

Article

Innovative Treatment of Ancient Architectural Wood Using Polyvinyl Alcohol and Methyltrimethoxysilane for Improved Waterproofing, Dimensional Stability, and Self-Cleaning Properties

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Abstract: This study introduced a novel two-step treatment to enhance the waterproofing, dimensional stability, and self-cleaning capabilities of ancient architectural wood. The process was initiated with the immersion of wood in an organic hybrid sol, composed of an acidic methyltrimethoxysilane (MTMS)-based silica sol and polyvinyl alcohol (PVA), which effectively sealed the wood's inherent pores and cracks to mitigate degradation effects caused by aging, fungi, and insects. Subsequently, the treated wood surface was modified with an alkaline MTMS-based silica sol to form a functional superhydrophobic protective layer. The modification effectiveness was meticulously analyzed using advanced characterization techniques, including scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX), Fourier-transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD). The results demonstrated substantial improvements: the modified wood's water contact angle (WCA) reached 156.0°, and the sliding angle (SA) was 6.0°. Additionally, the modified wood showed a notable reduction in water uptake and moisture absorption, enhancing its dimensional stability. The superhydrophobic surface endowed the wood with excellent self-cleaning properties and robust resistance to pollution. Enhanced mechanical durability of superhydrophobic surface was observed under rigorous testing conditions, including sandpaper abrasion and tape peeling. Furthermore, the modification improved the thermal stability, compressive strength, and storage modulus of the wood. Collectively, these enhancements render this modification a potent methodology for the preservation and functional augmentation of historic architectural woodwork.

Keywords: ancient architecture; wood component; PVA; MTMS; organic hybridization; superhydrophobic; self-cleaning



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1. Introduction

Historic wooden buildings are vital components of cultural tourism and serve as significant conduits for understanding ancient civilizations [1,2]. However, the wooden components of these historic buildings are vulnerable to damage from various environmental factors such as acid–base water erosion, ultraviolet degradation, and microbial or insect infestation, due to the inherent biological characteristics of wood [3,4]. These challenges can drastically reduce the lifespan of wood components and, in severe cases, may even precipitate the collapse of wooden structures [5–7]. Consequently, the reinforcement and preservation of wooden components in historic buildings are of paramount importance.

Degradation typically progresses from the exterior to the interior of wood, eventually leading to structural compromise [8,9]. In order to alleviate this problem, researchers have recently developed several methods to deal with ancient building wood. For instance, Hamed et al. [10] employed a novel reinforcement agent composed of hydroxypropyl cellulose (Klucel E) and nanocellulose (NC) at a specific concentration to treat archaeological wood, effectively minimizing color alterations and substantially enhancing its compressive strength. Zhou et al. [9] used a hybrid sol composed of polyvinyl alcohol (PVA), ethyl orthosilicate (TEOS), and methyl triethoxysilane (MTES) to impregnate ancient wood, effectively enhancing its mechanical properties and thermal stability. Chen et al. [11] applied a coating of polyurethane acrylate (PUA), in situ polymerized with dihydroxy-functionalized organo-montmorillonite (OMMT), to the surface of ancient wood. This coating exhibits self-healing properties when damaged externally, thereby providing effective protection for the wood. Additionally, Chen et al. [12] significantly enhanced the water resistance of ancient wood by painting a waterborne siloxane-modified polyurethane coating, achieving a water contact angle of 107.6° . Despite numerous reports on protecting ancient architectural wood using various methods, there is a scarcity of research concerning anti-fouling and self-cleaning functionalities. It is well known that in practical applications, there is a pressing need to protect the surface of historic wooden buildings from the impact of polluting liquids, dust, and other contaminants. Therefore, studying the construction of superhydrophobic coatings on traditionally reinforced wood surfaces to enhance their overall performance is highly meaningful.

Polyvinyl alcohol (PVA) is a flexible polymer with multiple hydroxyl ($-\text{OH}$) groups [13]. Owing to its robust adhesive characteristics, PVA is readily formulated into a film that fills the porous structures of wood [14,15]. However, its significant water absorption [16] and poor thermal stability [17] limit its application. In contrast, methyltrimethoxysilane (MTMS) silica sol obtained by hydrolysis under acidic conditions can penetrate wood cell walls [18] and form a hydrophobic film [19], but the resulting polymethylsilsesquioxane (PMSQ) [20,21] may exhibit a certain brittleness [22]. Recent studies have demonstrated that organic composites of PVA and MTMS exhibit exceptional thermal stability and mechanical properties [23]. If the PVA and acidic MTMS silica sol are synergistically applied to reinforce decayed wood, it is possible to fill the inherent pores and cracks exacerbated by aging and other damages in historic wood structures, thereby enhancing both dimensional stability and internal waterproofness. Additionally, due to the film-forming properties of PVA and acidic MTMS silica sol, it may not be feasible to impart self-cleaning functionality to the substrate. Typically, self-cleaning requires the construction of a micro/nano-structured superhydrophobic surface [24]. Interestingly, the MTMS silica sol obtained under alkaline conditions not only exhibits high reactivity but can also form biomimetic superhydrophobic micro-nano rough structures [25,26], thereby providing self-cleaning properties to the substrate. Therefore, by further treating the modified wood with alkaline MTMS silica sol, it may compensate for the functional deficiencies present in modifications made with acidic MTMS silica sol and PVA, thereby potentially generating synergistic reinforcement effects.

Based on the aforementioned ideas, this study proposed a two-step process that began with the infusion of a composite modifier comprising PVA and acidic MTMS silica sol to reinforce the wood's internal structure, followed by the application of an alkaline MTMS silica sol which created a durable superhydrophobic surface. A comprehensive analysis of the modified wood's physicochemical properties, including waterproofing, dimensional stability, self-cleaning capabilities, and mechanical strength tests, along with a series of characterization techniques (such as SEM, EDX, FT-IR, XRD, and XPS characterization), was conducted to evaluate the modification's effectiveness. This innovative treatment is expected to offer a significant new method for the protection of wooden components in historic buildings.

2. Experimental Section

2.1. Raw Materials

The pine wood (*Pinus yunnanensis* Franch) components utilized in this study were procured from the deteriorated hangings of historical buildings, such as the “Liu Family Courtyard” in Heshun Ancient Town, Tengchong City, Yunnan Province, China (Figure 1). Experimental wood samples, processed from areas showing slight decay and characterized by an air-dried density of approximately 0.455 g/cm^3 (the corresponding density of un-degraded wood is $\sim 0.487 \text{ g/cm}^3$) and a moisture content of 8.0%, were meticulously cut into three different sizes to meet specific experimental needs (Figure 1). For the mechanical tests, the dimensions were set to 30 mm (Longitudinally: L) $\times$ 20 mm (Radially: R) $\times$ 20 mm (Tangentially: T) and 50 mm (L) $\times$ 10 mm (R) $\times$ 5 mm (T). For all other tests in the experiment, the dimensions were set to 20 mm (L) $\times$ 20 mm (R) $\times$ 20 mm (T). Each test was repeated at least five times.

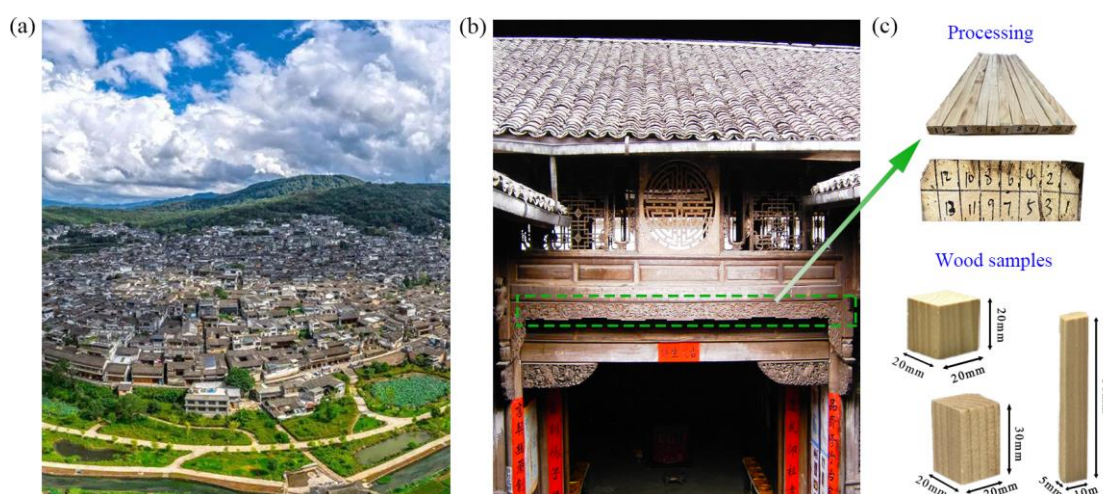


Figure 1. (a) The overlooking view of ancient town. (b) Location of collecting wood components. (c) Wood component processing and test samples.

Methyltrimethoxysilane (MTMS, 98%) and polyvinyl alcohol (PVA, alcoholysis degree: 87.0~89.0 mol%; viscosity: 40.0~48.0 mPa·s) were acquired from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Hydrochloric acid solution (HCl, 0.1 mol/L) was sourced from Guangzhou Howei Pharma Tech Co., Ltd. (Guangzhou, China). Ammonium hydroxide solution (NH_4OH , 25%–28%) was obtained from Shanghai Yien Chemical Technology Co., Ltd. (Shanghai, China). Anhydrous ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99.7%) was procured from Guangdong Guanghua Sci-Tech Co., Ltd. (Shantou, China). All chemical reagents were utilized as received, without further purification. Distilled water was made in the laboratory using an ultra-pure water machine (model AEX-1001-B) from Chongqing Ever Young Enterprise Development Co., Ltd. (Chongqing, China).

2.2. Preparation of the Samples

2.2.1. Acidic MTMS–Silica Sol/PVA Impregnation

As outlined in Figure 2, the preparation process began with the mixing of MTMS and a 90 wt.% ethanol aqueous solution in a volume ratio of 1:2. This mixture was subjected to magnetic stirring for 30 s. Subsequently, a 0.1 mol/L HCl solution was added quickly in a ratio of $V(\text{MTMS}): V(\text{HCl}) = 5:1$ to form acidic MTMS–silica sol, then stirred for an additional 5 min. Following this, a 5 wt.% PVA aqueous solution was introduced to the acidic sol at a 3:7 v/v ratio and stirred for another 5 min. The wood samples were then immersed in the obtained PVA/MTMS–silica sol composite solution, with the impregnation process completed under a pressure of 0.6 MPa for 20 min. After impregnation, the samples were removed and cured in an oven at 103°C for 10 min.

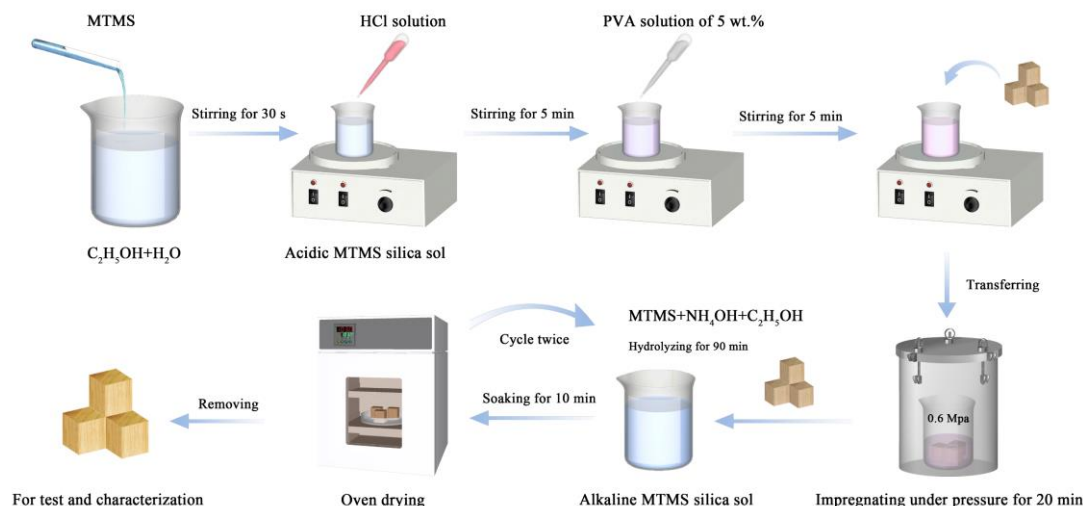


Figure 2. The schematic of preparation process.

2.2.2. Construction of Superhydrophobic Surface

The samples prepared in the previous step were immersed in alkaline MTMS–silica sol at atmospheric pressure for 10 min, followed by a curing phase which took place at 103 °C for 10 min. This immersion and curing process was repeated twice to ensure an adequate thickness of the superhydrophobic surface. Finally, the samples were dried at 103 °C for 3 h to complete the final sample preparation.

The above alkaline MTMS–silica sol was prepared by mixing MTMS, ammonium hydroxide (NH₄OH), and anhydrous ethanol (C₂H₅OH) in a 1:25:25 *v/v/v* ratio. The mixture was pre-stirred at room temperature for 90 min.

For comparative analysis, five groups of wood samples were prepared with varying treatments: sample I was treated with PVA; sample II was treated with acidic MTMS–silica sol; sample III was treated with a combination of PVA and acidic MTMS–silica sol; sample IV was treated with alkaline MTMS–silica sol; sample V was the final sample prepared using a two-step method. Additionally, an untreated wood set was used as the control.

2.3. Morphological Observation

The surface morphological characteristics of the as-prepared samples were examined using a scanning electron microscope (SEM, TESCAN MIRA LMS, Tescan, Brno, Czech Republic). The distribution of chemical elements on the wood surface was analyzed with an accompanying energy-dispersive X-ray spectrometer (EDX). Additionally, the changes in surface roughness before and after wood modification were assessed using a three-dimensional (3D) laser microscopic imaging system (VK-150K, Keyence, Osaka, Japan). Measurements of arithmetic mean surface roughness (Ra) and 3D topographic images were obtained over a tested area of 518 µm × 692 µm. The analysis regions of all the samples mentioned above were earlywood.

2.4. FTIR, XRD and XPS Investigation

Attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectra of the wood samples were obtained using a Nicolet iN10 MX (Thermo Fisher Scientific, Waltham, MA, USA) spectrometer. For each spectrum, 32 scans were conducted at a resolution of 4 cm^{−1}, ranging from 4000 cm^{−1} to 675 cm^{−1}. The crystal structure of the wood was analyzed using copper Kα radiation (40 kV, 40 mA, λ = 1.54056 Å) on an X-ray diffractometer (XRD, Rigaku Ultima IV, Rigaku Co., Ltd., Tokyo, Japan). Additionally, the chemical bonding states of the surfaces were examined using an X-ray photoelectron spectrometer (XPS, Nexsa G2, ThermoFisher, Waltham, MA, USA) at high-resolution scans with a monochromatic Al-Kα (1486.6 eV) X-ray source. The obtained spectra were calibrated using a reference voltage for C1s at 284.8 eV. All the above tests were conducted on the tangential sections of the samples.

2.5. Wettability Characterization

The water contact angles (WCA) of different samples were measured using a 5 μ L water droplet on a contact angle measuring instrument (JC2000D3R, Shanghai Zhongchen Digital Technology Apparatus Co., Ltd., Shanghai, China) at room temperature. Data were recorded immediately after the droplet was deposited on the surface and continually until 300 s. Additionally, the sliding angle (SA) of the superhydrophobic surface was measured using a 10 μ L water droplet [26]. The results of the WCA and SA are the averages of five measurements taken at different locations on the tangential sections of the wood samples.

2.6. Water Uptake/Moisture Absorption Measurement

According to the Chinese standard GB/T 1934.1—2009 “Method for determination of the water absorption of wood”, the following procedure was employed. The oven-dried specimens with dimensions of 20 mm (L) $\times$ 20 mm (R) $\times$ 20 mm (L) from both the control and modified groups were initially weighed (designated as W_1). These specimens were then submerged in water to a depth of 50 mm below the surface. After specific intervals, the specimens were removed and weighed again, and recorded as W_t (the immersion lasted 7 d). Each group consisted of five replicates, and the average value was calculated. The water uptake (WU) was calculated using Equation (1) with an accuracy of 0.1%.

$$WU = [(W_t - W_1)/W_1] \times 100\% \quad (1)$$

where W_t represents the weight of the sample after the predetermined water uptake time; W_1 states the initial oven-dried weight of the sample, i.e., the moisture content is 0%.

Moisture absorption testing was conducted in accordance with GB/T 1934.2—2009 “Method for determination of the swelling of wood”. The oven-dried specimens were weighed and recorded as M_1 . They were then placed in a constant-temperature and -humidity chamber (HD-E702–100B40, Haida International Equipment Co., Ltd., Dongguan, China) set at 20 $^{\circ}$ C and 85% relative humidity for 7 d. Periodically, the specimens were removed from the chamber and weighed, and the resulting weight was denoted as M_t . The moisture absorption (MA) was calculated using Equation (2) with an accuracy of 0.1%.

$$MA = [(M_t - M_1)/M_1] \times 100\% \quad (2)$$

where M_t suggests the dynamic mass of the specimen after moisture absorption; M_1 illustrates the initial oven-dried mass of the specimen.

2.7. Dimensional Stability Determination

During the water uptake and moisture absorption testing, the volume of the specimens was also measured by a digital vernier caliper. The volume swelling coefficient (VSC) was calculated according to Equation (3) and reported with an accuracy of 0.1%.

$$VSC = [(V_t - V_1)/V_1] \times 100\% \quad (3)$$

where V_1 refers to the primary volume of the specimen before water uptake or moisture absorption; V_t denotes the dynamic volume of the specimen after water uptake or moisture absorption.

The dimensional stability of the specimens is characterized by the anti-swelling efficiency (ASE). The ASE of the modified specimens is calculated from the oven-dried condition to the condition after water absorption or moisture absorption, according to Equation (4), and is reported with an accuracy of 0.1%.

$$ASE = [(VSC_1 - VSC_2)/VSC_1] \times 100\% \quad (4)$$

where VSC_1 and VSC_2 are the volume swelling coefficients of the control sample and the modified sample, respectively.

2.8. Anti-Fouling and Self-Cleaning Test

The anti-fouling performance of the final superhydrophobic sample was evaluated by measuring the contact angles of various common liquid contaminants, including acidic water (pH = 2), alkaline water (pH = 12), cola, milk, and coffee. Both the superhydrophobic and control samples were placed on tilted glass slides at a dip angle of 10° and sprinkled with chalk dust. Water droplets were then continuously dispensed onto the contaminated surfaces using a pipette. The process of removing the contaminant powder was documented to assess the self-cleaning performance of the samples.

2.9. Superhydrophobic Surface Durability Test

The durability of the superhydrophobic surface was evaluated through sandpaper abrasion and adhesive tape peeling tests. The sandpaper abrasion test was conducted by placing a superhydrophobic sample, loaded with a 50 g weight, on 1000# sandpaper. The sample was pushed horizontally at a consistent speed of 1 cm/s over a distance of 5 cm for one testing cycle. This process was repeated five times, and the WCA and SA were measured after each cycle. For the adhesive tape peeling test, adhesive tape was applied to the surface of the superhydrophobic sample and rolled back and forth using a 50 g weight to ensure firm adhesion. Then, the tape was carefully peeled away from the surface of the sample; this completed one cycle. This process was repeated for a total of 100 cycles, and the WCA and SA data were recorded every 20 cycles.

2.10. Thermal Stability Test

To compare the thermal stability of wood before and after modification, thermogravimetric (TG) and differential thermogravimetric (DTG) analyses were conducted using a thermogravimetric analyzer (Netzsch STA449F3, Selb, Germany) in a nitrogen atmosphere. The powders of each sample were progressively heated from room temperature to 800 °C at a rate of 10 °C/min.

2.11. Compressive Strength Test

In order to ensure that the modified wood components meet the mechanical performance requirements for practical applications, the compressive strengths parallel to the grain (longitudinal) and perpendicular to the grain (radial and tangential) were measured by using an electronic universal testing machine (UTM5105, Shenzhen SUNS Technology Stock Co., Ltd., Shenzhen, China). These measurements were conducted in accordance with the national standards GB/T 1935-2009 “Method of testing in compressive strength parallel to grain of wood” and GB/T 1939-2009 “Method of testing in compression perpendicular to grain of wood”.

2.12. Dynamic Mechanical Thermal Test

The dynamic mechanical thermal properties, including the storage modulus (E') and loss factor ($\tan \delta$), were measured using a dynamic mechanical analyzer (DMA, Q800, TA Instruments Inc., New Castle, DE, USA). The tests were conducted in three-point bending mode (the loading direction was along the tangential direction) over a temperature range from 30 °C to 120 °C, with a heating rate of 5 °C/min, an oscillating frequency of 1 Hz, a proportional factor of 1.3, a displacement amplitude of 60 µm, a dynamic force of 2 N, and a static force of 0 N. The experimental data were automatically recorded by the software integrated into the instrument.

3. Results and Discussion

3.1. Morphologies Observation

The SEM images depicted in Figure 3 provide a comprehensive visual representation of the surface morphology across different samples, including the control sample and samples I through V. Figure 3(a₁,a₂) reveals the inherent anisotropic nature of wood, which is characterized by interconnected cellular structures. In its longitudinal section, wood

displays a ridge-like protrusion (cell walls) and a groove-like depression (cell cavities) in an alternating pattern, while the cross-sectional view resembles a honeycomb structure. The surfaces of cells in non-decayed natural wood are often smooth and the cells are tightly packed [27,28]. Therefore, on the surface of the control wood, residue caused by decay can be observed (see inset in Figure 3(a₁)), along with larger gaps between the cells (Figure 3(a₂)). In contrast, after undergoing a treatment with pure polyvinyl alcohol (PVA), the surface of sample I appears smoother (Figure 3(b₁)), with the tracheid lumens effectively sealed off (Figure 3(b₂)), showcasing successful pore and crack filling, which helps mitigate the impacts of decay. For sample II, treatment with acidic MTMS silica sol resulted in the deposition of a uniform polymethylsilsesquioxane (PMSQ) coating in the longitudinal section (Figure 3(c₁)), which closely resembles the morphology observed in sample I. However, the cross-section (Figure 3(c₂)) reveals unsealed tracheid lumens but thicker cell walls and significantly filled cell gaps (vs. control), indicating effective penetration and binding of MTMS within the wood structure. In Figure 3(d₁,d₂), it can be observed that the treatment with PVA/acidic MTMS silica sol composite system also leads to the surface pores of sample III being covered by an organic hybrid polymer coating to some extent, which indicates that PVA and acidic MTMS silica gel are compatible with each other. This is further supported by the uniform distribution of Si elements, as demonstrated by EDX detection (Figure 3(d₃)). Moreover, this provides a relatively flat substrate for the construction of further superhydrophobic coatings. The application of alkaline MTMS silica sol on sample IV leads to a deposition of a substantial amount of PMSQ particles on the wood surface, creating a desired micro–nano rough structure, as depicted in Figure 3(e₁,e₂). Indeed, consistent with expectations, by further utilizing alkaline MTMS silica sol treatment on the basis of sample III, the surface of sample V obtained through the two-step method (Figure 3(f₁,f₂)) not only exhibits a finely nano/micro-scale rough structure but also achieves the further filling of surface grooves and pores, thereby effectively protecting the wood.

According to SEM observations (Figure 3), sample V exhibits significantly greater surface roughness compared to other samples. To quantify this attribute, a three-dimensional laser microscopic imaging system was employed. Figure 4 demonstrates that the Ra value for Sample V increased obviously from 7.308 μm in the control wood to 9.476 μm . According to the principle of superhydrophobicity [29], an increase in surface roughness facilitates the formation of a superhydrophobic surface.

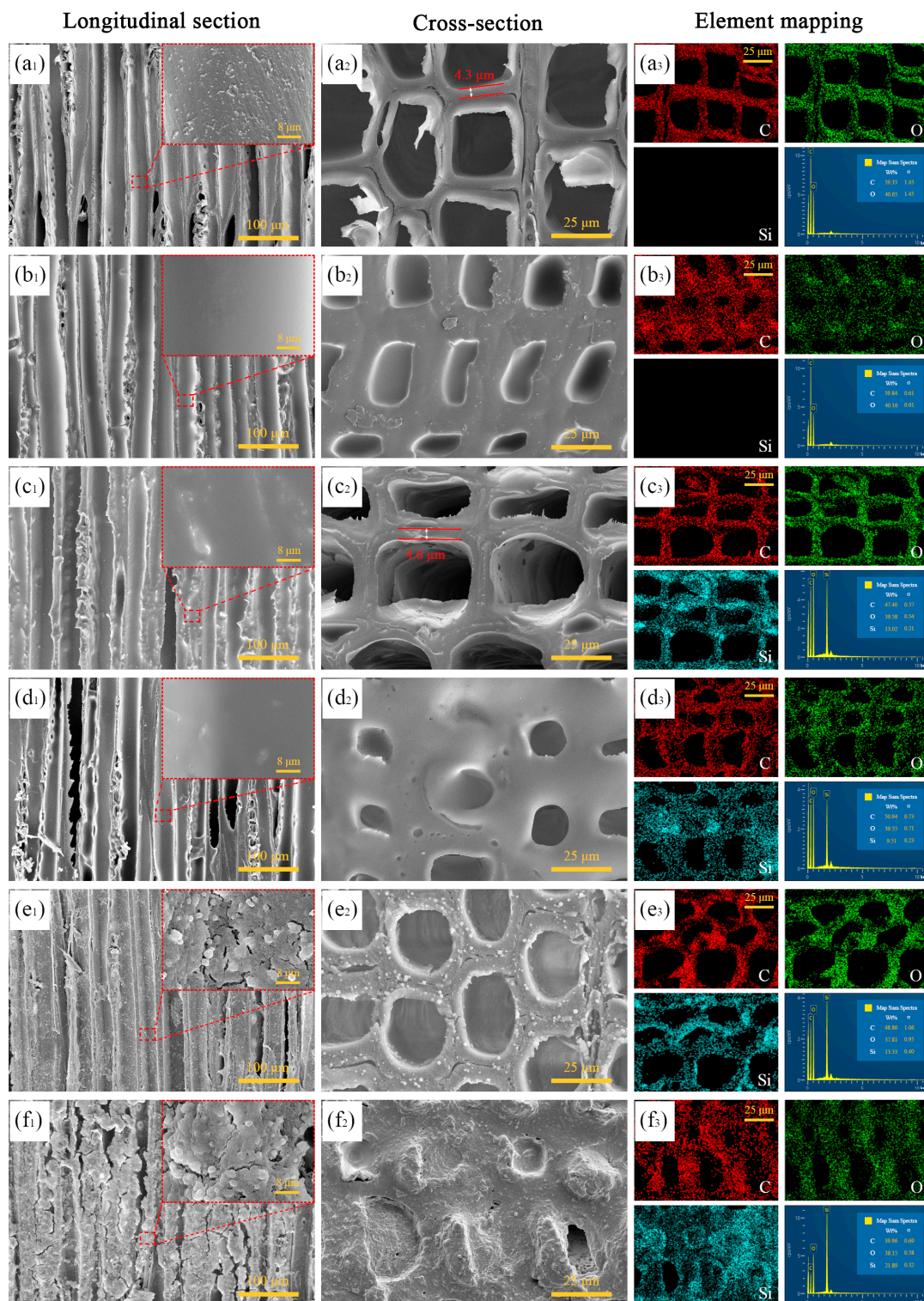


Figure 3. Surface SEM images and EDX element distribution maps of the (a₁–a₃) control wood sample, (b₁–b₃) sample I, (c₁–c₃) sample II, (d₁–d₃) sample III, (e₁–e₃) sample IV, and (f₁–f₃) sample V.

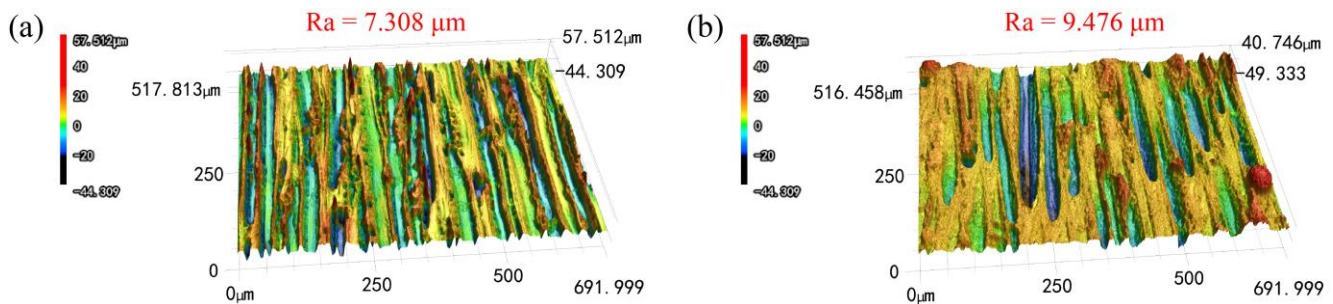


Figure 4. Surface 3D topographic images and corresponding arithmetic mean surface roughness (Ra) values of the (a) control wood sample and (b) sample V.

3.2. FT-IR Analysis

The chemical functional groups on the surface of the wood before and after modification were characterized using FT-IR spectra, and the results are presented in Figure 5. The control sample displayed a broad and intense vibrational peak at 3350 cm^{-1} , which was indicative of the hydrophilic -OH functional groups in wood [30]. In the IR spectrum of sample I, the -OH stretching vibration peak shifted from 3350 cm^{-1} to 3300 cm^{-1} , suggesting the formation of hydrogen bonds between the -OH groups of PVA and those in the wood [31]. An enhanced peak at 1734 cm^{-1} was attributed to the stretching vibration of the C=O-O bond from the vinyl acetate group in PVA [32], while the reduced intensity of the wood absorption peak was due to the masking effect of the PVA film. In sample II, characteristic peaks at 1269 cm^{-1} and 773 cm^{-1} were observed, corresponding to Si-CH_3 functional groups from MTMS [33]. The -OH absorption peak disappeared, indicating a chemical reaction between the acidic MTMS silica sol and wood components, resulting in the formation of a PMSQ coating with a Si-O-Si crosslinking network structure (1009 cm^{-1}) [34]. However, the reaction was incomplete, as evidenced by the appearance of a characteristic Si-OH absorption peak at 893 cm^{-1} [35]. The spectrum of sample III, modified by PVA/acidic MTMS silica sol, revealed the presence of characteristic bands for both PVA and MTMS. Not only did the Si-CH_3 characteristic peaks appear, along with the Si-OH stretching vibration at 899 cm^{-1} , but an enhanced peak attributed to the C=O-O bond from PVA also appeared near 1734 cm^{-1} . This further indicated excellent blending of PVA with the acidic MTMS silica gel, signifying the formation of a hybrid polymer. Importantly, the presence of the residual hydrophilic -OH and Si-OH groups laid a chemical foundation for further surface modification. As for sample IV, not only did Si-CH_3 characteristic peaks appear, but the peaks corresponding to -OH groups and Si-OH groups were both absent. This indicated a more complete reaction between alkaline MTMS silica sol and wood components by the sol-gel process. In contrast, sample V not only lacked the hydrophilic -OH and Si-OH groups, but also exhibited strong characteristic absorption peaks of Si-CH_3 . These indicate the full reactivity of alkoxy groups and the complete polymerization of MTMS with its other molecules and wood components after the two-step synergistic modification.

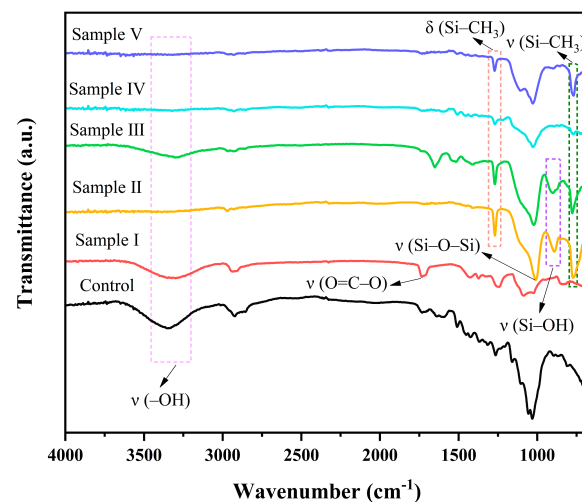


Figure 5. FT-IR spectra of control and modified wood.

3.3. XRD Analysis

The XRD patterns of all samples are shown in Figure 6. Distinct peaks at diffraction angles of approximately 16.0° , 22.5° , and 35.0° in the control wood and all modified wood curves were assigned to the (101), (002), and (040) crystal planes of the wood cellulose, respectively [36]. After modification, the diffraction peak positions for wood samples I to V remained unchanged, indicating that the crystalline structure of the wood was not disrupted, although crystallinity decreased. This decrease is attributed to the modifier PVA/MTMS penetrating the wood cell wall, causing the cellulose crystallization area to swell and affecting the orderly arrangement of microfibrils within this area. At the same time, the modifier PVA/MTMS reacts with the $-OH$ groups of the wood cellulose molecular chain, destroys the hydrogen bonds within the cellulose itself, and weakens the intermolecular interactions between the cellulose molecular chains, thus reducing the crystallinity of the wood [37]. For modified sample V, the reduction in crystallinity is more pronounced than in the other modified samples. This greater decrease can be inferred as resulting from the larger swelling effect in the crystalline region and the effective consumption of cellulose $-OH$ groups caused by the synergistic two-step modification process. This result is also consistent with the FT-IR results.

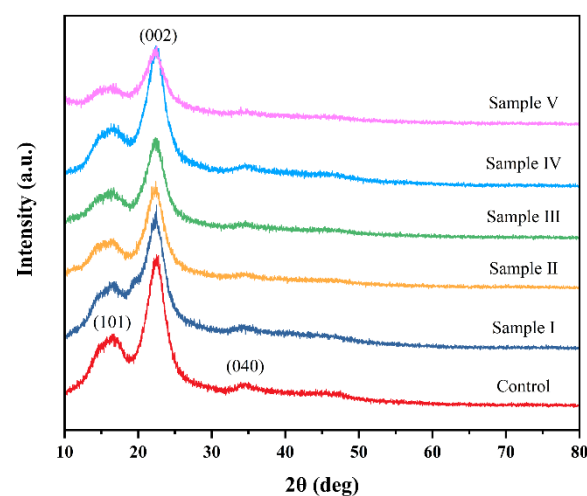


Figure 6. XRD patterns.

3.4. XPS Analysis

Wood is a natural polymer material composed of cellulose, hemicellulose, lignin, and a small amount of extractives [38]. The XPS detection results, shown in Figure 7 and Table 1, confirm the presence of carbon (C1s) and oxygen (O1s) on the surface of the untreated wood (control). Hydrogen (H) is also present on the wood surface but cannot be detected by the XPS technique. For sample I, the introduction of high –OH content PVA resulted in an increased oxygen content. In addition to sample I, all other modified samples contained silicon (Si2s and Si2p), confirming the bonding of organosilane MTMS to the wood. Among these, the modified sample V not only had high Si content (38.63%) but also a relatively high C/Si ratio (0.75), indicating that the dual-step modification enriched the Si elements on the wood surface while effectively grafting hydrophobic –CH₃ groups onto the wood, which is beneficial, as it improves its hydrophobicity.

Table 1. Surface chemical compositions and their relative contents in control wood and modified wood samples.

Sample Label	Elements (at.%)			Ratio	Carbon Components (at.%)			
	C	O	Si		C1	C2	C3	C4
Control	74.47	25.53	-	-	58.53	32.98	7.24	1.25
Sample I	69.41	30.59	-	-	60.24	28.11	5.51	6.14
Sample II	29.41	32.58	38.01	0.77	52.98	35.48	7.05	4.49
Sample III	39.92	34.00	26.08	1.53	58.65	19.11	15.75	6.49
Sample IV	27.28	33.00	39.72	0.69	74.21	17.19	5.99	2.61
Sample V	29.03	32.34	38.63	0.75	75.15	19.19	4.26	1.40

The high-resolution XPS C1s spectra and corresponding component percentages are displayed in Figure 7b–g and Table 1. Carbon (C) atoms in wood can be classified into four binding forms based on their respective bonding states [39,40]: The C1 component is mainly associated with lignin and wood extractives such as fatty acids, waxes, and terpenes, with C atoms bonded as C–C or C–H. The C2 component is primarily related to C atoms in cellulose molecules bonded to only one non-carbonyl oxygen atom (C–O). The C3 component represents C atoms bonded to either one carbonyl oxygen atom or two non-carbonyl oxygen atoms (C=O or O–C–O). The C4 peak represents C atoms simultaneously bonded to one carbonyl oxygen atom and one non-carbonyl oxygen atom (O=C–O). In contrast to the control, modified sample I shows a significant increase in C4 content, which can be attributed to the residual acetate (–O–CO–CH₃) groups from PVA, consistent with the FT-IR result. For the modified samples II to V, the C1 content gradually increases, with the highest increment observed in sample V. This result suggests that the hydrophilic –OH groups in wood undergo chemical reactions with the applied modifier, resulting in an increase in C–H and C–C structural content. This provides additional evidence for the effective reduction of hydrophilic groups in wood after the two-step synergistic modification.

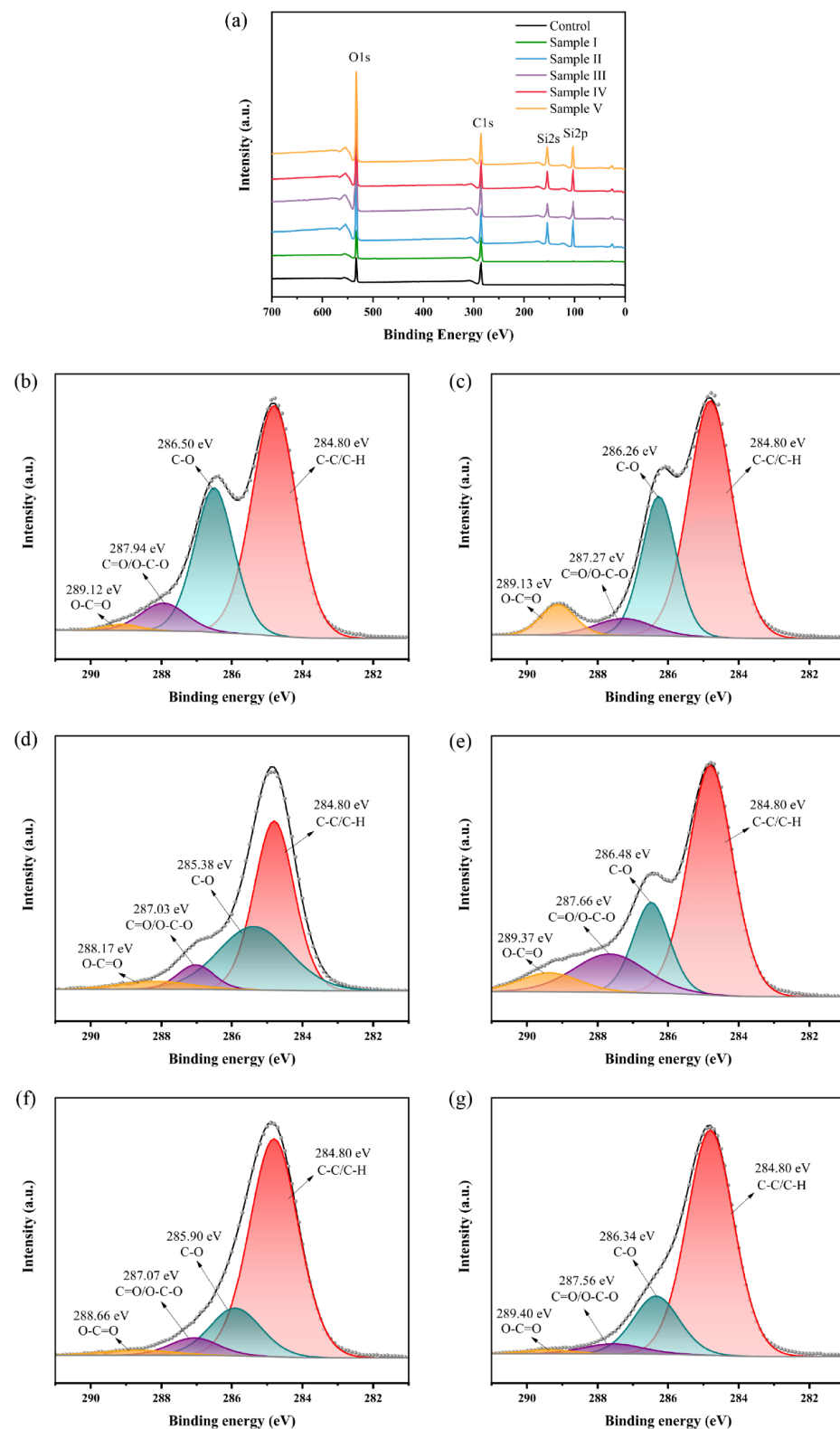


Figure 7. (a) XPS survey spectra. High-resolution C1s spectra for various samples: (b) control sample, (c) sample I, (d) sample II, (e) sample III, (f) sample IV, and (g) sample V.

3.5. Modification Mechanism Analysis

Based on the above analysis, the modification mechanism of this experiment can be clearly understood. Initially, MTMS was hydrolyzed under acidic conditions to produce

$\text{CH}_3\text{Si}(\text{OH})_3$, which subsequently formed an MTMS-based silica sol featuring reactive silanol ($\text{Si}-\text{OH}$) groups [41]. A PVA solution was then added to this acidic MTMS silica sol, where the $\text{Si}-\text{OH}$ groups interacted with the $-\text{OH}$ groups on the PVA chain, forming an organic hybrid sol [42,43]. This sol permeated the wood, where MTMS hydrolyzed oligomers (forming $\text{Si}-\text{O}-\text{Si}$ bonds) and PVA molecules interacted with the wood components through $\text{Si}-\text{O}-\text{C}$ bonds or hydrogen bonding. Upon solidification, a branched polymer network composed of PMSQ and PVA molecules formed inside the wood, effectively sealing pores and cracks. In the second step of immersion, the $\text{Si}-\text{OH}$ groups generated by the alkaline MTMS silica sol reacted with the residual $-\text{OH}$ groups from the PVA/acidic MTMS silica sol composite polymer and the wood itself. This reaction introduced a superhydrophobic micro–nano rough structure on the surface of the smooth composite polymer. The possible modification mechanism for the entire process is illustrated in Figure 8.

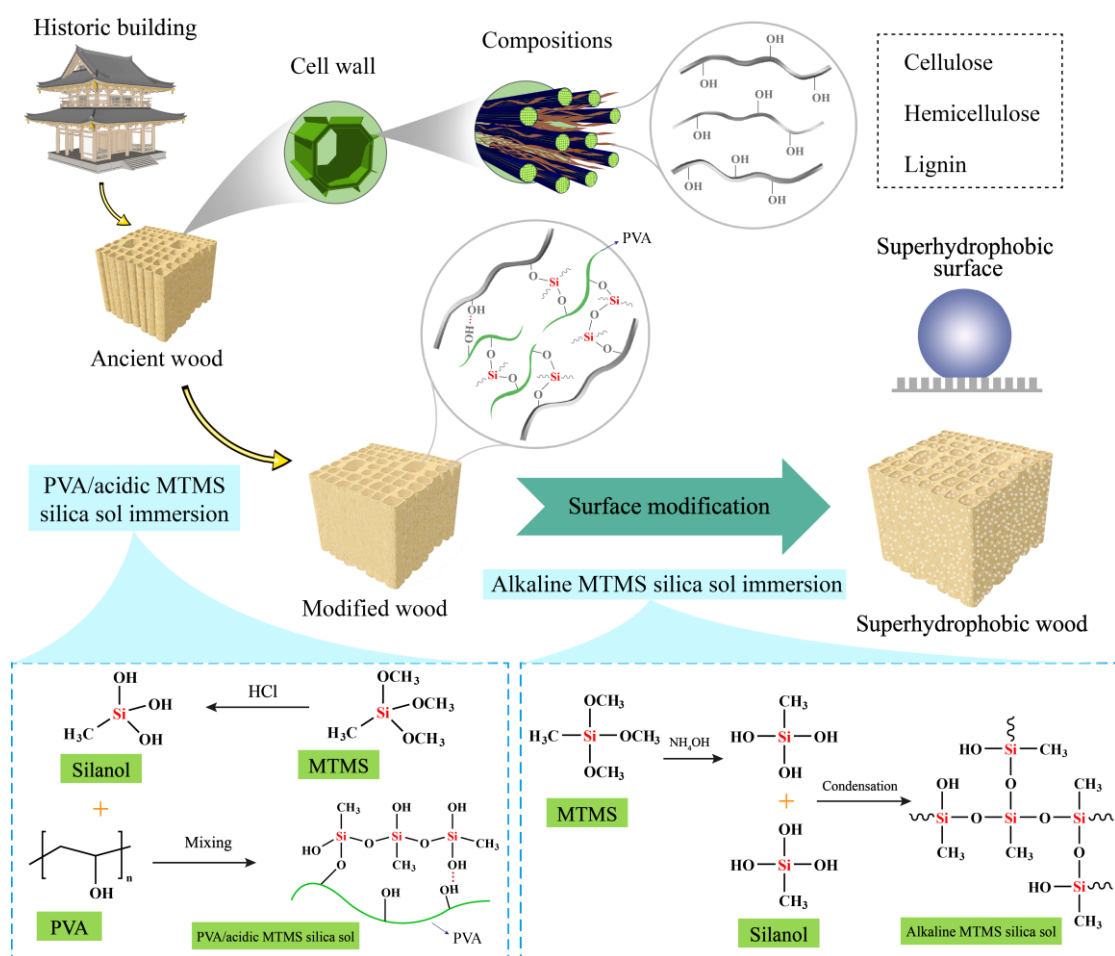


Figure 8. Schematic diagram of possible modification mechanism.

3.6. Dynamic Wettability Analysis

The water contact angle (WCA) values on the surfaces of wood samples from different groups changed over time, as shown in Figure 9. It was evident that the untreated control wood was hydrophilic, with an initial WCA of only 80.0° , and the water was absorbed by the wood within 40 s. Due to the hydroxyl nature of PVA, the surface of sample I treated with pure PVA still exhibited hydrophilic characteristics. However, the WCA of sample I increased, which can be attributed to the closure of wood pores by the PVA film, delaying the penetration of water into the wood matrix; this finding was consistent with the research results of Yang et al. [28]. SEM, FTIR, and XPS analyses demonstrated that the acidic MTMS silicon sol infiltrated the wood and polymerized to form a hydrophobic PMSQ coating. As a result, sample II exhibited a higher WCA compared to the control

and sample I. Furthermore, the WCA of sample II remained hydrophobic (96.1°) even after 300 s. However, due to the flat surface, achieving superhydrophobicity was not feasible. From Figure 9, it can be observed that the initial WCA (114.6°) of sample III, treated with a combination of PVA and acidic MTMS silicon sol, was higher than that of sample II. However, it immediately decreased and reached 68.0° at 300 s. This result indicates that the combination of PVA and acidic MTMS silicon sol effectively sealed the wood pores, but the residual hydrophilic functional groups contributed to increased wettability. In contrast, the water droplet on the surface of sample IV exhibited a round shape, and the WCA curve remained stable even after 300 s, with the WCA remaining greater than 150° . This stability can be attributed to the formation of PMSQ particles on the wood surface under alkaline conditions. These particles effectively trapped air within the pores, preventing water droplet penetration. Compared to modified samples I, II, III, and IV, wood sample V exhibited highly stable superhydrophobicity over time. This stability was due to the further depositing of the superhydrophobic PMSQ layer, which is the product of the alkaline MTMS silicon sol, onto the wood surface pre-treated with PVA/acidic MTMS silicon sol. This combination resulted in the formation of a dual-layer waterproof system, enhancing the long-term stability of superhydrophobicity.

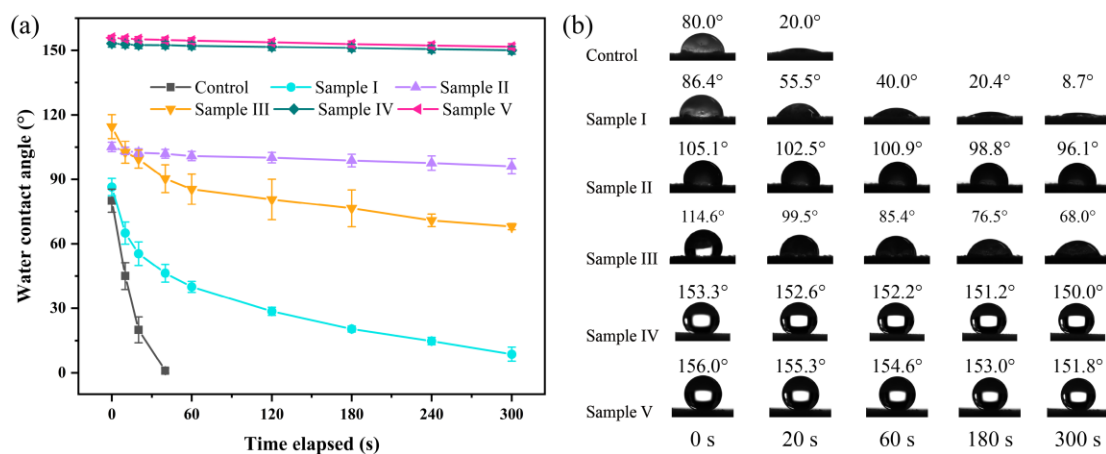


Figure 9. (a) The change of WCA value on the surface of wood sample with the elapsed time and (b) the corresponding contact angle images at different times (0 s, 20 s, 60 s, 180 s, and 300 s).

3.7. Water Uptake (WU) and Moisture Absorption (MA) Analysis

The WU and MA of the wood samples were measured to investigate their water/moisture resistance properties. Figure 10a illustrates the WU change curve, showing that the WU of each sample gradually increased with prolonged immersion time. At 168 h, the WUs of samples I, II, III, IV, and V were 137.6%, 117.9%, 121.4%, 115.0%, and 91.9%, respectively. Compared to the control sample (143.4%), these values were reduced by 4.0%, 17.8%, 15.3%, 19.8%, and 35.9%, respectively, indicating that the modified wood samples exhibited improved waterproofing performance. There are two main reasons for the decrease in the WU of the modified wood. Firstly, the modification agent underwent polymerization and curing within the wood, filling the wood pores and reducing the available space for water accommodation. Secondly, as indicated by the FT-IR spectra, the modification agent formed crosslinks with the $-OH$ groups in the wood, reducing the accessibility of water-absorbing $-OH$ groups. Notably, sample V exhibited the lowest WU, indicating that after treatment with acidic MTMS silica sol in conjunction with PVA (reducing the porosity), the construction of a superhydrophobic barrier on the surface using alkaline MTMS silica sol further prevented water from entering the wood, thereby significantly reducing the water uptake.

In addition, the MA under high relative humidity (RH) conditions (RH = 85%, 20°C) was also monitored, and the results are shown in Figure 10b. Compared to the control wood, sample I exhibited a moderate increase in MA (Figure 10b). The higher MA may be

attributed to the smaller size of water vapor molecules, which makes them more prone to forming hydrogen bonds with the –OH groups. Samples II, III, and IV had lower MAs (10.9%, 11.5%, and 10.7%, respectively) compared to the control sample (12.4%). However, sample V still had the lowest MA (8.9%), which was reduced by 28.3% compared to the control wood. This result is consistent with the WU test findings.

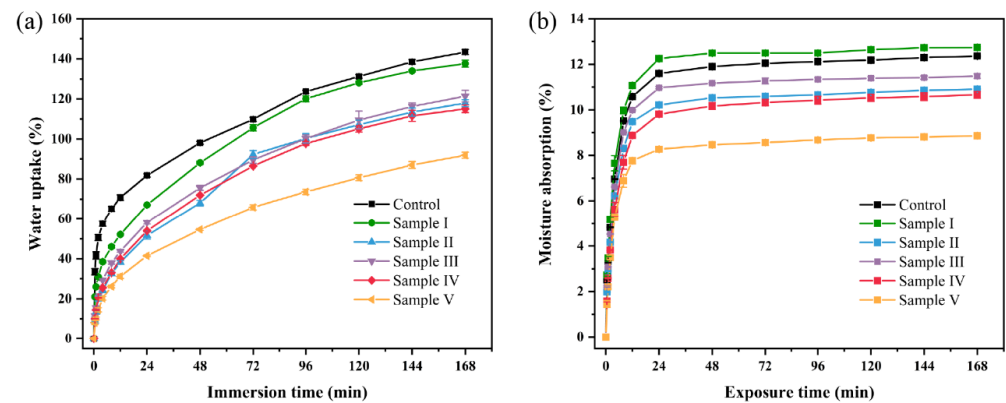


Figure 10. (a) Plots of water uptake versus immersion time of wood samples. (b) Graphs of moisture absorption versus exposure time of wood samples.

3.8. Dimensional Stability Analysis

The results of the volume swelling coefficient (VSC) tests during 168 h of water immersion and moisture exposure for the control and all modified wood samples, demonstrating the dimensional changes caused by water influence during simulated wood usage, are presented in Figure 11. From Figure 11a,b, it was observed that the VSCs of the control wood under water immersion and high-humidity conditions were higher than those of all the modified woods. The results indicate that treatments with PVA, acidic MTMS silica sol, PVA/acidic MTMS silica sol, alkaline MTMS silica sol, and PVA/acidic MTMS silica sol/alkaline MTMS silica sol all improved the dimensional stability of wood. Sample V exhibited the lowest VSC (best dimensional stability), with a value of 7.7% and an anti-swelling efficiency (ASE_{WU}) of 38.9% under water-immersion conditions. Under a high-humidity environment, it had a value of 5.0% with a corresponding anti-swelling efficiency (ASE_{MA}) of 39.0%. This superior performance was attributed to the PVA/acidic MTMS silica sol system penetrating the wood and forming a crosslinked network, which limited the dimensional changes of the wood. Additionally, the superhydrophobic layer formed on the surface by the alkaline MTMS silica sol further reduced the volumetric swelling caused by water uptake and moisture absorption, resulting in the most significant synergistic effect on dimensional stabilization.

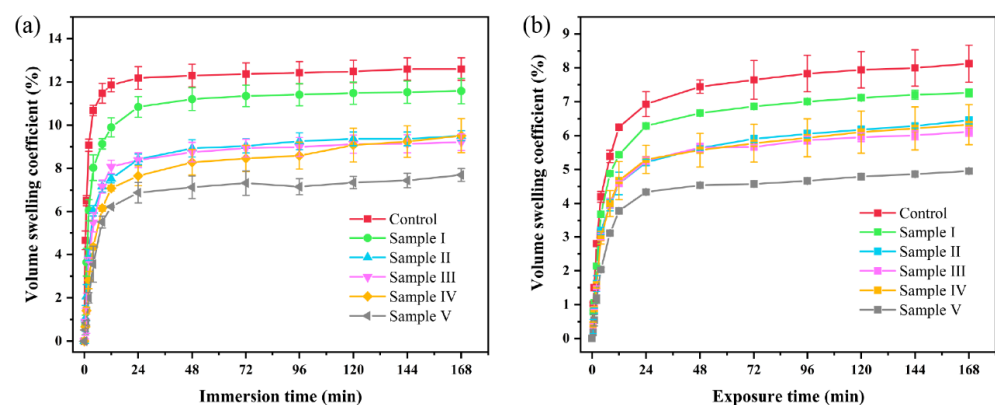


Figure 11. The changes in the volume-swelling coefficient of wood samples (a) under the water-immersion condition and (b) in a high-humidity environment.

3.9. Anti-Fouling and Self-Cleaning Performance Analysis

Considering the advantages of the superhydrophobic modified wood obtained by the two-step treatment, it was selected for further application experiments. Figure 12a displays photographs of various daily liquid droplets on the surface of sample V. It was observed that these droplets exhibited a round and spherical shape on the surface, indicating that the modified wood had strong resistance to pollutants. Meanwhile, Figure 12b demonstrates excellent water adhesion resistance. From the figure, it can be seen that water droplets in contact with the superhydrophobic wood surface easily detached from the surface without adhering to it. This excellent anti-adhesive property can be attributed to the presence of air pockets that formed at the hierarchical structured interface of the superhydrophobic surface, as well as the low surface-energy contributed by the $-\text{CH}_3$ functional groups, resulting in its repellency. Additionally, a self-cleaning test was conducted, as shown in Figure 12c,d. Figure 12c reveals that on the untreated wood surface, water droplets mixed with chalk dust, wetting the surface without effectively removing the pollutants. In contrast, due to the low adhesion of the superhydrophobic surface, spherical water droplets swiftly rolled off the surface under gravity, simultaneously absorbing pollutants (Figure 12d), thus facilitating the self-cleaning process.

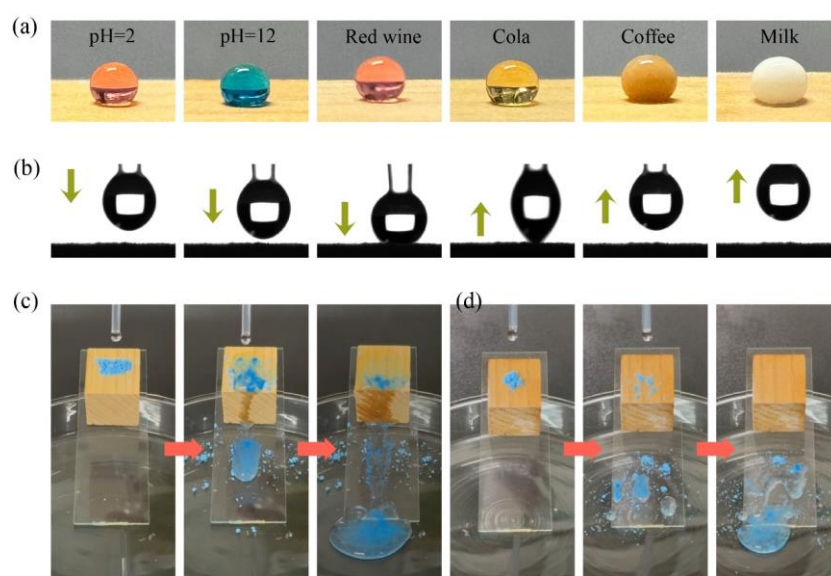


Figure 12. (a) Optical photos of common liquids on the superhydrophobic wood, including acidic water, alkaline water, red wine, cola, coffee, and milk. (b) The process of water droplets advancing, contacting, deforming, recovering, and detaching from the superhydrophobic wood surface. Self-cleaning test process: (c) control wood and (d) superhydrophobic wood.

3.10. Durability Analysis

Maintaining surface dirt resistance and self-cleaning functionality requires robust mechanical durability. Therefore, this study evaluated the mechanical durability of superhydrophobic wood surfaces through sandpaper abrasion and tape peeling tests. Figure 13a illustrates the abrasion test, while the corresponding data are shown in Figure 13c. From the results, it was evident that the superhydrophobic wood maintained a WCA greater than 150° and a SA less than 10° even after five abrasion cycles, indicating excellent durability. To further evaluate the mechanical stability of the prepared superhydrophobic wood surfaces, peel tests were conducted using transparent 3M Scotch 600 tape, as shown in Figure 13b. As depicted in Figure 13d, it was observed that even after 100 cycles, the wood maintained its excellent superhydrophobic performance. Therefore, it can be concluded that the superhydrophobic wood surface exhibits satisfactory mechanical durability, with its excellent durability attributed to the strong covalent grafting reaction between PVA/MTMS and the wood.

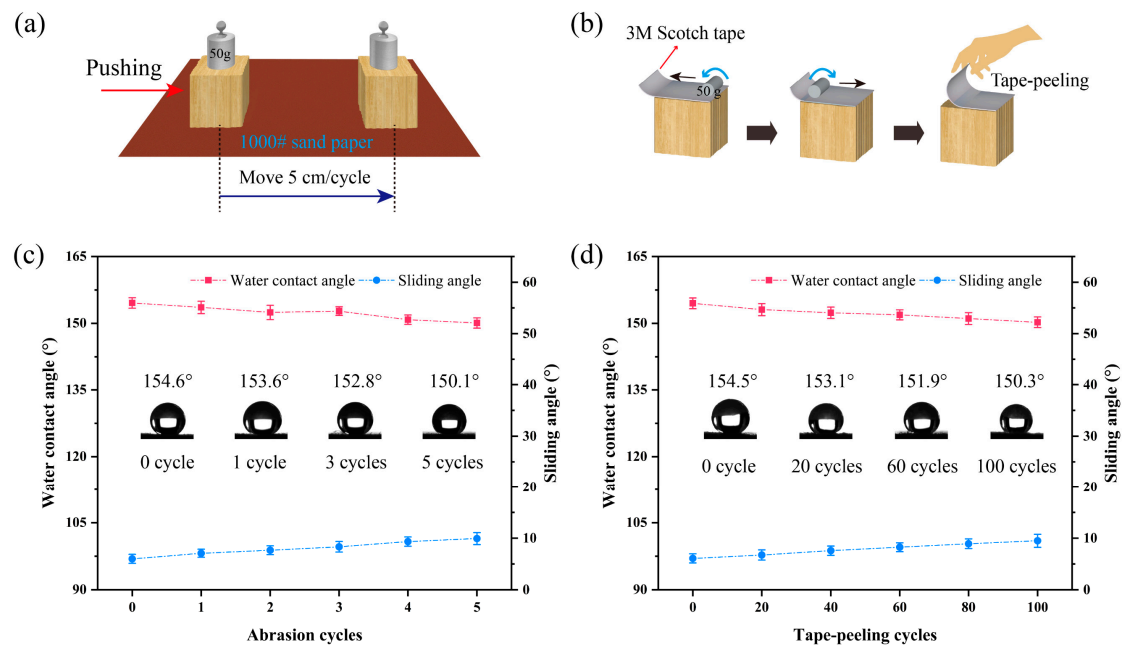


Figure 13. (a) Schematic of sandpaper abrasion test. (b) Diagram of the tape-peeling test. (c) Changes in WCA and SA on the surface of superhydrophobic wood during 5 wear cycles. (d) The WCA and SA vary with the cycle of tape-peeling iterations on superhydrophobic wood surface.

3.11. Thermostability Analysis

Good thermal stability contributes to the wood's resistance against complex temperature variations in the environment. Figure 14 illustrates the thermogravimetric analysis plots of wood before and after modification. Wood components degrade in three stages [44]. The first stage, from 100 °C to 250 °C, shows a low pyrolysis rate and mass loss, primarily due to the partial degradation of hemicellulose and lignin. The second stage, from 250 °C to 400 °C, involves the rapid degradation of cellulose along with the continuous degradation of lignin. In the third stage, which begins at 400 °C, the remaining wood components continue to aromatize and carbonize, gradually reaching stability. Based on the figure, it was evident that the modified wood exhibited a significantly slower mass loss across the entire temperature range, with a 45.5% residual mass at 800 °C, which is 2.6 times that of the control wood (17.2%). This can be attributed to the modification treatment, which resulted in a high content of SiO₂ in the wood residue [45]. Meanwhile, from the DTG curves, it was observed that the maximum weight loss rates and corresponding temperatures for the control and modified wood were 11.96%/min at 362.8 °C and 5.65%/min at 362.4 °C, respectively. Not only were the degradation temperatures nearly identical, but the maximum weight loss rate was also significantly reduced. This indicates that the PVA/MTMS polymer can act as a flame retardant, delaying the combustion of wood components and exhibiting fire-resistant effects. Based on the above thermal analysis results, it is evident that the modified wood demonstrates excellent thermal stability.

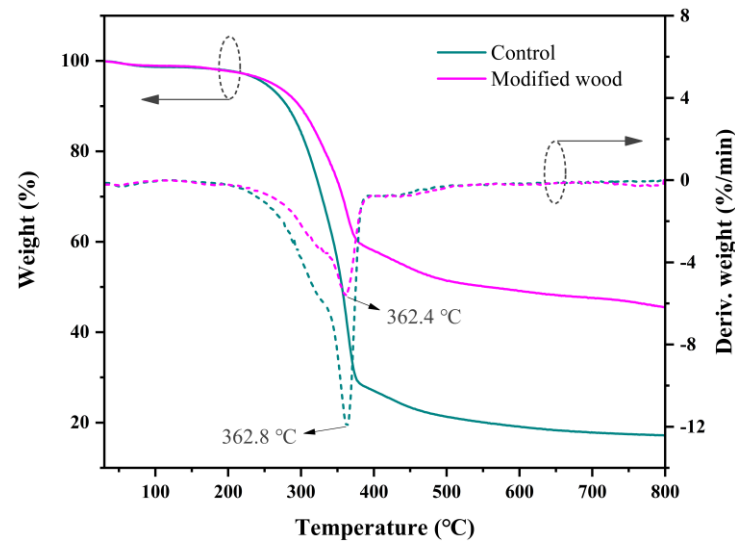


Figure 14. TG and DTG curves of wood samples.

3.12. Compressive Strength Analysis

It is essential to carry out modifications for wooden structures under the premise of ensuring the mechanical properties of wood. The experimental results are shown in Figure 15. The results show that the longitudinal compressive strength, radial compressive strength, and tangential compressive strength of the modified wood samples were 49.1 MPa, 5.8 MPa, and 2.7 MPa, respectively, and these were improved by 41.7%, 36.8%, and 30.2% compared to the control wood, indicating that the superhydrophobic modified wood possessed excellent mechanical properties. The results are straightforward and can be attributed to the modification agent penetrating the wood cell wall pores and cracks, reacting with the $-OH$ groups of the components, enhancing the connectivity of the network structures such as cellulose and hemicellulose in wood and thereby improving the mechanical properties of the wood.

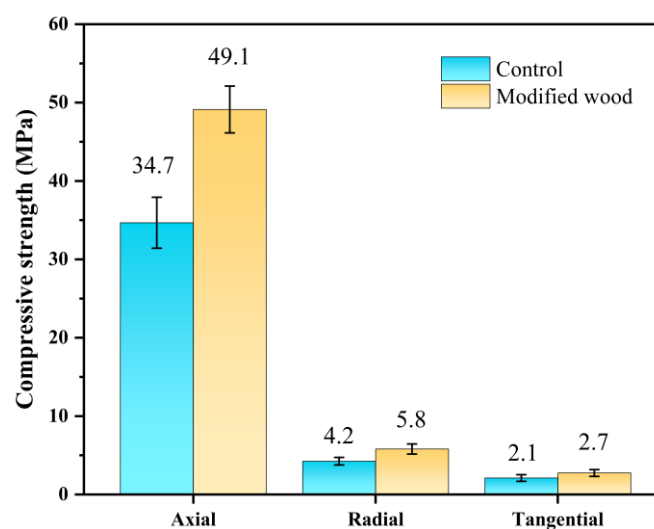


Figure 15. Mechanical properties.

3.13. Dynamic Mechanical Thermal Analysis

The viscoelastic behavior of wood was studied through DMA, focusing on two primary parameters: storage modulus (E') and loss factor ($\tan \delta$). E' serves as a crucial indicator of the material's capacity to store energy following elastic deformation [44]. Figure 16 illustrates the relationship between the E' of wood and temperature, revealing a declining trend in E' as temperature increases. This decrease is primarily due to the enhanced chain

mobility of cell wall polymers—namely cellulose, hemicelluloses, and lignin—in wood [46]. Notably, E' of the modified wood significantly surpasses that of the control, indicating an improvement in the stiffness of the modified wood. Additionally, Figure 16 depicts the variation of $\tan \delta$ with temperature. The glass transition temperature (T_g) for both control and modified wood is identified at the temperature corresponding to the peak of the $\tan \delta$ versus temperature plot. The T_g of the modified wood shifts from 99 °C in the control to 88 °C, likely due to the integration of polyvinyl alcohol (PVA), which itself has a lower glass transition temperature of 79 °C [47].

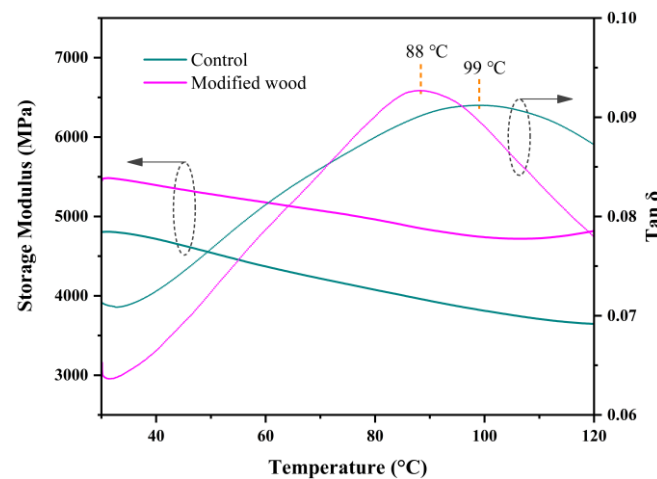


Figure 16. Temperature dependence of storage modulus (E') and loss factor ($\tan \delta$) for control and modified wood.

4. Conclusions

This study successfully demonstrates the functional modification of historical building wooden components using a two-step impregnation method with polyvinyl alcohol (PVA) and methyltrimethoxysilane (MTMS). Through comprehensive analyses including SEM-EDX, FTIR, XRD, and XPS, we have shown that the PVA/acidic MTMS silica sol forms a crosslinking system within the wood, effectively sealing cracks and pores while preserving specific hydroxyl groups. This consolidation treatment provides a structural and chemical basis for the subsequent construction of a superhydrophobic surface with the application of an alkaline MTMS silica sol. The modified wood achieved a superhydrophobic state, evidenced by a water contact angle of 156.0° and a sliding angle of 6.0°. Moreover, water uptake was reduced by 35.9%, and moisture absorption decreased by 28.3%, thereby substantially improving the wood's dimensional stability with anti-swelling efficiencies of 38.9% (ASE_{WI}) and 39.0% (ASE_{MA}). The superhydrophobic treatment endowed the wood with exceptional self-cleaning and anti-fouling properties, which remained largely unaffected even after rigorous mechanical challenges, including 5 cycles of sandpaper abrasion and 100 cycles of tape peeling. The thermal stability of the modified wood was significantly enhanced, with an increase in residual mass from 17.2% to 45.5% and a reduction in the maximum weight loss rate from 11.96%/min to 5.65%/min. The mechanical properties also saw remarkable improvements: the longitudinal compressive strength increased by 41.7%, radial compressive strength by 36.8%, and tangential compressive strength by 30.2% compared to the control wood. The storage modulus of the wood was also notably enhanced. Overall, the enhancement of these properties significantly contributes to the protection of wooden components in ancient buildings, meeting practical application requirements. Additionally, the use of this simple impregnation method provides a direct reference for the preservation of wooden decorative components in historical structures.

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administration, L.X.; Funding acquisition, L.X. All authors have read and agreed to the published version of the manuscript.

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