfill the simultaneous requirements of high mechanical strength and good fire safety in modern construction.

4. Experimental Section

**Materials:** Basswood (Midwest Products Co.), sodium hydroxide (≥97%, Sigma–Aldrich), sodium sulfite (≥98%, Sigma–Aldrich), and commercial h-BN micropowder (Momentive Inc.) were used in this experiment.

**BN-Densified Wood Preparation:** The densified wood was prepared by a chemical delignification and hot-pressing treatment following our previous studies. Then, 10 g of h-BN powder was dispersed in deionized water (1000 mL) by sonication for 48 h, followed by centrifugation at 5000 rpm for 2 min. After centrifugation of the dispersion, the supernatant was collected. To obtain an aqueous h-BN paste with a solid concentration of 10 wt%, the vacuum filtration and drying process were used to remove the rest of water. The obtained BN paste was coated on the densified wood surface using a brush and sandwiched between two pieces of stainless steel, then hot pressed under a pressure of 5 MPa at 60 °C until it was completely dried.

**Characterization:** The morphology of the samples was studied by SEM and TEM using a Hitachi SU-70 SME and JEOL JEM 2100 TEM. ATR-FTIR spectra were obtained (Thermo Nicolet NEXUS 670 FT-IR) as the result of the accumulation of 32 scans with the interferometer mirror speed of 0.6329 mm s⁻¹, a resolution of 4 cm⁻¹, in the range of 4000–650 cm⁻¹. The tensile strength of the BN-densified wood (100 mm × 5 mm × 1.5 mm) was determined using a Tinius Olsen HS KT tester. Adhesion tests were performed in accordance with ASTM D3359 (Test Method B). The thermal conductivities of wood samples were measured via the steady-state method.

**Cone Calorimetry Measurements:** The combustion test used a cone calorimeter with heat fluxes of 20, 30, and 40 kW m⁻², according to ASTM E1354. The wood specimens (100 × 100 × 6 mm) were used in this experiment. Time and HRR are recorded by a data collection (Fluke ITS-90). A conical radiant electric heater and an electric ignition spark plug were used to ignite the wood samples.

**Heat-Transfer Tests:** Thermal diffusion tests were conducted for the two kinds of wood samples. The dimensions of the samples were approximately 50 mm × 50 mm × 5 mm. Here, the 50 × 50 mm surface is called the front surface and the 50 × 5 mm surfaces are called the lateral surfaces. A 465 nm diode-pumped solid state laser was used for the energy input on the wood samples. Two sets of tests were conducted. In the first set of tests, the laser spot was aimed at the center of the front surface. The central area was covered by a layer of black coating with a square shape (3 mm × 3 mm) and an emissivity of 0.9. The temperature distribution of the front surface was measured and mapped by a FLIR Merlin MID IR camera system. In the second set of tests, the laser spot was aimed on the edge of the front surface where a 3 mm × 3 mm square area was also coated. The temperature distribution of the nearest lateral surface was measured and mapped. The temperature distributions were recorded by the IR camera when the samples were at a steady state. The power of the laser was 167 mW for all tests.

**Supporting Information**

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

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

W.G., C.C., and Z.W. contributed equally to this work. L.H., W.G., and C.C. designed the experiments. W.G., C.C., and J.S. contributed to wood processing and mechanical measurements. Z.W. and P.B.S. contributed to the fire resistance measurements and analysis. W.G., Y.P., and B.Y. contributed to the heat-transfer tests. B.Z. and S.D. contributed to the thermal expansion tests. W.G. and J.D. created the 3D illustrations. W.P., Y.Y., and S.H. provided characterizations via SEM, TEM, and FTIR. W.G., C.C., and L.H. collectively wrote the paper. All authors commented on the final manuscript.

Keywords

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