

ADVANCED MATERIALS

Supporting Information

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Precision Imprinted Nanostructural Wood

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Supporting Information

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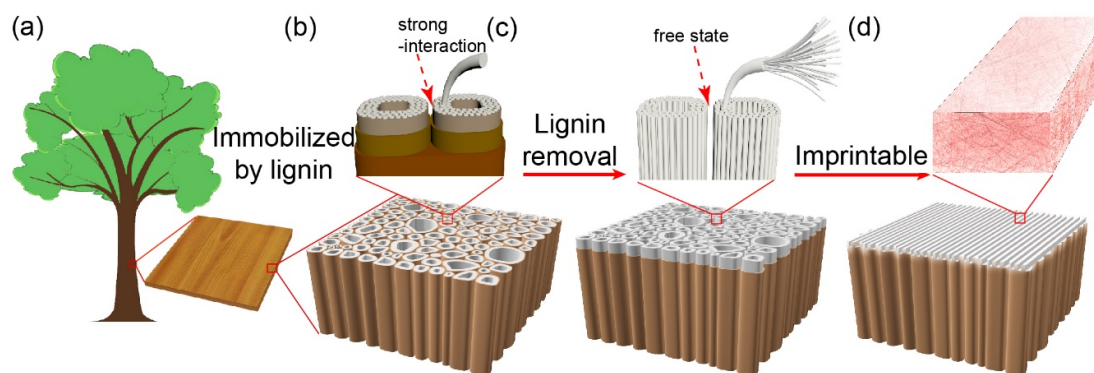


Figure S1. Schematic of pattern fabrication on the wood surface. Because cellulose has no thermal plastic deformation property, we developed a novel method to pattern the wood based on the plastic deformation behavior of delignified wood.

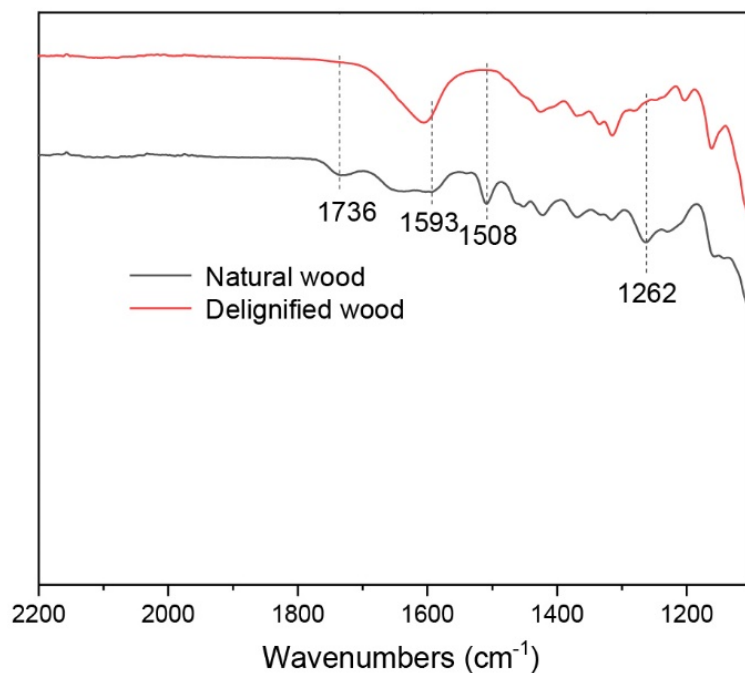


Figure S2. FT-IR spectra of natural wood and delignified wood.

FT-IR measurements were carried out to evaluate the delignification grade of the samples. FT-IR spectra show that the peaks at 1736 and 1262 cm^{-1} for carbonyl stretching and C–O stretching are significantly reduced, which reflects the removal of hemicellulose after NaClO treatment. Meanwhile, the disappearance of peaks at 1593 and 1508 cm^{-1} is indicative of an aromatic skeleton, indicating the removal of lignin during NaClO treatment.

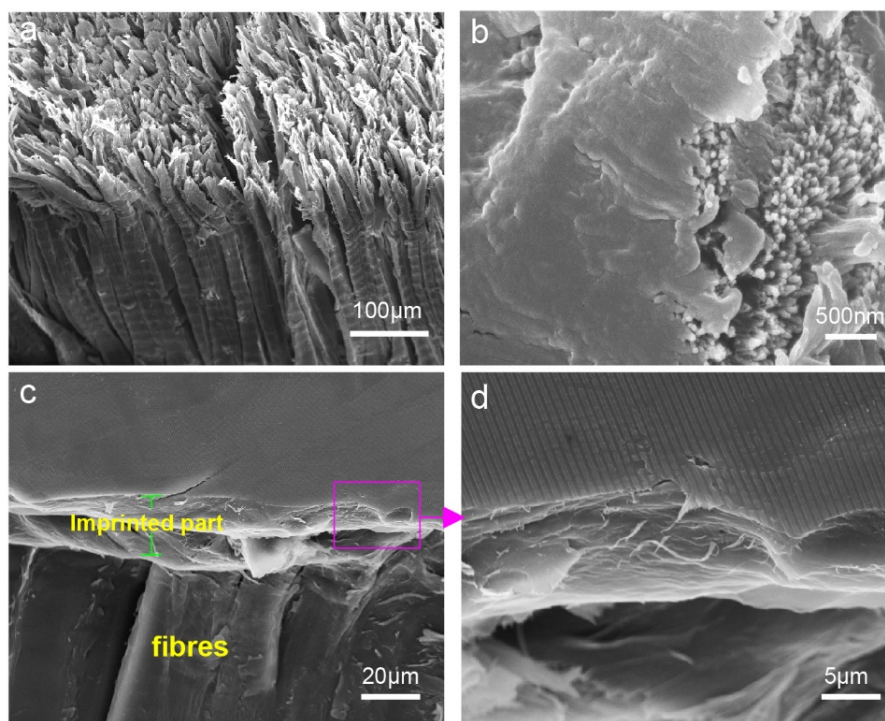


Figure S3. SEM images of the microstructures of delignified wood under pressure. (a) Partly broken structure on the top wood layer under very weak pressure; (b) Comparison of the tightly packed part and its surrounding nanostructures; (c) and (d) imprinted wood on side view.

The experimental basis presented below to support the schematic of Figure 1d.

- (1) The deformation of fibres and vessels according to the pressing force: As shown in Figure S3a, when the direction of the pressure is parallel to the fibres/vessels axis, fibres/vessels tend to rupture the structure to relax the energy.
- (2) The deformation of fibril aggregates according to the pressing force: As shown in Figure S3b, since the hydrogen bonds between the fibrils in the water are destroyed, the force between them is very weak, and the fibrils are easily moved relative to each other under pressure, eventually forming an isotropic aggregate. Figure S3b also shows both the pressed part and the uncompressed part, the fibrils of the pressed part become very dense, and they are unable to distinguish by SEM. In contrast, the fibrils are clearly visible in the uncompressed part.
- (3) Figure S3c and S3d show both the nanoimprinted part and the fibres.

Based on these experimental results, we have obtained a schematic diagram of the fibres/vessels being pressed shown in the manuscript of Figure 1d. When the lignin is removed, the binding of the cellulose fibres/vessels is relieved. Under the pressure of a small external force, the wet lignin removed wood undergoes great deformation, and the deformation cannot be recovered, showing a typical plastic deformation behavior. This is consistent with the experimental results of mechanics (Figure 2g, red line). Of course, there are still a lot of details, and here we are only schematically showing the basic principles.

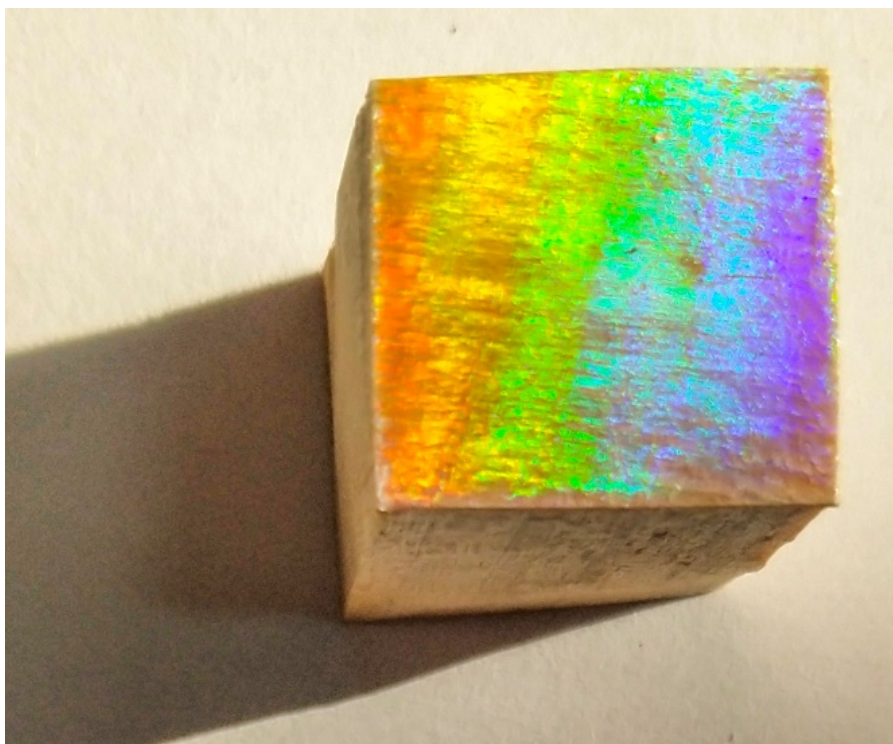


Figure S4. Photo of the patterned wood. The color originates from light diffraction by the line array imprinted on the wood surface.

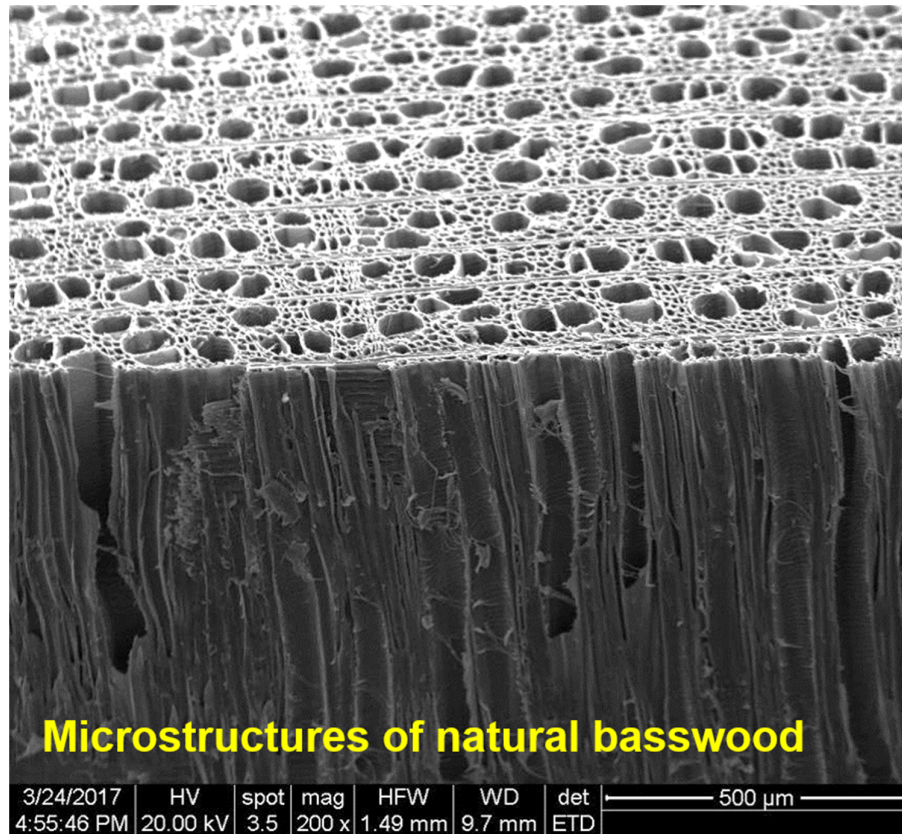


Figure S5. SEM image of the microstructures of natural basswood, demonstrating the micro-sized aligned fibres and vessels.

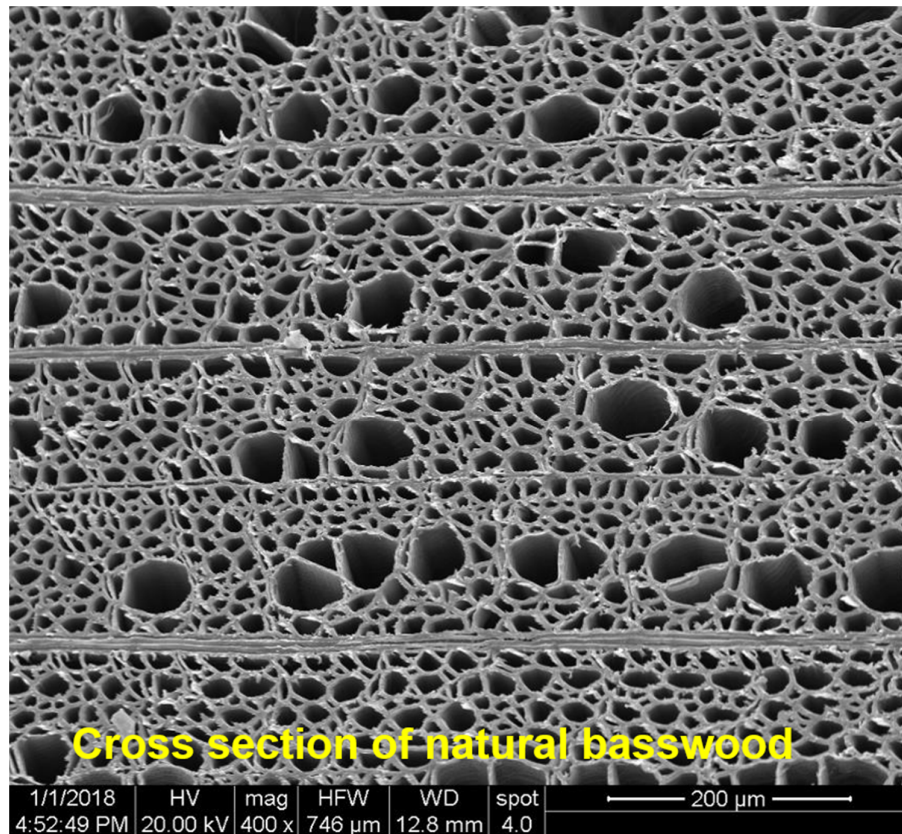


Figure S6. Cross-sectional SEM image of natural basswood, showing a top-view of the fibres and vessels.

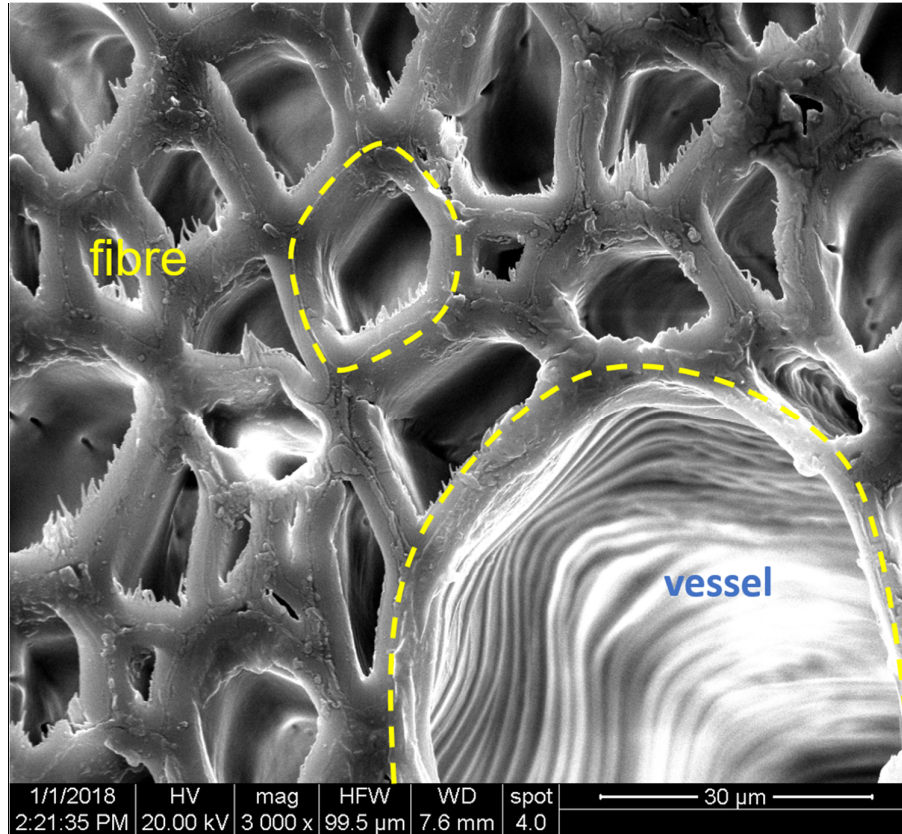


Figure S7. Magnified cross-sectional SEM image demonstrating the detailed structure of the natural basswood.

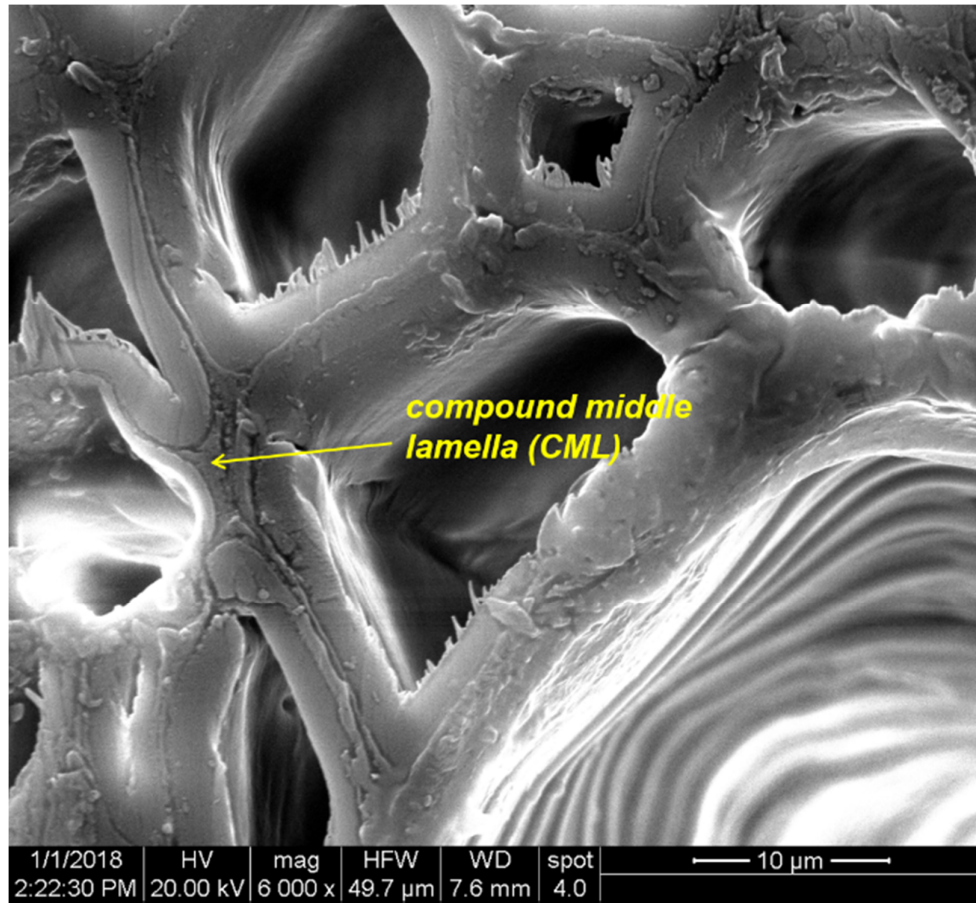


Figure S8. Top-view SEM image of natural basswood, demonstrating the CML (middle lamella + primary cell walls) between the adjacent fibres. The fibres are connected by the CML, forming wood's strong structures.

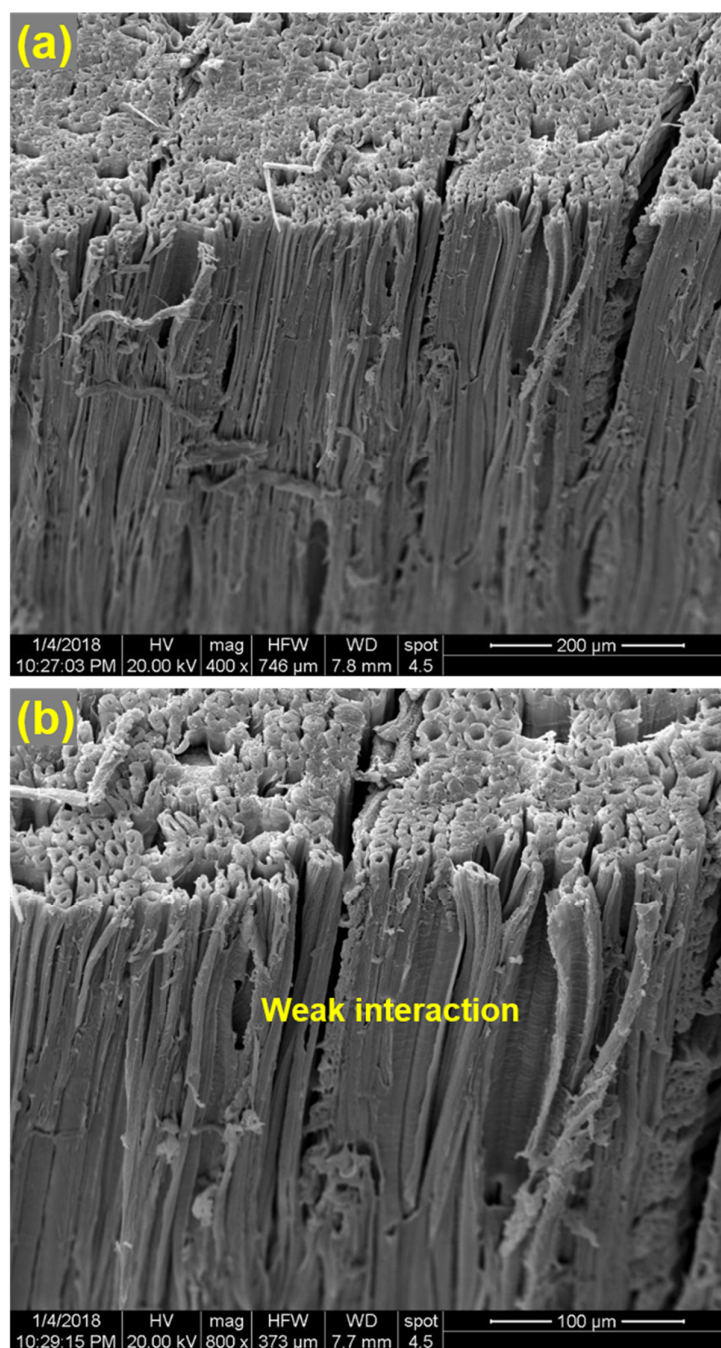


Figure S9. (a) SEM image of the delignified basswood, indicating that the basic microstructures are maintained even after losing the binding lignin. (b) A magnified SEM image shows that the fibres are isolated after losing the binding effect of lignin.

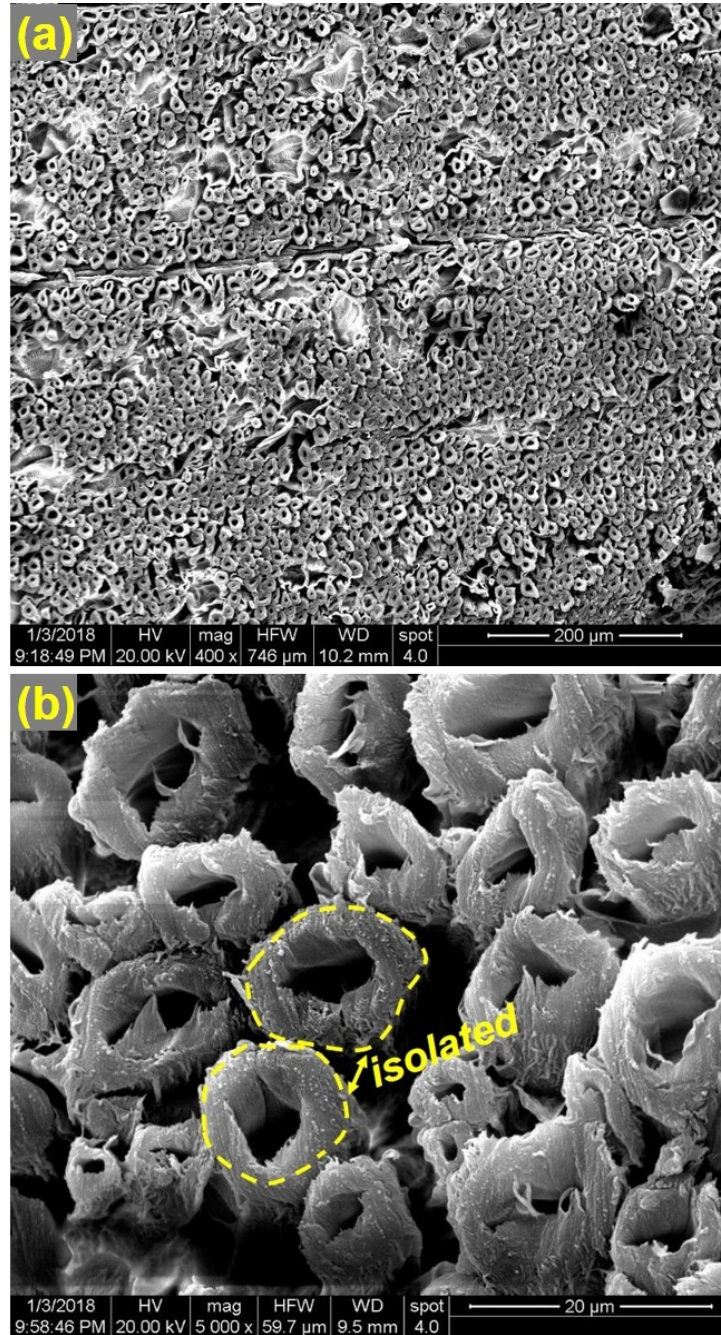


Figure S10. (a,b) Top-view SEM images of the delignified basswood. After lignin removal, the fibres are nearly isolated from each other and can easily change their relative position with very little applied force.

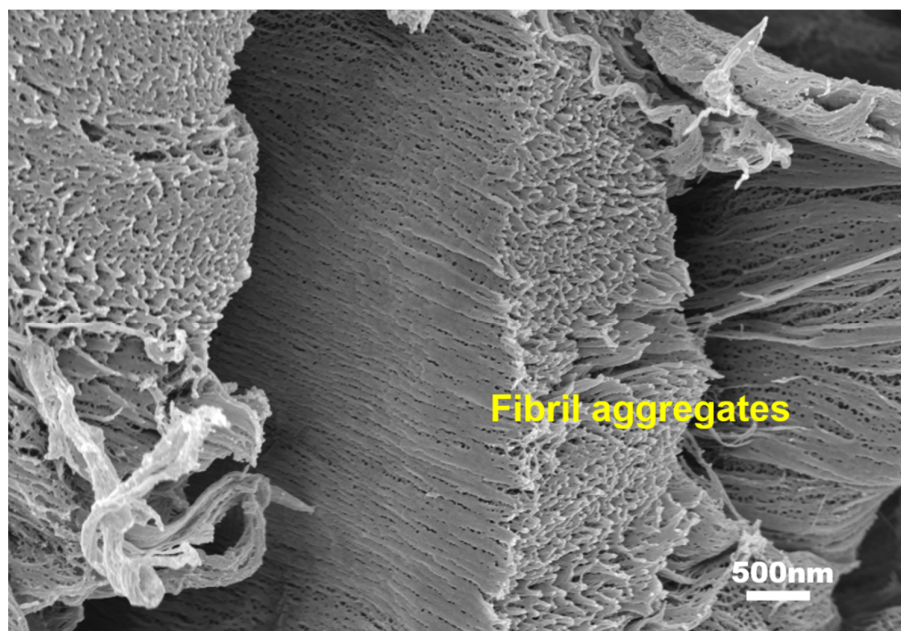


Figure S11. SEM image of the fibril aggregates in the delignified basswood. These fibril aggregates are the main content of the cell walls. The nanosized fibrils enable the resulting wood to be patterned with nanoscale resolution. Additionally, the fibrils feature weak interaction after lignin removal, allowing their relative positions to be changed easily. These effects endow the delignified wood with more plasticity, enabling them to deform with applied force, such as that imposed during the imprinting process.

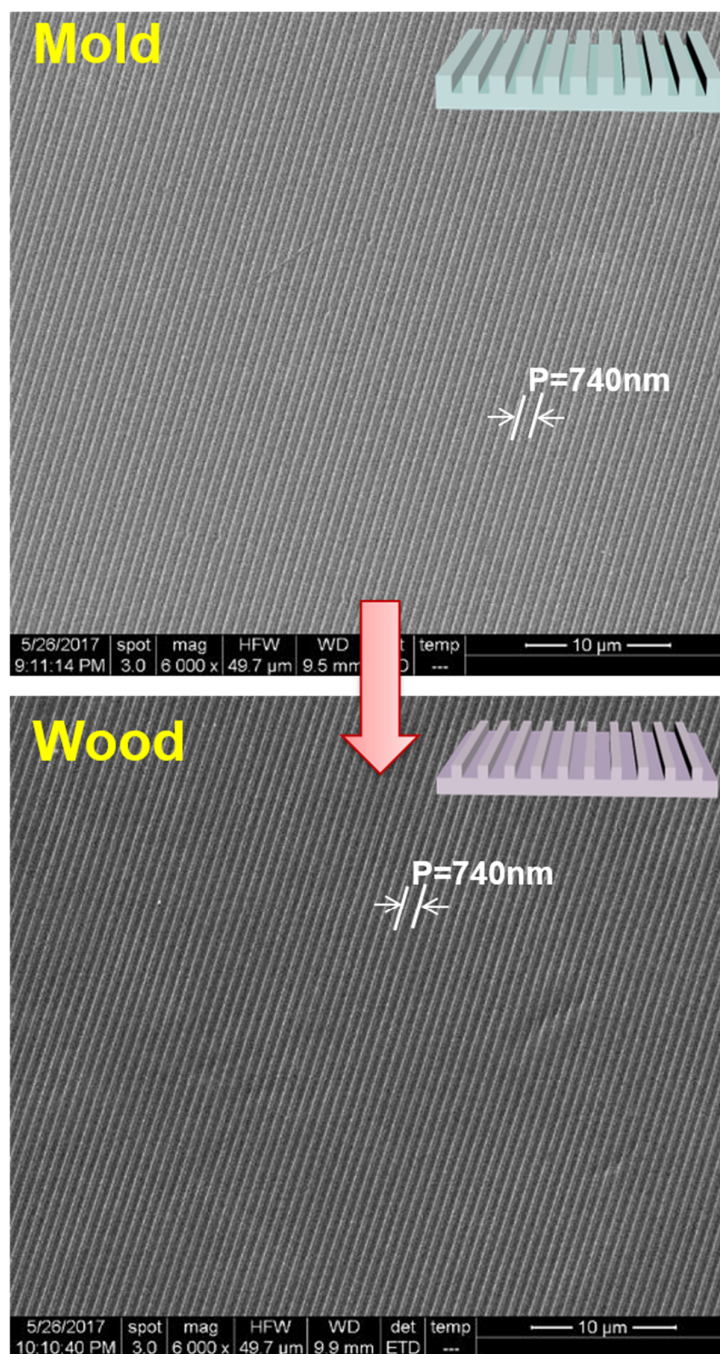


Figure S12. SEM image of the printing mold and the resulting patterns on the wood surface. The line patterns are successfully transformed from mold to wood in a conformal way.

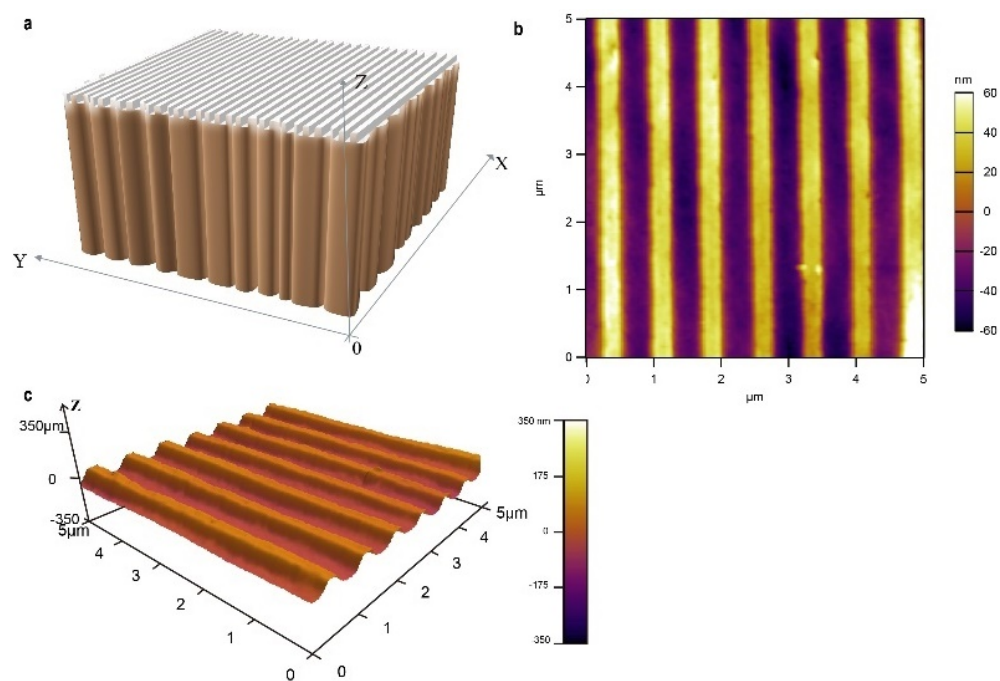


Figure S13. AFM image of the wood patterned with a line array. The line period is about 740 nanometers. (a) Model of wood; (b) and (c) AFM image of imprinted wood.

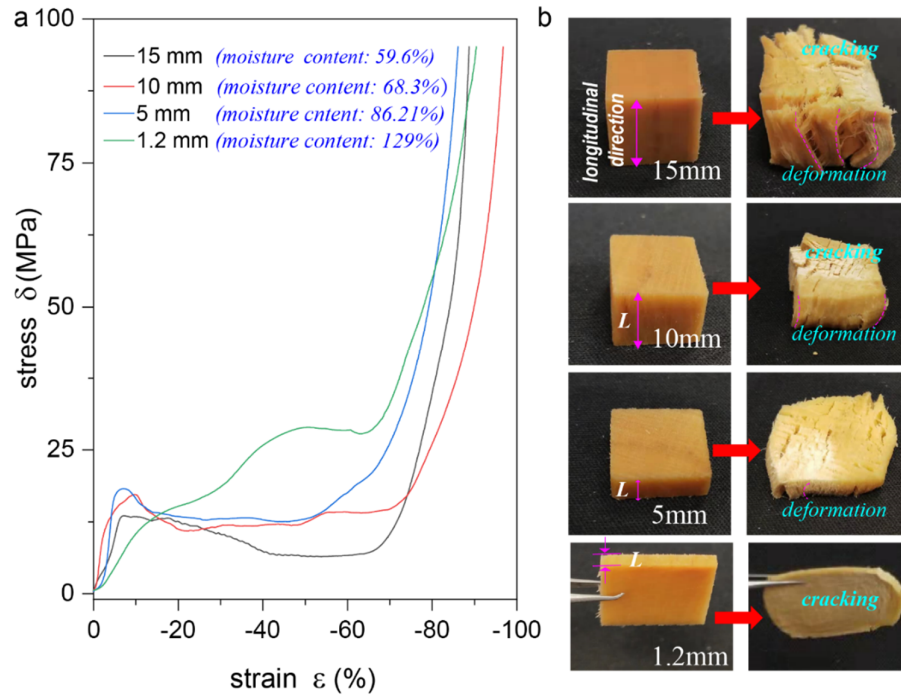


Figure S14. The compression curves are related to the thickness of the wet natural wood. (a) The stress-strain curve of different thickness wet natural wood. (b) Sample photos before and after compression.

The wood compression curve can be divided into three parts: the elastic deformation stage, the plastic deformation stage, and the densification stage. During the compression tests, the wood is only confined laterally by the jaws of the testing device. However, with the increase of the wood thickness, the impact of the lateral confinement of jaws is less, and the wood expands to the surroundings more easily. The lack of rigid lateral confinement leads to a larger compression strain (over 80%) than previous reports (*J. Wouts, G. Haugou, M. Oudjene, D. Coutellier, H. Morvan. Strain rate effects on the compressive response of wood and energy absorption capabilities – Part A: Experimental investigations; Composite Structures 149 (2016) 315–328; J. Wouts, G. Haugou, M. Oudjene, H. Morvan, D. Coutellier. Strain rate effects on the compressive response of wood and energy absorption capabilities – Part B: Experimental investigation under rigid lateral confinement; Composite Structures 204 (2018) 95–104.*).

By comparing the longitudinal compression curves of wood with different thicknesses, Figure S14 shows that the mechanical test results are related to the thickness to width ratio. For samples with a high thickness to width ratio, they exhibit plastic behavior during compression. For flaky samples, wet wood exhibits a certain degree of elasticity when compressed. Since our imprinted areas are thin delignified areas, wet wood sheets with similar thickness are selected for comparison. Such wet wood sheets show partial elastic behavior in the compression curve.

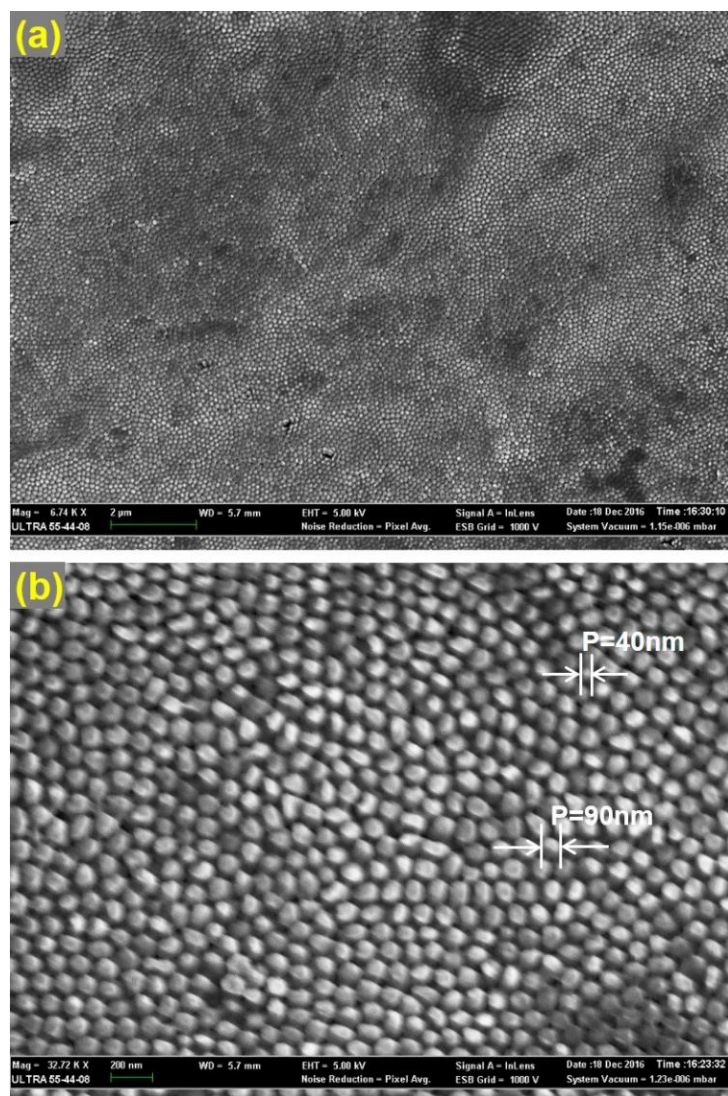


Figure S15. (a,b) SEM images of an imprinted wood sample patterned with a nanopillar array. These features were imprinted using an AAO template with a hole diameter of ~40–90 nanometers.

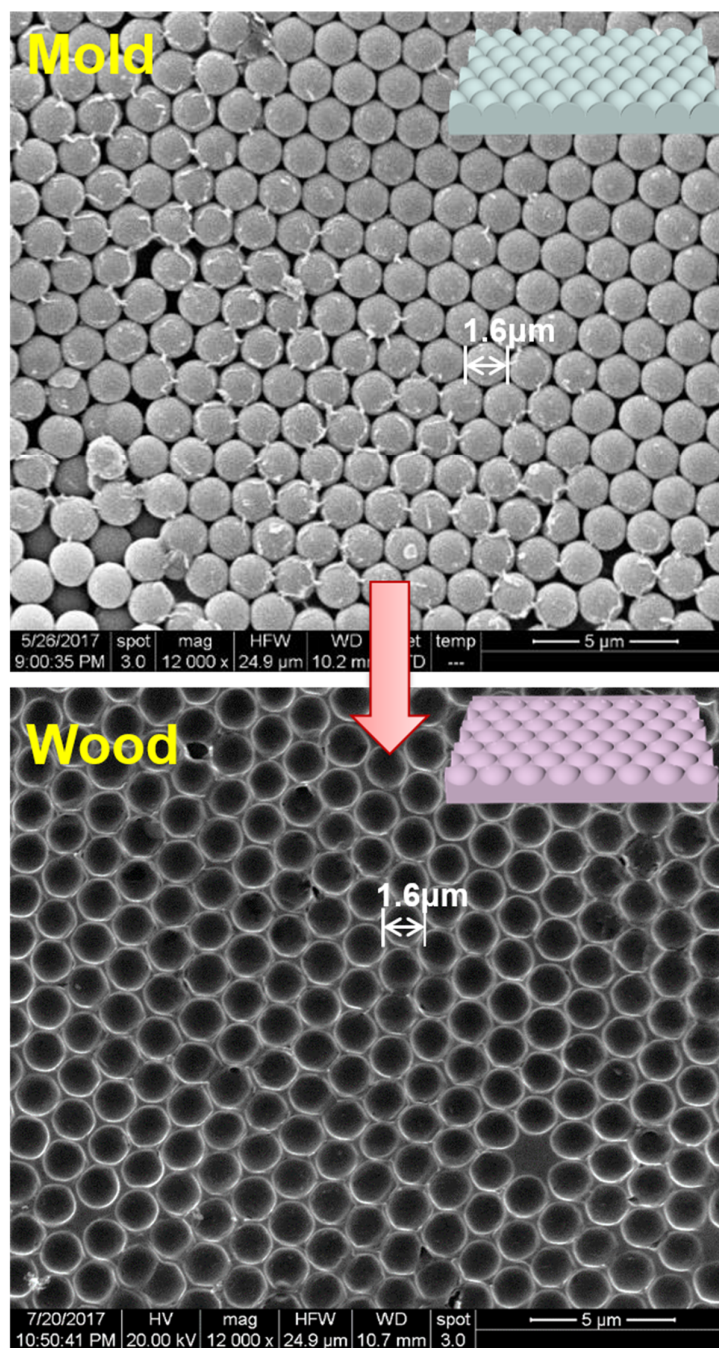


Figure S16. SEM image of the imprinting mold and the resulting patterned wood. The mold is composed of two-dimensional colloidal crystals of silica spheres with an average diameter of about 1.6 μm.

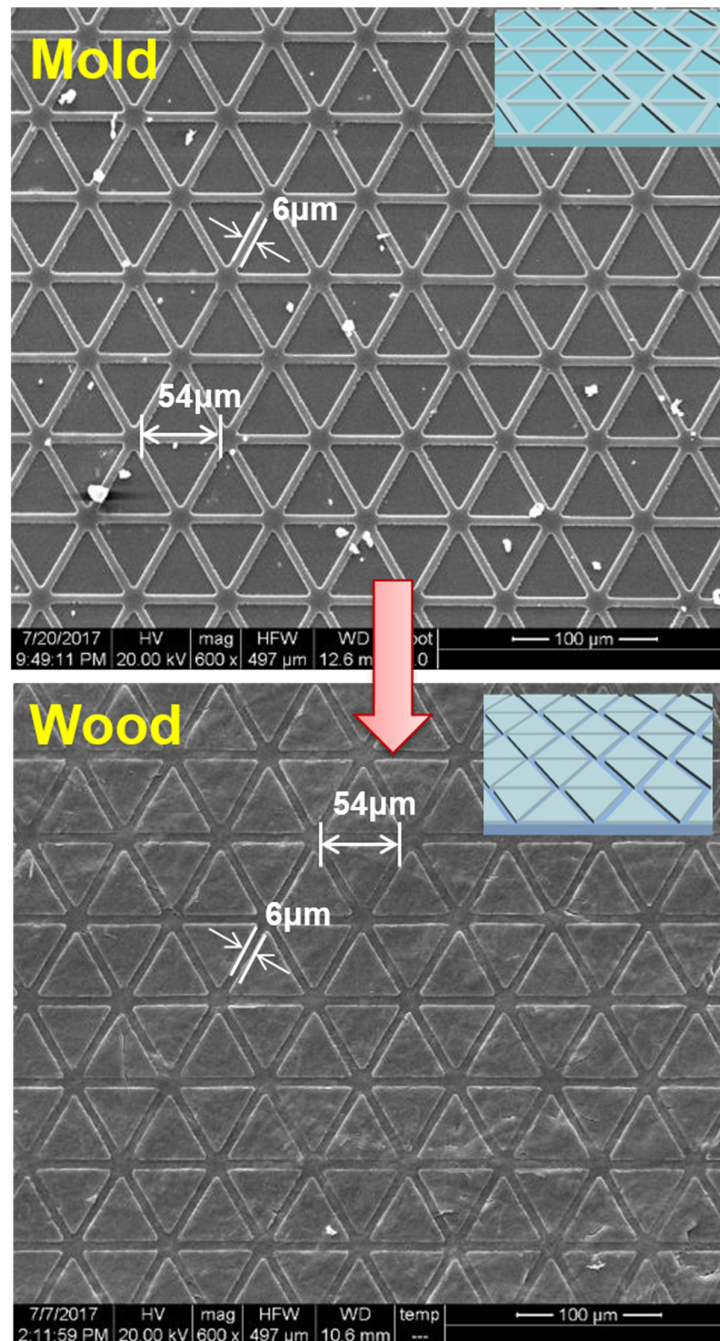


Figure S17. SEM images of the imprint mold and the resulting triangular-patterned wood. The side length of each triangle is $\sim 50 \mu\text{m}$, which demonstrates the capability of the delignified wood to be patterned with large unit size.

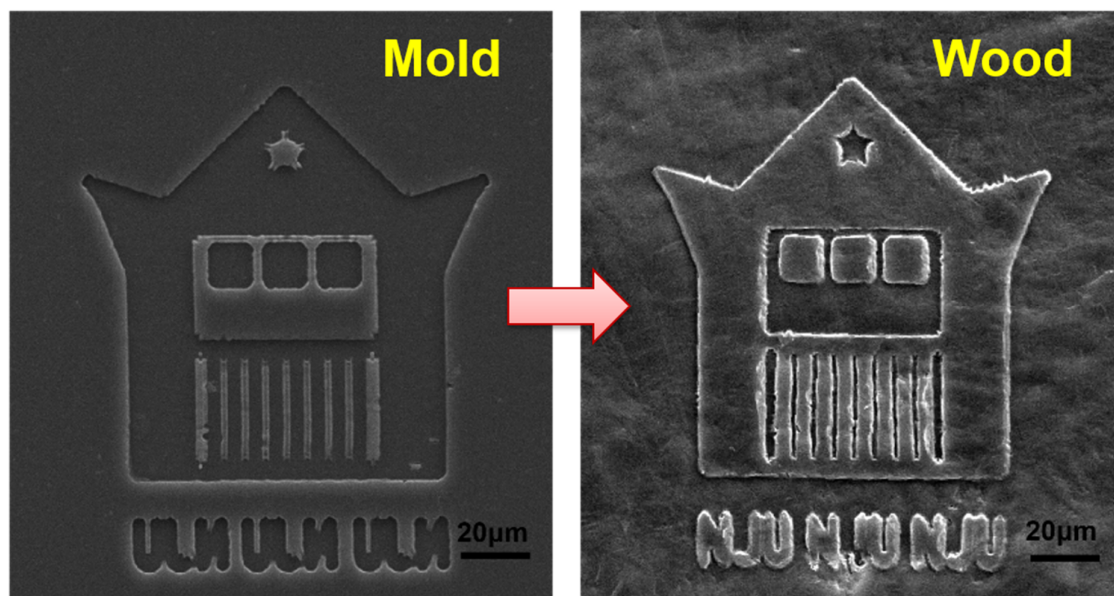


Figure S18. SEM image of the imprint mold and the resulting complex patterned wood.

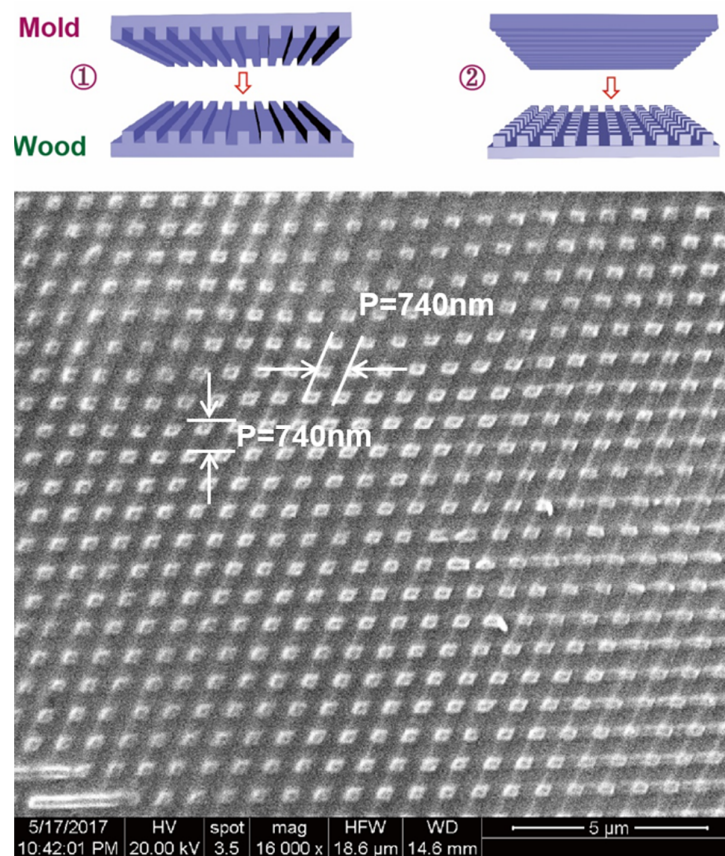


Figure S19. The process and result of generating a nanodot array using a line template. The wood is imprinted by the line template first, then the mold is rotated at an angle and imprinted again.

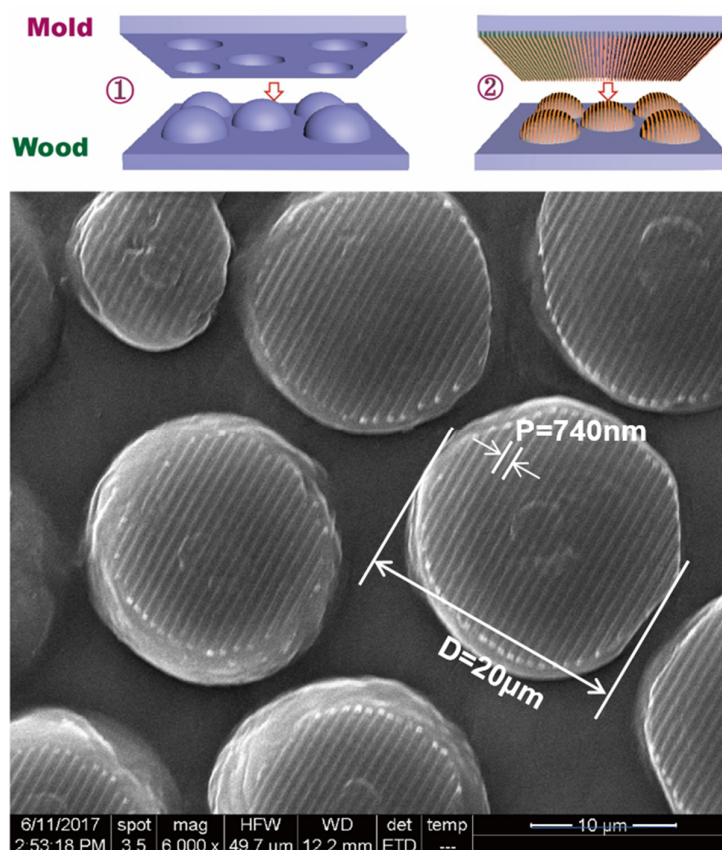


Figure S20. The process of fabricating multi-scale structures on a wood surface. Microsized hemispheres are generated on wood surface by imprinting firstly, then nanolines are imprinted on the surface of hemispheres. The SEM image shows the resulted multi-scale structures, which demonstrate the pattern generation ability on wood surface.

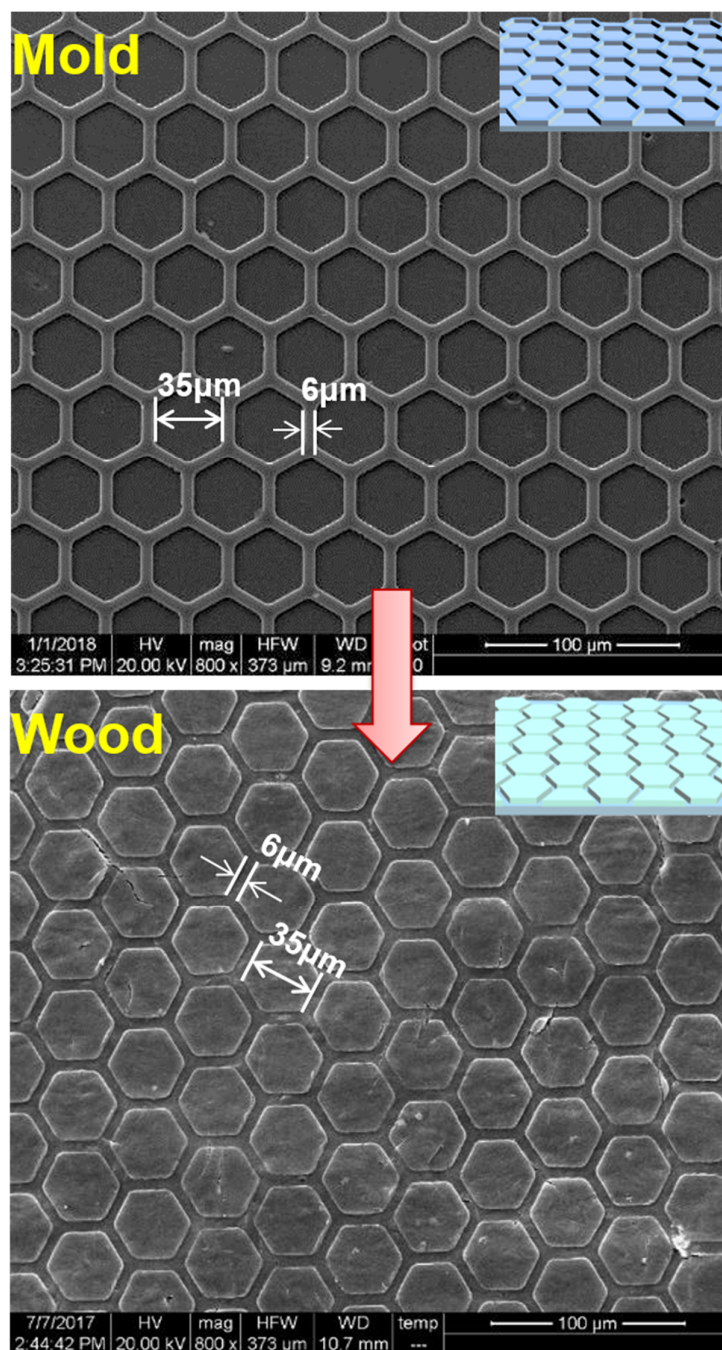


Figure S21. SEM images of the imprint mold and patterned wood, featuring a hexagonal array. The patterns are copied to the wood in a conformal way.

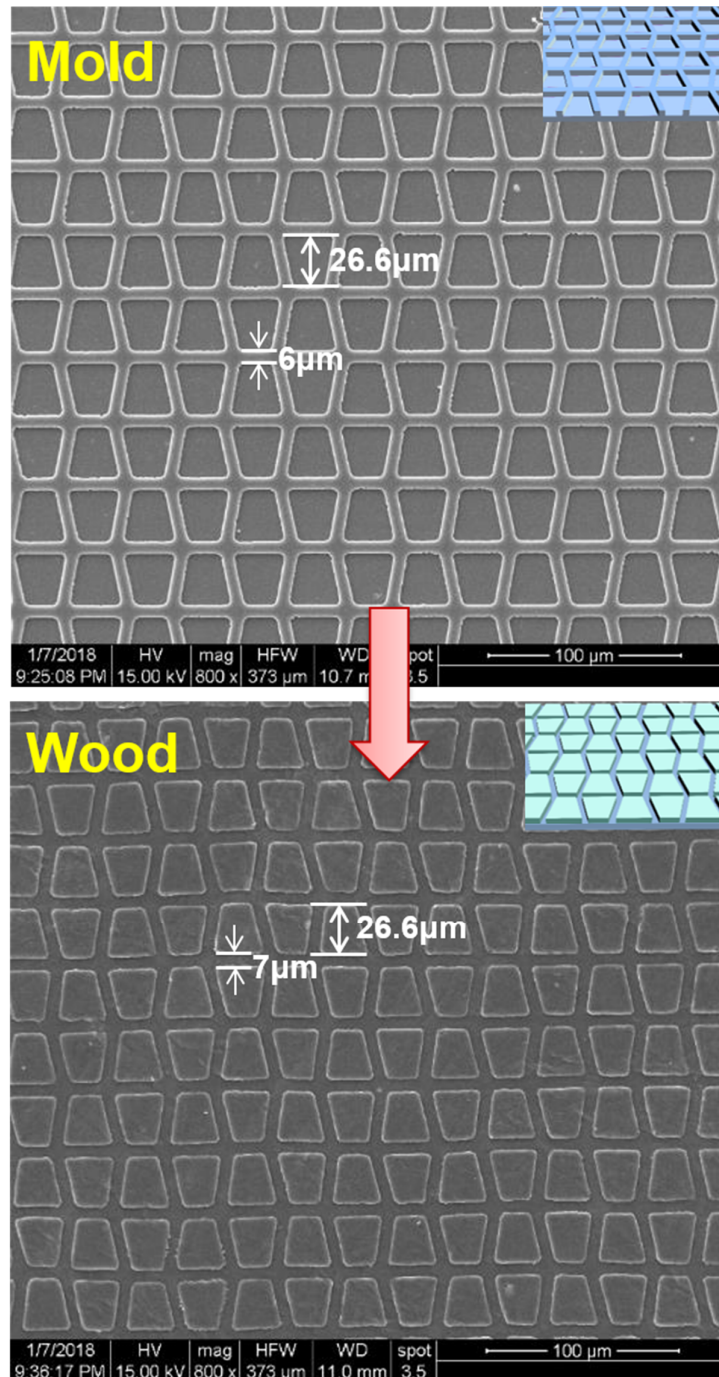


Figure S22. SEM images of the imprint mold and the patterned wood, featuring a trapezoid array.

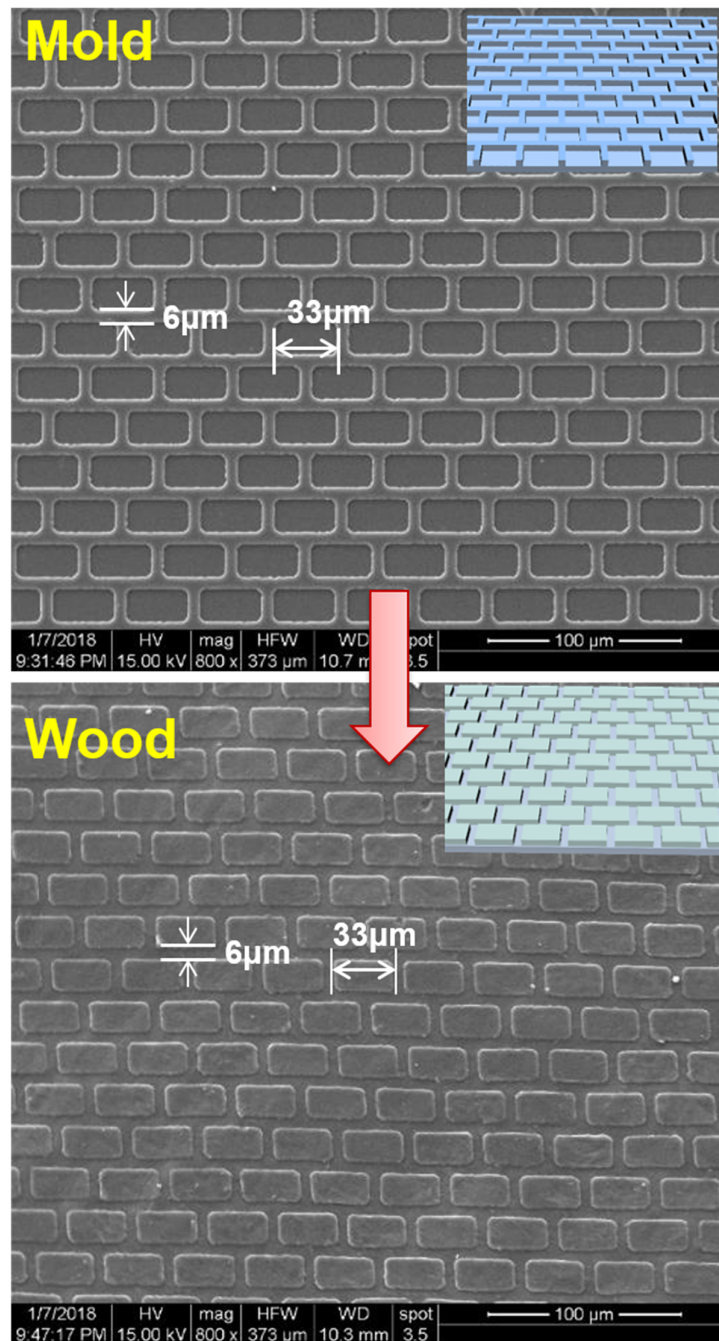


Figure S23. SEM images of the imprint mold and the patterned wood, featuring a rectangular array.

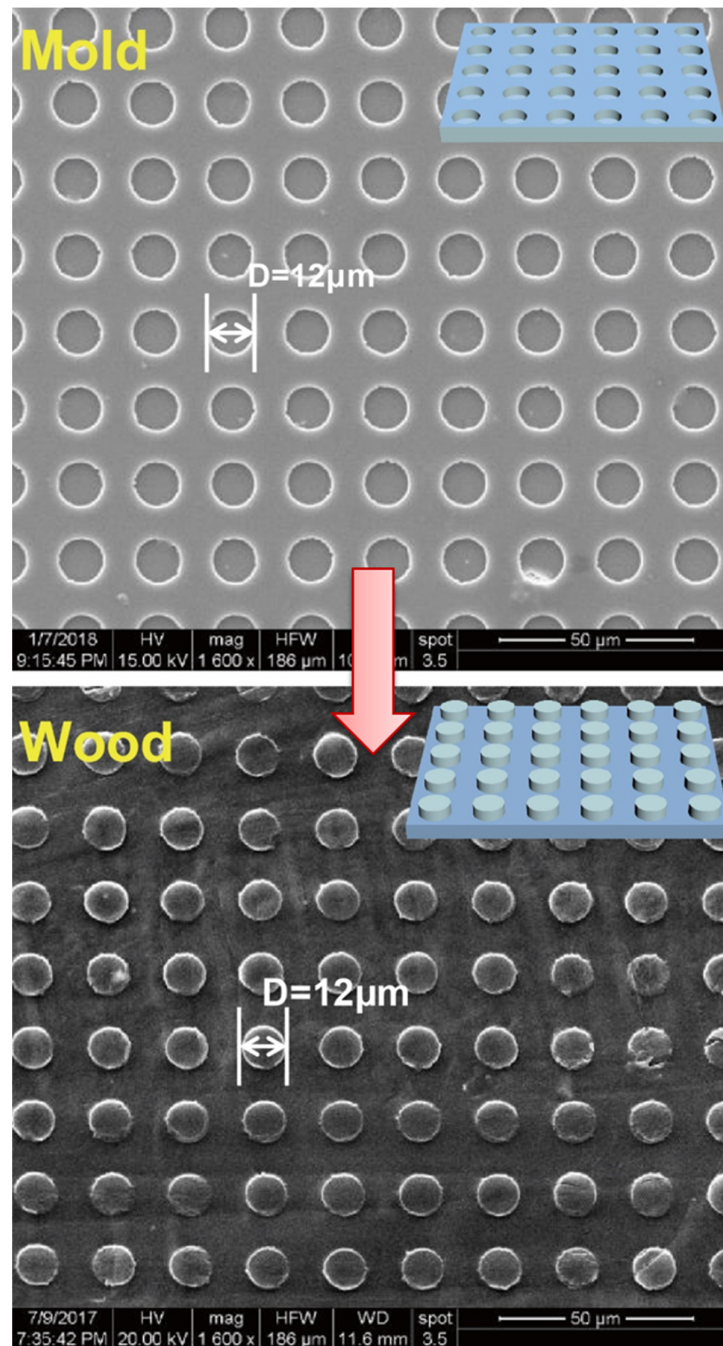


Figure S24. SEM images of the imprint mold and the patterned wood, featuring a circular array.

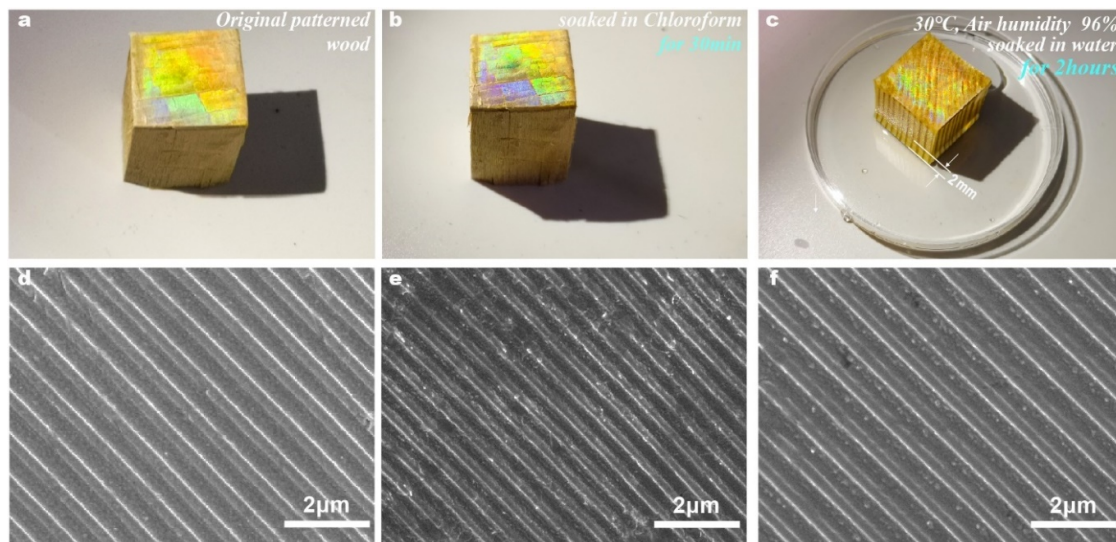


Figure S25. Optical and SEM images of imprinted woods treated at different environments. (a, d) origin imprinted wood and its surface patterns, respectively; (b, e) Imprinted wood treated in the organic solvents for 30 minutes and its surface patterns, respectively; (c, f) Imprinted wood treated in 96% air humidity and water for 2 hours and its surface patterns, respectively.

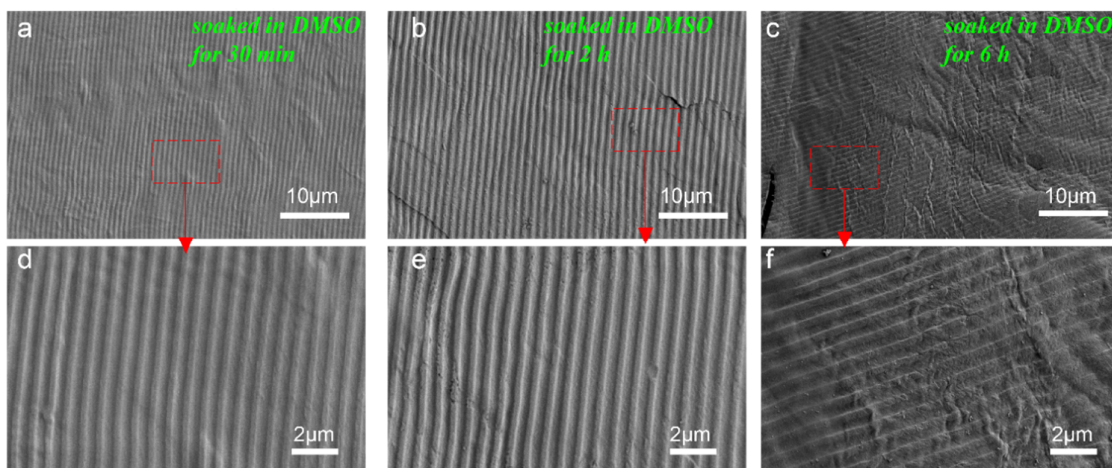


Figure S26. SEM images of wood imprinted sample which soaked in DMSO for different times. (a, d) SEM images of imprinted wood soaking in DMSO for 30 minutes. (b, e) SEM images of imprinted wood soaking in DMSO for 2 hours. (c, f) SEM images of imprinted wood soaking in DMSO for 6 hours

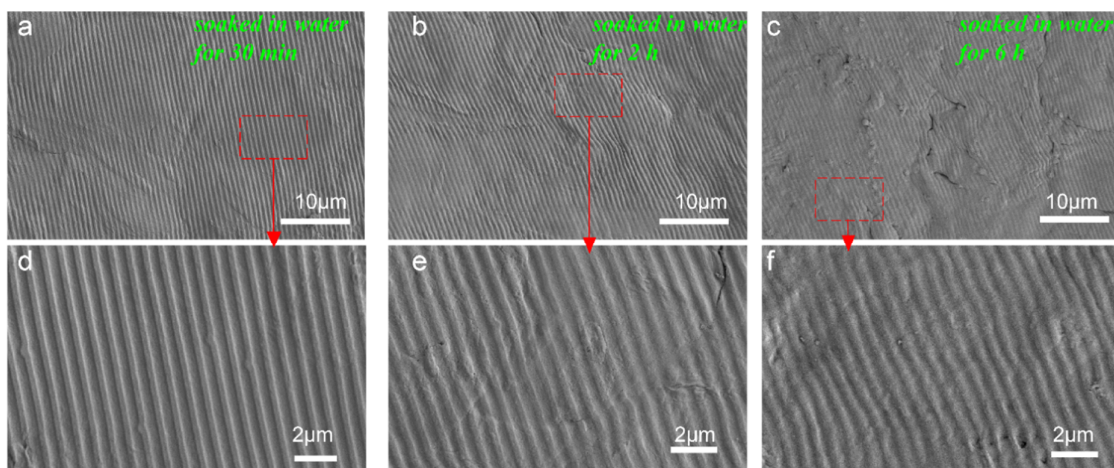


Figure S27. SEM images of wood imprinted sample which soaked in water for different times. (a, d) SEM images of imprinted wood soaking in water for 30 minutes. (b, e) SEM images of imprinted wood soaking in water for 2 hours. (c, f) SEM images of imprinted wood soaking in water for 6 hours

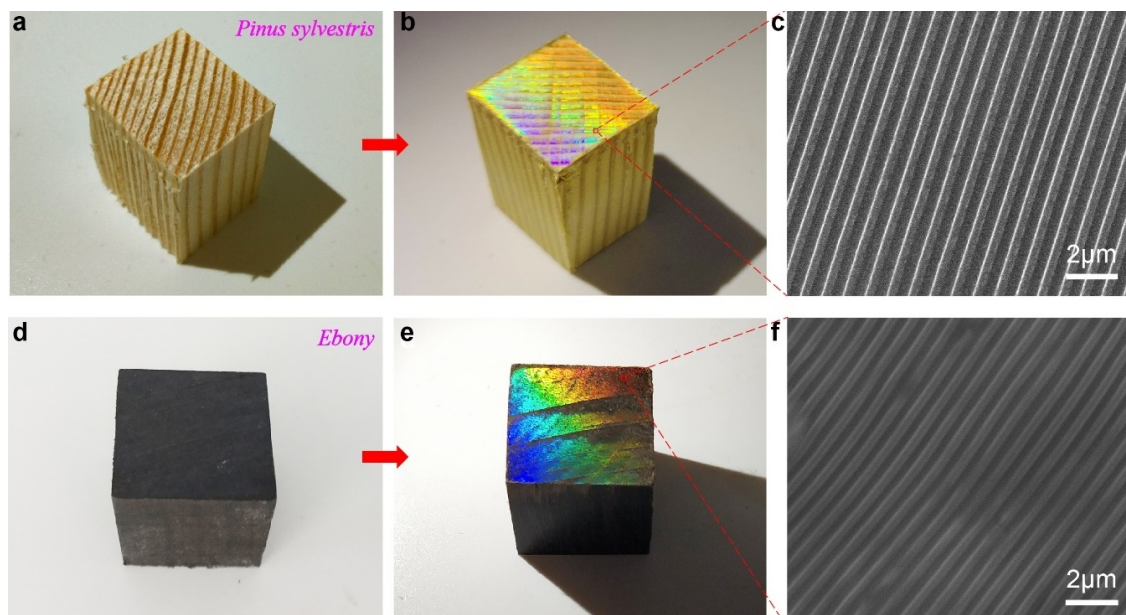


Figure S28. Some other kinds of wood can also be imprinted, demonstrating the universality of our method. (a,d) Photo of natural pinus sylvestris and ebony wood, respectively. (b, e) Photo of patterned wood made from pinus sylvestris and ebony wood, respectively. The color originates from light diffraction by the line array imprinted on the wood surface. (c,f) SEM image of the colorful surface of patterned pinus sylvestris and ebony wood, respectively.

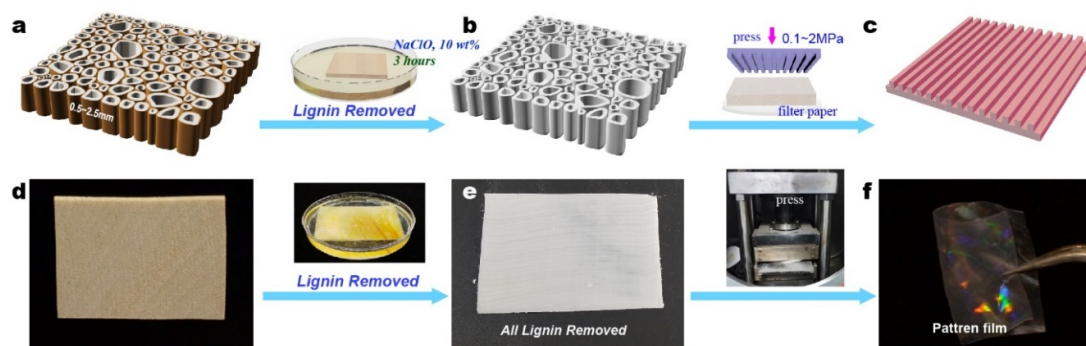


Figure S29. The procedure and set-up used for fabrication of imprinted wood film. (a) Model of natural wood; (b) Model of delignified wood; (c) imprinted mold; (d) Photo of wood; (e) Photo of delignified wood; (f) Photo of imprinted wood film.