

Superflexible Wood

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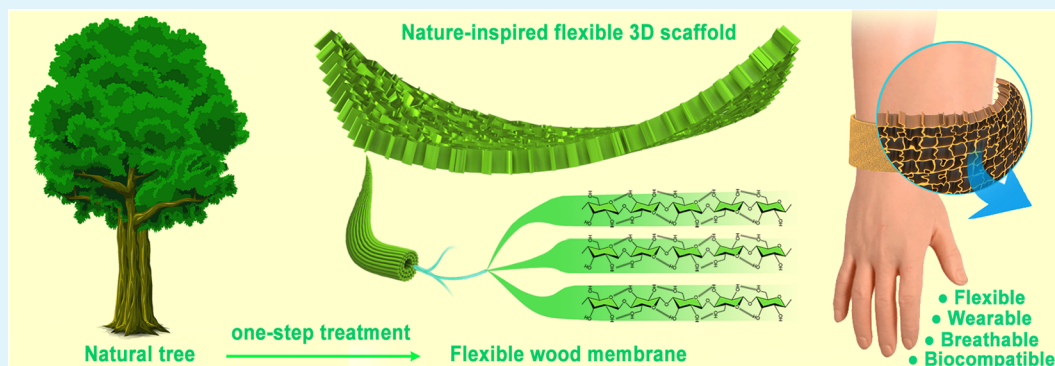
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S Supporting Information



ABSTRACT: Flexible porous membranes have attracted increasing scientific interest due to their wide applications in flexible electronics, energy storage devices, sensors, and bioscaffolds. Here, inspired by nature, we develop a facile and scalable top-down approach for fabricating a superflexible, biocompatible, biodegradable three-dimensional (3D) porous membrane directly from natural wood (coded as flexible wood membrane) via a one-step chemical treatment. The superflexibility is attributed to both physical and chemical changes of the natural wood, particularly formation of the wavy structure formed by simple delignification induced by partial removal of lignin/hemicellulose. The flexible wood membrane, which inherits its unique 3D porous structure with aligned cellulose nanofibers, biodegradability, and biocompatibility from natural wood, combined with the superflexibility imparted by a simple chemical treatment, holds great potential for a range of applications. As an example, we demonstrate the application of the flexible, breathable wood membrane as a 3D bioscaffold for cell growth.

KEYWORDS: wood chemistry, 3D porous structure, cellulose nanofibers, biocompatible, flexible

INTRODUCTION

Materials with high mechanical flexibility, biocompatibility, and porous structure are urgently needed for the development of portable energy storage devices,¹ sensors,^{2,3} flexible electronics,^{4–6} and three-dimensional (3D) bioscaffolds.^{7–9} Recently, many efforts have been dedicated to the fabrication of various flexible membranes including inorganics, polymers, and biological materials with additional functionalities. For example, conductive sponges have been demonstrated with excellent flexibility and charge transport for microbial fuel cells.¹⁰ Among the flexible membranes that have captured recent interest, natural biological materials have been regarded as one of the most promising candidates due to their inherently high biocompatibility, renewability, and source material abundance.

Cellulose-based flexible membranes, for example, have been widely investigated in energy storage devices^{11–17} and flexible

electronics,^{18,19} showing excellent flexibility, biocompatibility, and renewability. Despite the aforementioned merits, the fabrication process of cellulose-based membranes generally involves multiple steps including the disintegration of cellulose fibers using chemical,²⁰ mechanical,²¹ or biological methods,²² dispersion of cellulose fibers into solution, and reconstruction via a bottom-up approach. Although the bottom-up approach can enable fine control of the membrane structure, the multistep fabrication process is relatively costly yet has a low fabrication yield efficiency, positioning it as a less competitive method for scalable applications. In this context, a low-cost,

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scalable, simple yet effective fabrication approach is highly desirable but also challenging to design.

In addition, the growing demands for tissue engineering, including tissue regeneration and repair, have driven the search for bioscaffold materials with excellent biodegradability and biocompatibility. Among them, natural biological materials have been regarded as one of the most promising candidates due to their inherently high biocompatibility. In addition to the requirements of biodegradability and biocompatibility, porous 3D structure is highly desirable for bioscaffold materials to provide abundant space for cell growth and tissue formation.^{7–9} Recently, many efforts have been dedicated to the fabrication of various 3D nanomaterials for tissue engineering and regenerative medicine.

For the first time, a simple yet effective top-down chemical approach is developed to construct a superflexible, biodegradable, and biocompatible 3D porous membrane directly from cellulose-based natural wood material via a one-step chemical treatment. The flexible wood membrane demonstrates a unique 3D porous structure with numerous channels, excellent biodegradability and biocompatibility enabled by the cellulose-based wood precursor, and superior flexibility induced by partial lignin/hemicellulose removal. These structural merits contribute to excellent biocompatibility and efficient cell adhesion properties, demonstrated by the successful attachment of HEK293 cells in abundance onto the flexible wood membrane, indicating the great potential of flexible wood for 3D cell carriers. Moreover, the superflexible wood membrane can potentially enable a range of applications beyond bioscaffolding, such as structural materials and flexible electronics.^{4–6,23,24}

RESULTS AND DISCUSSION

Cellulose-based natural wood material is one of the most abundant resources on earth and is widely used in buildings,^{25,26} cellulose industry,^{27–29} energy storage,^{30–35} and water treatment applications.^{36,37} The lignocellulosic composition endows natural wood materials with excellent biodegradability and biocompatibility. Additionally, they commonly possess a unique 3D porous structure with multiple channels, including tracheids and vessel cells in the xylem, with the cell types depending on the species.^{32,38} Interestingly, when we look at flexible porous membrane materials, especially 3D bioscaffolds, it is not hard to notice that biodegradability, biocompatibility, and 3D porous structure are three key features. This has inspired us to develop a flexible membrane material directly from natural balsa wood.³⁹ Figure 1a graphically illustrates the nature-inspired design concept and straightforward one-step top-down fabrication approach of the superflexible wood membrane directly from natural wood. Due to the excellent biocompatibility and unique 3D porous structure with multiple channels, the flexible wood membrane can find a range of promising applications, especially for 3D bioscaffolds. Another benefit of the wood-based flexible membrane is its superflexibility. As demonstrated in Figure 1b,c, the natural wood membrane breaks easily upon bending, while the modified flexible wood can totally recover its shape even upon severe folding and twisting, suggesting superflexibility. The superflexibility enables the wood membrane to have excellent mechanical properties and tunable shapes for wearable devices. More excitingly, even a large thickness (4 mm) sample of the modified flexible wood membrane can still be totally recovered after severe twisting, demonstrating the

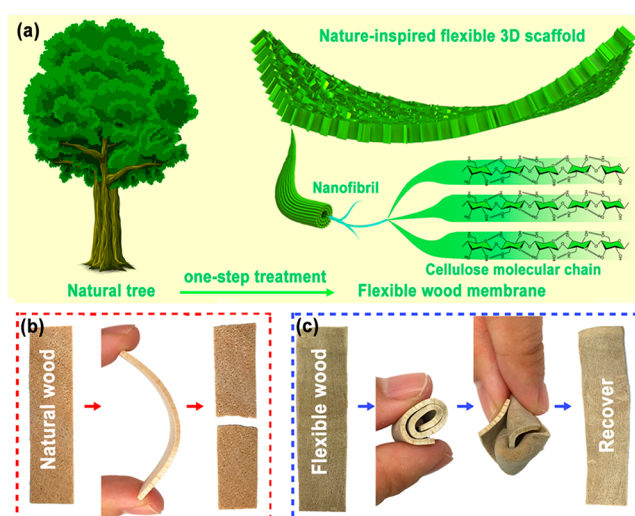


Figure 1. Graphical illustration and photo images of flexible wood through a simple yet effective chemical treatment. (a) Graphical illustration of the nature-inspired flexible wood-based membrane material directly from natural wood with multiple aligned channels and cellulose nanofibers via a one-step chemical treatment. (b) Photo images of natural wood before bending, under bending, and breaking upon bending. (c) Photo images of flexible wood before bending, under severe folding/twisting, and after recovery.

great potential of the flexible wood membrane for thick wearable devices (Figure S1). Additionally, the alignment of cellulose nanofibers gives the flexible wood membrane unique anisotropic properties, holding great promise for flexible electronic, energy storage device, sensor, and 3D bioscaffold applications.

The fabrication process of the flexible wood membrane is quite simple yet effective, involving only a one-step chemical treatment (see Experimental Section for synthetic details). Typically, the pre-cut natural balsa wood membrane was immersed into a mixed solution of NaOH and Na₂SO₃ for 1 h and then washed with deionized (DI) water and dried in air to obtain the final product of flexible wood (Figure 2a). Significant shrinkage was observed during the drying process, associated with dehydration of the wood membrane (Figure S2). The morphology and microstructure of the wood membranes before and after chemical treatment are characterized by scanning electron microscopy (SEM), as shown in Figure 2b–e. Natural balsa wood shows a unique 3D porous structure with irregular hexagonal cell lumina of 30–50 μ m in diameter along the tree-growth direction (Figure 2b,c and Figures S3 and S4). After chemical treatment, the multi-channelled 3D porous structure can be well preserved but with distinct evolution from open latticed hexagonal cell lumina to crumpled ones with irregular shape and shrunken diameters (Figure 2d,e and Figures S5 and S6). This unique crumpled, shrunken cell lumen structure is expected to contribute to the superflexibility of the modified wood membrane. Moreover, the mechanical tensile strength of the modified wood membrane can be significantly enhanced by ~ 7 times in contrast to untreated natural wood membrane simultaneously, further emphasizing the advantages of the chemical treatment method presented in this work (Figure S7 and Table S1). Meanwhile, the modulus of the wood membrane decreases from 134 to 116 MPa after chemical treatment, suggesting softening of the treated wood. The structure of flexible wood is similar to cork

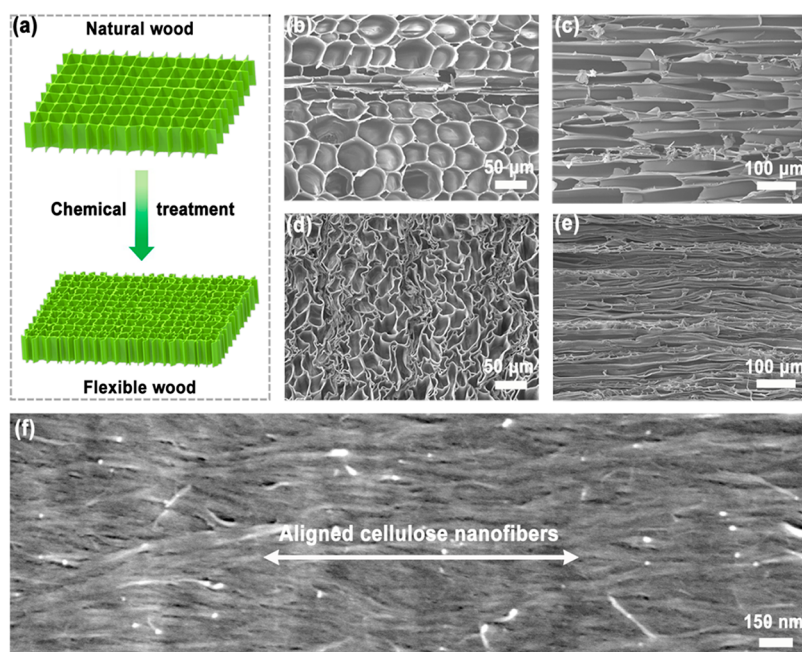


Figure 2. Structural characterization of natural and flexible wood after one-step chemical treatment. (a) Schematic illustration of treatment process for superflexible wood. (b, c) SEM images of natural wood: (b) cross-sectional image showing hexagonal fiber cells and (c) longitudinal image that shows elongated cell lumina. (d–f) SEM images of flexible wood: (d) cross-sectional image showing crumpled fiber cells, (e) longitudinal image that shows narrowed cell lumina, and (f) magnified SEM image showing aligned cellulose nanofibers in flexible wood. The thickness of wood membrane is 1 mm.

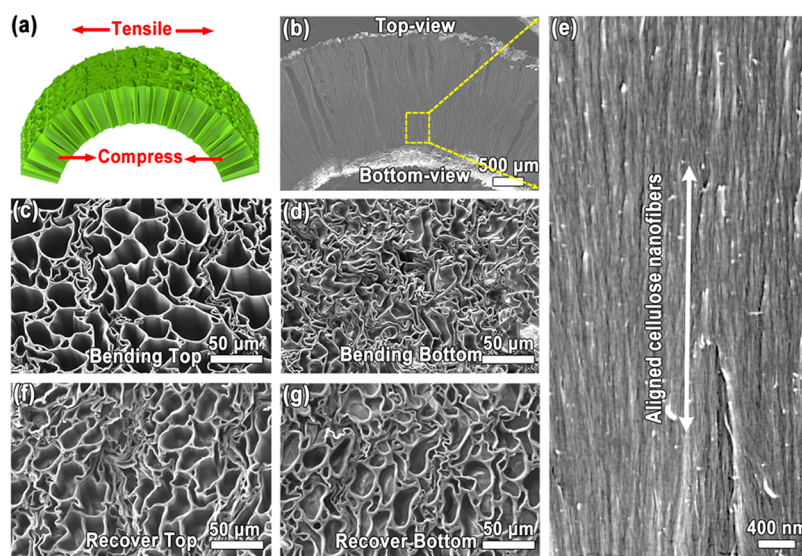


Figure 3. Flexible wood under bending and after release. (a) Graphical illustration of flexible wood under bending condition. (b–e) SEM images of flexible wood under bending: (b) cross-sectional view, (c) top view, (d) bottom view, and (e) magnified SEM image showing alignment of cellulose nanofibers. (f, g) SEM images of flexible wood after release: (f) top view and (g) bottom view.

(an impermeable buoyant material) but with a different composition.

We have also performed three-point bending tests and bending durability analysis of wood. As shown in Figure S8, natural wood is easy to break with a small bending radius, while the flexible wood membrane can be totally recovered after bending. Moreover, the flexible wood shows excellent durability after undergoing 1000 bending cycles, suggesting the outstanding structural stability of the flexible wood membrane against multiple cycles of bending. The bending radius of natural wood is 5.1 mm (curvature 0.195 mm^{-1}) and that of

flexible wood is 0.06 mm (curvature 16.7 mm^{-1}), further confirming the superflexibility of flexible wood membrane (Figure S9). Note that the aligned cellulose nanofibers in natural wood can be well preserved even after chemical treatment (Figure 2f). Meanwhile, numerous nanopores between the cellulose nanofibers are generated due to partial removal of lignin/hemicellulose.

To gain further insights into the superflexibility of the flexible wood membrane, we carried out ex situ SEM measurements to monitor the microstructural evolution upon bending and releasing. As mentioned above, the unique crumpled cell

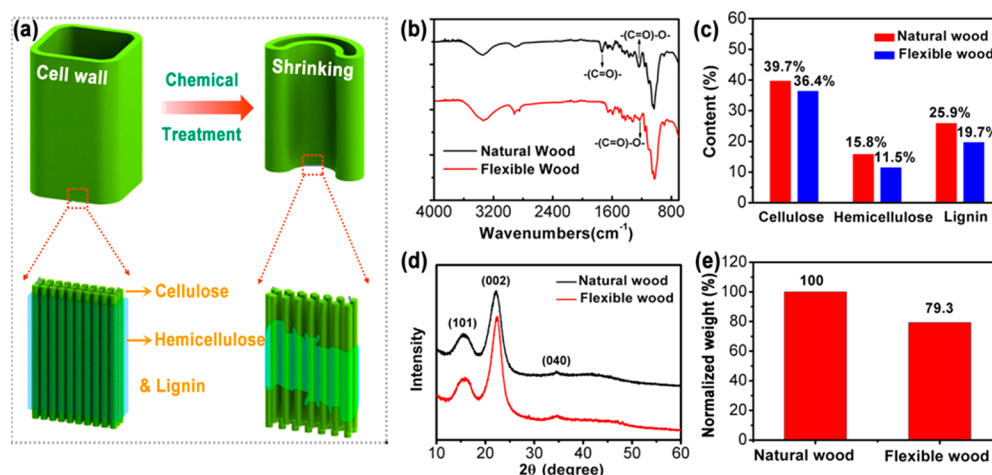


Figure 4. Chemical characterization of natural and flexible wood. (a) Schematic to illustrate before and after chemical treatment of the wood cell wall. (b) FT-IR spectra of the natural wood and flexible wood. (c) Cellulose, hemicellulose, and lignin content evolution from natural wood to flexible wood. (d) XRD patterns of both natural and flexible wood. (e) Weight loss of wood samples before and after chemical treatment.

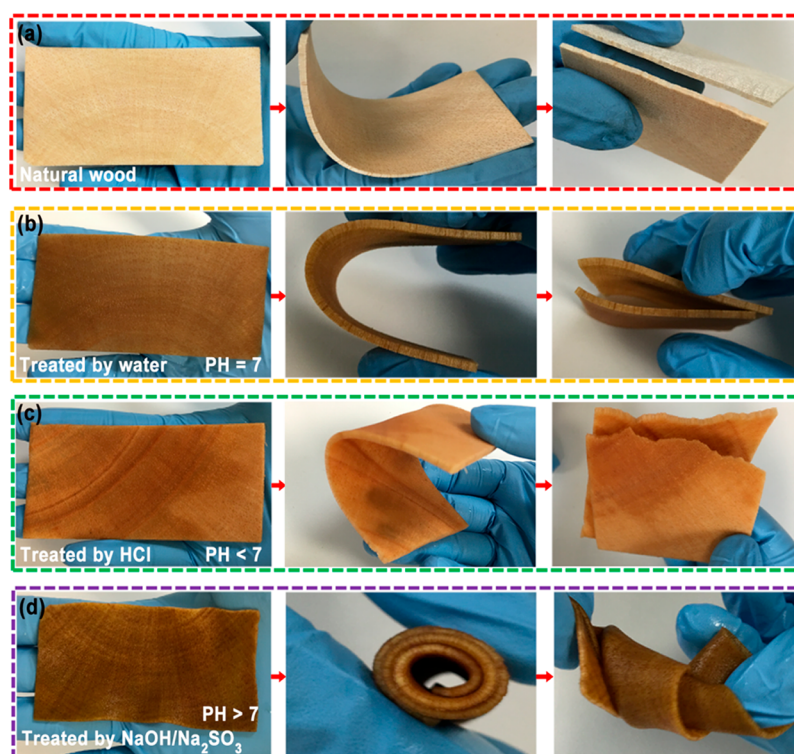


Figure 5. pH-responsive mechanical properties of treated wood membrane. (a) Natural wood membrane breaks upon bending. (b) Water-treated wood membrane breaks upon bending. (c) HCl-treated wood membrane breaks upon bending. (d) NaOH/Na₂SO₃-treated wood membrane becomes highly flexible upon bending. The dark color of the wood membrane in panel d is due to absence of washing by water and drying.

lumina are beneficial to flexibility of the flexible wood membrane. Upon bending, the top side of the flexible wood membrane will sustain tension force while the bottom side bears compression force (Figure 3a). As a result, the top side of the lumina will expand whereas the bottom side shrinks, demonstrating multiple cone-shaped channels (Figure 3b). Top-view SEM image of the bent flexible wood membrane provide further evidence that the upper part of the channels is more open than in their original state (Figure 3c). The crumpled cell walls in the original flexible wood membrane are partially straightened due to the upper tension induced by bending, returning partly to the hexagonal cell shape as

observed before chemical treatment. On the contrary, the bottom parts of the lumina are heavily compressed to almost total closure with more severe curving of cell walls (Figure 3d). Meanwhile, the well-aligned cellulose nanofibers are maintained with smaller gaps due to compression of the bottom part (Figure 3e). When released, the flexible wood can be totally recovered without suffering any damage to the structure. Both the top and bottom parts of the lumina can be recovered to the original crumpled state, indicating excellent structural recoverability of the flexible wood membrane (Figure 3f,g).

In addition to the microstructure, the chemical composition change during treatment is also vital for achieving super-

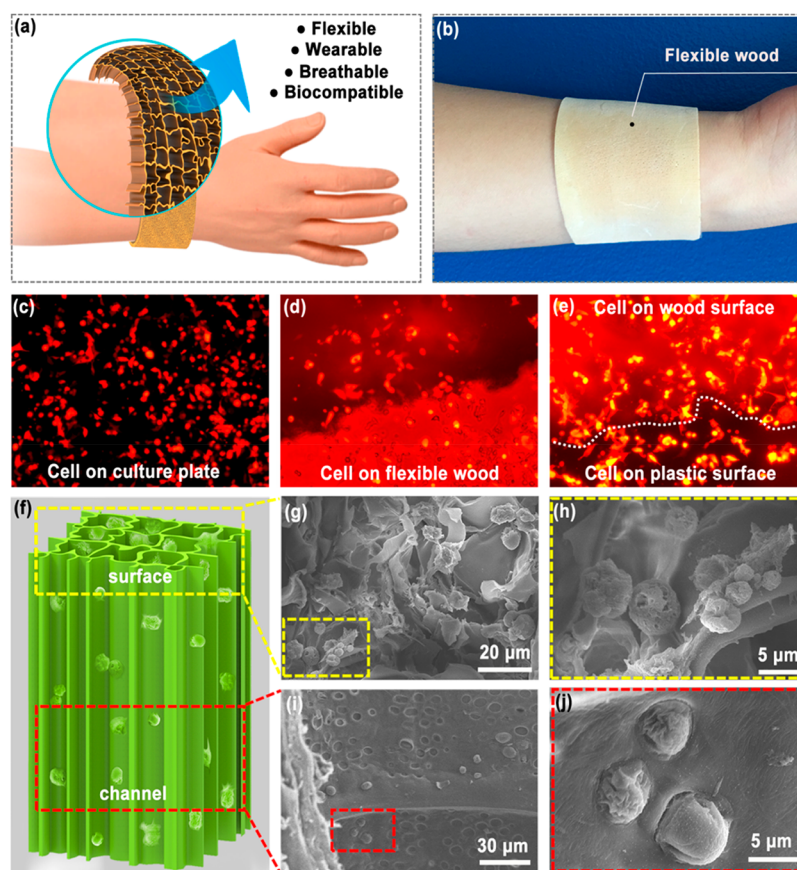


Figure 6. Cell culturing performance of flexible wood 3D bioscaffold. (a, b) Graphical illustration and photo image of flexible wood membrane being worn, showing the flexible, wearable, breathable, and biocompatible properties. (c–e) Fluorescent microscopic images of HEK293 cells on flexible wood. (f) Schematic illustration of cells on flexible wood. (g, h) SEM images of HEK293 cells cultured on flexible wood surface. (i, j) SEM images of HEK293 cells cultured in wood lumen.

flexibility of the flexible wood membrane. We have performed various measurements including Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), and high-performance liquid chromatography (HPLC) to investigate the evolution of chemical composition of wood membranes before and after chemical treatment. As we know, the cell walls of wood are mainly composed of cellulose, hemicellulose, and lignin (Figure 4a). These three main components intertwine with each other, forming a strong and rigid cell wall structure. Cellulose is the crystalline fibril with long, crystalline slender chains of glucose.^{32,40} Hemicellulose is a type of amorphous heteropolysaccharide, while lignin is a polyphenol-based material filling in the spaces between cellulose and hemicellulose and acting as an adhesive agent in cell-wall structure.^{32,41} After partial removal of hemicellulose and lignin, nanopores between the aligned cellulose nanofibers are generated, and thus the channel wall become soft and flexible (Figure 2f and Figure S10). Further drying leads to the shrinkage of cell walls with closely packed cellulose nanofibers, resulting in the unique crumpled cellulose-nanofiber-dominant cell walls that could sustain both tensile and compression forces due to the flexibility of cellulose nanofibers and extensive interfiber hydrogen bonds (Figure 4a). FT-IR spectra of the wood membrane before and after chemical treatment show that the groups assigned to hemicellulose are partially reduced by the mixed solution of NaOH/Na₂SO₃ (Figure 4b). This can be further evidenced by the determination of cellulose, hemicellulose, and lignin content, which show that cellulose,

hemicellulose, and lignin are partially removed by chemical treatment (Figure 4c).⁴² The cellulose crystal structure, on the other hand, show negligible changes through chemical treatment, as confirmed by the almost identical XRD patterns of the two samples (Figure 4d). Due to the partial cellulose, lignin, and hemicellulose removal, the natural wood membrane underwent a total weight loss of 20.7% (Figure 4e).

Interestingly, we found that the mechanical flexibility of treated wood membrane was highly dependent on the pH of the treatment solution, as shown in Figure 5. Natural wood membrane without any chemical treatment is fragile and easily broken by bending (Figure 5a). When treated with water (pH = 7) and HCl (pH < 7) solutions, the mechanical flexibility of the wood membranes can be improved slightly, yet they remain rigid materials and can be broken upon violent bending, suggesting the inferior flexibility of water- and HCl-treated wood membranes (Figure 5b,c). The NaOH/Na₂SO₃-treated wood membrane, on the contrary, demonstrates superflexibility even under severe folding and twisting, which can be well maintained after being dried (Figures 5d and 1c). This unique pH response should be attributed to the distinct stabilities of wood components of cellulose, hemicellulose, and lignin in solutions with different pH values. The role of NaOH is to selectively degrade lignin and hemicellulose in wood materials, while having little effect on the cellulose components. The addition of Na₂SO₃ to NaOH solution can help remove the lignin component in wood. Meanwhile, the reaction time can be shortened to removing lignin with the addition of Na₂SO₃.

The reason is that the increase of sulfite groups (SO_3^{2-}) into the lignin side chains by means of sulfonation enables the lignin to be dissolved quickly in alkaline solution.^{43,44} Moreover, the interaction between $\text{NaOH}/\text{Na}_2\text{SO}_3$ and cellulose, hemicellulose, and lignin molecules can also swell the cell wall, making it softer for feasible bending, folding, or twisting. In contrast, cellulose, hemicellulose, and lignin are relatively stable in water and HCl solutions, which can be evidenced by the absence of color change of the solutions (Figure S11). The slight improvement in flexibility of water- and HCl-treated wood membranes is due to swelling of the cell wall by water molecules.

Additionally, due to the similarity in components for various kinds of wood materials, similar chemical treatment can help improve the flexibility of other various kinds of wood materials beyond balsa. We have also chemically treated basswood (hard wood) with the same process. As shown in Figure S12, the $\text{NaOH}/\text{Na}_2\text{SO}_3$ treated basswood becomes highly flexible, suggesting the universality of our demonstrated top-down approach.

The 3D porous flexible wood with cell lumen structure can potentially enable a range of applications, especially bio-applications, due to its excellent biodegradability, biocompatibility, superflexibility, breathability, wearability, and 3D porous microstructure (Figure 6a,b). To evaluate application of the flexible wood membrane as a 3D tissue engineering scaffold, a HEK293 cell line was selected as an example to test cell attachment and biocompatibility. The HEK293 cells, once transfected with tdTomato fluorescence reporter, were cultured on flexible wood for 24–48 h. The attachment and biocompatibility of the flexible wood were examined by use of a fluorescence microscope to investigate the cell living conditions on the flexible wood membrane. The fluorescent microscopic images in Figure 6c–e show that HEK293 cells can successfully adhere and proliferate on the surface of the flexible wood, indicating their excellent attachment and biocompatibility. The sharp contrast between the bright area, associated with adherence of HEK293 cells on the flexible wood membrane, and the dark area, assigned to the culture plate, emphasizes sufficient adherence of HEK293 cells (Figure 6e).

SEM observations provide further evidence of sufficient attachment of HEK293 cells both on the surface and inside the channels of the flexible wood membrane. Top-view SEM images (Figure 6g,h) clearly show the presence of HEK293 cells on the surface of the flexible wood membrane, while longitudinal SEM images (Figure 6i,j) demonstrate that HEK293 cells can also adhere inside the lumina. The above SEM observations suggest that efficient 3D adhesion and proliferation of cells on the flexible wood membrane can be realized, which is critical for 3D bioscaffolding and tissue engineering applications. Even after repeated bending of the flexible wood membrane, the HEK293 cells can still adhere, demonstrating a highly stable and sufficient attachment property (Figure S13a,b). Moreover, the superflexibility of the wood membrane can be well maintained after HEK293 cell culturing, suggesting excellent mechanical stability of the wood membrane (Figure S13c–e). The stability of flexible wood membrane immersed in water for 10 days also confirms the long-term culturing capability (Figure S14). All these cell experiments indicate that the flexible wood 3D bioscaffold can indeed support cell growth and proliferation due to the intrinsic excellent biocompatibility of cellulose in wood and the unique multichanneled 3D porous structure providing sufficient space

for cell adhesion. Additionally, the multiple direct micro- and nanochannels in the flexible wood membrane are beneficial for nutrient transportation and metabolic byproduct removal, positioning it as a potentially promising 3D bioscaffold material for tissue engineering.

CONCLUSION

In summary, a nature-inspired flexible 3D porous wood membrane has been successfully achieved for the first time via a facile one-step chemical treatment method directly from natural wood. Structural and compositional modifications were also investigated, which reveal the underpinning mechanism of the excellent flexibility in chemically treated wood. The utilization of natural wood as starting material endows the flexible wood membrane with excellent biocompatibility and unique multichanneled 3D porous structure, while further chemical treatment imparts the 3D bioscaffold with superb flexibility. All these structural merits are beneficial for efficient adhesion and proliferation of cells into the flexible wood membrane, transportation of nutrients, and removal of metabolic byproducts, all of which are vital for practical tissue engineering applications. Therefore, the flexible wood membrane demonstrated here is a promising candidate for an efficient bioscaffold material for tissue engineering and other clinical applications such as surgery mesh. We believe that the flexible, breathable wood materials can also be used for other applications, such as structural materials, flexible electronics, biosensors, and flexible 3D conductors.

EXPERIMENTAL SECTION

Materials and Chemicals. Balsa wood was used for the fabrication of flexible wood. Sodium hydroxide (>97%, Sigma–Aldrich), sodium sulfite (>98%, Sigma–Aldrich), and deionized (DI) water were used for processing the wood.

Treatment Process for Flexible Wood Membrane. Wood slices were immersed in a mixed aqueous solution of NaOH and Na_2SO_3 and quickly transferred into a vacuum chamber. Vacuum was used to let the liquid flow into the wood lumina. The chemically treated wood was immersed in boiling DI water several times to remove the chemicals. Wood slices were then dried in air to form the final product of superflexible wood membrane.

HEK293 Cell Culture in Flexible Wood Membrane. HEK293 cells were seeded into the wells of a 6-well cell culture plate with 90% confluence, and the plate was incubated overnight in an incubator with 5% CO_2 at 37 °C. The cells were transfected next morning with a plasmid containing tdTomato fluorescence reporter gene by use of DNA-In transfection reagent (VistaScientific Inc.), following the manufacturer's protocol, and incubated for 24–48 h. In a new 6-well cell culture plate, several autoclaved pieces [(2–4) × (2–4) mm² in size] of flexible wood membrane were lined in the bottom of each well of the culture plate. The wood pieces were held down in place by sterilized custom-made metal rings. The transfected cells were detached by use of 0.05% trypsin and transferred to wells of the plate containing wood pieces. The cells and the pieces of wood were cocultured for another 24–48 h. The growth of cells on the surface of the wood membranes was examined and photographed by use of a fluorescent microscope (Nikon, TS100). For SEM observations, phosphate-buffered saline (PBS) was used to wash the samples, and 2.5 wt % glutaraldehyde was used to fix the samples for 24 h. After that, PBS was used again to wash them 6 times, and then the samples were immersed in increasing concentrations of ethanol (50–99%). After that, *t*-BuOH was used to wash them three times, followed by freeze-drying.

Measurements and Characterization. A scanning electron microscope (SEM, Hitachi SU-70) was used to characterize the morphologies of the wood samples. XRD were measured on a Rigaku

Ultima III equipped with a curved detector manufactured by Rigaku Americas Corp. The carbohydrates and lignin content were measured by two-step sulfuric acid hydrolysis as described previously.⁴² A Thermo Nicolet Nexus 670 FT-IR was used to measure the FT-IR spectrum. Mechanical tensile properties were measured on a Tinius Olsen HSKT tester, and mechanical bending properties were measured with a dynamic mechanical analyzer.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b06529.

Fourteen figures showing digital photo images of thick flexible wood, areal size change, and color change, SEM images for wood micro- and nanostructure, tensile stress-strain curves, three-point bending performance, and photo images to show the flexibility and structural stability of flexible wood; one table comparing mechanical properties (PDF)

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Author Contributions

#J.S. and C.C. contributed equally. L.H. and J.S. conceived the idea. J.S. and C.C. contributed the wood treatment and mechanical measurements. C.W., Y.F.Li, F.J., E.H., Y.Z., and B.L. contributed the characterizations of the materials. Y.K. contributed the 3D illustrations. Y.J.Li and C.C. contributed the SEM characterization. H.B. and J.Y.Zhu contributed the compositional analysis. J.Zhang contributed the cell culturing. L.H., J.S., and C.C. contributed the paper writing. J.L. helped revise the manuscript. All authors commented on the final manuscript.

Notes

The authors declare no competing financial interest.

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