

Article

In Situ Fabrication of a Superhydrophobic ORMOSIL Coating on Wood by an Ammonia–HMDS Vapor Treatment

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Abstract: A superhydrophobic ORMOSIL (organically modified silicate) coating was in situ fabricated on a wood surface by ammonia–hexamethylisilazane (HMDS) vapor treatment. The wood was immerged in tetraethoxysilane (TEOS), and then the TEOS absorbed on the wood surface was hydrolyzed and condensed to hydrophobic SiO₂ nanoparticles with ammonia and HDMS vapor treatment. The effect of the treatment temperature and time on the hydrophobicity of wood was investigated. At a treatment temperature of 50 °C, a superhydrophobic surface was achieved on the wood with a treatment time longer than 2 h. SEM images indicated that there were SiO₂ nanoparticles fabricated on the wood surface, and FTIR revealed that the hydrophobic –Si(CH₃)₃ groups were incorporated on the wood surface. The ORMOSIL-modified wood possessed improved liquid repellency. The water absorption decreased significantly from 72.3% to 31.9% after modification.

Keywords: superhydrophobic; wood; hexanethylisilazane; self-cleaning; vapor treatment

1. Introduction

Wood is a natural bio-material and is widely used as an engineering construction material [1]. However, the hydrophilic property of natural wood makes it absorb water from the environment very easily [2], which leads to deformation, discoloration, decay and the poor repellence of waterborne pollutants [3–6]. Heat treatment [7] and chemical modification methods are applied to overcome these disadvantages. Chemical modification methods include acetylation [8,9], furfurylation [10] and chemical modification with glutaraldehyde [11] and organosilicons [12,13]. These methods can significantly improve the hydrophobicity of wood, and therefore inhibit wood from absorbing water from the environment.

However, the properties of wood modified by these traditional methods still need to be improved. Natural and artificial superhydrophobic surfaces have gained wide attention [14,15]. The combination of a rough surface and low surface energy generates a surface with excellent repellence to water, which causes water to bounce and roll off the surface easily. This phenomenon is known as the lotus effect. The superhydrophobicity gives the surface self-cleaning, anti-sticking and anti-contamination properties. Recently, superhydrophobic wood has been also widely investigated. According to published papers, the most used method for the fabrication of superhydrophobic coatings on wood surfaces includes two steps: increasing the roughness of wood surface by the deposition of nanoparticles, and then improving the hydrophobicity of nanoparticles by chemical modification [16–20]. Among various kinds of nanoparticles, SiO₂ is mostly applied because of the convenient control of its particle size and its easy modification by various organosilanes [21–24]. The hydrophobic modified SiO₂ coatings afford wood excellent water-repellent and self-cleaning properties, and hence dimensional-stability and liquid



repellency. However, the stack of SiO_2 nanoparticles on wood surfaces are random, and the bonding between the SiO_2 coating and wood is quite weak [25].

In this work, an ammonia–HMDS vapor treatment was proposed to in situ fabricate ORMOSIL coatings on wood surfaces. Unlike the reported works, in this method SiO₂ nanoparticles were in situ fabricated on the wood surface by the hydrolysis and condensation of tetraethoxysilane (TEOS) in ammonia vapor. With this process, the binding forces between the SiO₂ nanoparticles and the wood surface and between SiO₂ nanoparticles would be increased, and therefore the mechanical stability of the ORMOSIL coatings would probably be improved. In addition, the SiO₂ nanoparticles on the wood surface would give a rough surface for the further fabrication of a superhydrophobic surface. After the in situ fabrication of SiO₂ nanoparticles on the wood surface, a further surface modification of SiO₂ nanoparticles would be replaced by hydrophobic –Si(CH₃)₃ groups with a low surface energy. Therefore, the ammonia–HMDS vapor treatment of the wood surface would probably fabricate a superhydrophobic surface on the wood surface. The treatment temperature and time of the wood in the ammonia and HMDS vapor were the key factors for the fabrication of ORMOSIL coatings on the wood surface, and therefore the effect of them on the hydrophobicity of wood was investigated.

Finally, a superhydrophobic ORMOSIL coating on the wood surface was realized. The superhydrophobic ORMOSIL coating significantly improved the liquid repellency and therefore the anti-contamination property of wood.

2. Materials and Methods

2.1. Materials

Chinese *Cunninghamia lanceolata* slices ($20 \times 20 \times 15$ mm) were purchased from Fujian, China. High-purity TEOS was purchased from Kermel (Tianjin, China). Analytical grade ammonia–water with an NH₃ content of 25%–28% and hexamethylisilazane (HMDS) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

2.2. Preparation of ORMOSIL Coating on Wood

In a vacuum oven, wood slices were immerged into TEOS for 30 min at room temperature to adsorb TEOS. Then, as shown in Figure 1, the wood slices were placed successively in a desiccator (with a diameter of 120 mm) containing 10 mL ammonia–water and then a desiccator containing 10 mL HMDS at 25, 50 and 75 °C for 0.5, 1, 2, 3, 6 and 12 h. Finally, the wood slices were heat-treated at 100 °C for 1 h to remove ammonia, water and HMDS from the wood slices. For each experiment, three slices were modified.



Figure 1. Schematic representation of the fabrication process of superhydrophobic wood by the ammonia–hexamethylisilazane (HMDS) two-step catalytic process. TEOS: tetraethoxysilane.

2.3. Characterization

The FTIR spectra were recorded using the KBr pellet method, ranging from 4000 to 400 cm⁻¹ at a 4 cm^{-1} resolution for 32 scans. In detail, 1 mg of wood powder was scraped from the radial section of wood and mixed with 100 mg of KBr, and then pressed into a slice and placed in the FTIR spectrometer. The surface morphology of the wood samples at radial section were examined using a scanning electron microscope (SEM, ZEISS Z500) (Jena, Germany) in high vacuum mode at an acceleration voltage of 5 kV. A thin aurum (Au) layer was sputtered onto the sample surfaces to improve conductivity prior to observation. The water contact angle (WCA) of the wood slices at the radial section was measured on a commercial contact angle meter (HARKE-SPCA-1, Beijing, China) at room temperature. The WCA was tested at five different points. A small droplet of distilled water (5 μ L) was used for the measurement. In order to evaluate the water-repellent property of wood, the water absorption of the wood samples at 1, 2, 3, 5, 8 and 24 h was examined according to the following equation:

Water Absorption =
$$\frac{m_1 - m_0}{m_0} \times 100\%$$

where m_0 and m_1 are the weight of the wood slices before and after being immerged in water for 1, 2, 3, 5, 8 and 24 h, respectively.

3. Results and Discussion

3.1. Schematical Diagram

The aim of this work was to fabricate superhydrophobic ORMOSIL coatings on wood surfaces. To fabricate a superhydrophobic surface, there were two requirements: a hierarchical rough structure and low surface energy. In this work, an ammonia–HMDS vapor treatment was used, as shown in Figure 1. First, wood was immerged in TEOS to absorb TEOS on the surface of the wood. Second, the wood with TEOS was placed in a desiccator containing ammonia–water. In this process, as shown in Figure 1b, TEOS on the wood surface was converted to SiO₂ particles after hydrolysis and a condensation reaction. The SiO₂ particles on the wood surface provided a rough surface. Third, the ammonia-treated wood was placed in a desiccator containing HMDS. As shown in Figure 1c, the hydrophilic \equiv Si–OH groups on the SiO₂ particles were converted to hydrophobic \equiv Si–O–Si(CH₃)₃ groups, which significantly decreased the surface energy of the wood surface. Therefore, it could be deduced that superhydrophobic wood would be realized with the ammonia–HMDS two-step catalytic process with suitable conditions.

3.2. Chemical Property of Wood Surface

The samples for FTIR characterization were scraped from the wood surface, and the FTIR results indicated the change in the chemical property of the wood surface before and after modification. Figure 2 shows the FTIR spectra of the original and modified wood. For the original wood, there were obvious absorption bands at 3376 cm⁻¹ (stretching vibration of the –OH groups), 2901, 1732, 1604, 1509, 1463, 1426 and 1023 cm⁻¹. The broad band at 3376 cm⁻¹ was attributed to the –OH stretching of cellulose. C–H stretching in the –CH₂– groups was found at 2901 cm⁻¹. The absorption bands at 1742 cm⁻¹ were attributed to the C=O stretching vibration. The absorption bands at 1604, 1509, 1463, and 1426 cm⁻¹ indicated the existence of aromatic rings and C–H bonds [26]. The peak at 1023 cm⁻¹ was associated with both the C–O stretch in cellulose and the C–O deformation in the primary alcohols of lignin [27]. For the modified wood, there were three additional absorption bands at 2850, 1086 and 460 cm⁻¹. The absorption band at 2850 cm⁻¹ was assigned to –Si–CH₃, and those at 1086 and 460 cm⁻¹ were associated with the symmetric stretching vibration and rocking mode of Si–O–Si. These indicated that the TEOS on the wood surface was hydrolyzed and condensed to SiO₂ with ammonia treatment. Also, the hydrophobic –Si(CH₃)₃ groups were grafted onto SiO₂ with a further HMDS treatment.



Figure 2. FTIR spectra of original and modified wood.

3.3. Morphology of Wood Surface

FTIR spectra revealed the the change in the chemical property of the wood after the ammonia–HDMS two-step catalytic process. Specifically, the FTIR spectra indicated that the hydrophobic –Si(CH₃)₃ groups were incorporated onto the wood surface, which significantly lowered the surface energy of the wood. The other requirement for the fabrication of a superhydrophobic surface was a rough surface; therefore, the surface morphology of the wood before and after modification was characterized by SEM. Figure 3 shows the SEM images of unmodified wood and wood treated at room temperature for 12 h. As shown in Figure 3a, the vessels of unmodified wood were smooth. For the modified wood, the surface was covered by a layer of the coating. As shown in Figure 1, it can be deduced that the coating was composed of SiO₂ particles. As shown in Figure 3b, SiO₂ nanoparticles were found. The random stack of modified SiO₂ nanoparticles on the wood surface gave a rough surface. Therefore, SEM images combined with FTIR spectra demonstrated that the ammonia–HMDS two-step catalytic process fabricated a rough surface with a low surface energy on wood.



Figure 3. SEM images of the original (a) and modified (b) wood.

3.4. Effect of Treatment Temperature and Time on Hydrophobicity

The key factor was the hydrolysis and condensation of TEOS to SiO₂ nanoparticles. The chemical mechanism is represented in Formulas (1) and (2). In this work, the effect of treatment temperature and time on the hydrophobicity of the wood were investigated, as shown in Figure 4. At room temperature, the hydrophobicity of wood increased significantly with increasing the treatment time. By increasing the treatment time from 0.5 to 12 h, the water contact angle increased obviously from 98.4° to 157.6°. At room temperature, the wood was superhydrophobic when the treatment time was higher than 6 h. Increasing the treatment temperature benefitted the hydrolysis and condensation of TEOS to hydrophobic SiO₂. By increasing the treatment temperature from 25 to 50 °C, the treatment time for achieving superhydrophobicity was obviously decreased from 6 to 2 h. However, a further increment in the treatment temperature higher than 50 °C was of almost no benefit to the hydrophobicity.



Figure 4. Effect of treatment temperature and time on the water contact angle (WCA) of wood.

A superhydrophobic surface is one having a high WCA (>150°) and low sliding angle (SA < 10°). Figure 4 also reveals the SA value of the modified wood. The change in SA as a function of treatment time and temperature is similar to that of WCA. Increasing the treatment time and temperature is beneficial in fabricating a superhydrophobic surface with an SA lower than 10° .

$$Si(OCH_2CH_3)_4 + 4OH^{-} \xrightarrow{hydrolysis} Si(OH)_4 + 4CH_3CH_2OH$$
(1)

$$nSi(OH)_4 \xrightarrow{condensation} nSiO_2 + 4nH_2O$$
 (2)

3.5. Liquid Repellency

Wood is hydrophilic, and therefore it is easily polluted by waterborne pollutants. Figure 5 shows the liquid repellency of the original and modified wood to common household pollutants such as soy sauce, wine, coffee and milk. Chinese *Cunninghamia lanceolata* was porous and of low density. As shown in Figure 5, at the cross-section, the soy, wine, coffee and milk droplets were quickly absorbed as they were dropped on the original wood surface. At radial and tangential sections of original wood, although the soy sauce, wine, coffee, and milk droplets were not totally absorbed by the original wood, the contact angles of them on these two sections were lower than 90°. After absorbing the droplets from the surface with a tissue, stains were found on the original wood surface. Therefore, the liquid repellency of the original wood was demonstrated to be quite poor. The soy sauce, wine, coffee, and milk droplets were carefully dropped on the surface of the modified wood to capture the images shown in Figure 5; otherwise, the droplets would easily roll away from the modified wood surface. As shown in Figure 5, for the modified wood, the soy sauce, wine, coffee and milk droplets displayed good spherical shapes, which indicates that the modified wood had excellent repellence to these waterborne pollutants. After absorbing the droplets from modified wood with a tissue, there was no stain.



Figure 5. Liquid repellency of original and modified woods to soy sauce, wine, coffee and milk.

The change in the water absorption as a function of the immerging time of the original and modified wood in water is shown in Figure 6. As shown in Figure 6, the water absorption of the original wood significantly increased after being immerged in water. After being immerged in water for 24 h, the water absorption of the original wood was about 72.3%. This is because the original wood was porous and hydrophilic, and therefore it easily absorbed polar water. Compared with the original wood, the water absorption of the modified wood was much lower, at 31.9%.



Figure 6. Change in the water absorption of the original and modified wood as a function of the immersion time in water.

4. Conclusions

Ammonia–HMDS vapor treatment was applied to fabricate a superhydrophobic ORMOSIL coating on a wood surface. Treatment temperature and time had obvious effects on the hydrophobicity of modified wood. Superhydrophobic wood could be obtained when the treatment temperature was 50 °C and the treatment time was higher than 2 h. SEM images revealed that SiO₂ nanoparticles were formed on the wood surface by the ammonia–HMDS vapor treatment. The results of FTIR indicated that hydrophobic –Si(CH₃)₃ groups were incorporated onto the wood surface. The superhydrophobic

ORMOSIL coating afforded wood an excellent liquid repellency to waterborne pollutants and a good water-repellent property. The water absorption of the wood decreased significantly from 72.3% to 31.9% after modification.

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