coatings

MDPI

Article

# Fabrication of Hydrophobic ZnO/PMHS Coatings on Bamboo Surfaces: The Synergistic Effect of ZnO and PMHS on Anti-Mildew Properties

**Jingbing Chen, Yunyun Ma, Huiping Lin, Qingzhu Zheng, Xinxiang Zhang, Wenbin Yang * and Ran Li ***

College of Material Engineering, Fujian Agriculture and Forestry University, Fuzhou 350108, China; cjb8190925@163.com (J.C.); my448662507@163.com (Y.M.); 18450077642@163.com (H.L.); zjcf0911@163.com (Q.Z.); xxzhang0106@163.com (X.Z.)

* Correspondence: fafuywb@163.com (W.Y.); szylr@163.com (R.L.); Tel.: +86-591-8371-5175 (W.Y. & R.L.)

Received: 15 November 2018; Accepted: 27 December 2018; Published: 28 December 2018


**Abstract:** Poor mildew resistance has limited the application of bamboo materials. In this work, ZnO/PMHS coatings were fabricated on bamboo timber surfaces by hydrothermal synthesis method and hydrophobic modification with poly(methylhydrogen)siloxane (PMHS). The surface chemical characteristics and microstructure of the bamboo before and after modification were investigated using Fourier transform infrared spectroscopy, scanning electron microscopy, energy dispersive X-ray spectroscopy, X-ray diffraction, and water contact angle (WCA). The morphology results indicated that ZnO on the surface of bamboo forms flower-like aggregations. The WCA of ZnO/bamboo increased from 65° to 142° after PMHS hydrophobic modification, indicating that the hydrophobicity of bamboo was significantly improved. The original bamboo had poor anti-mildew properties when exposed to *Trichoderma viride*, *Aspergillus niger*, and *Penicillium citrinum*. After depositing ZnO onto the surface of the bamboo, the anti-mildew properties were significantly improved. Furthermore, it was found that after PMHS hydrophobic modification, ZnO/bamboo had excellent anti-mildew properties when exposed to the three mold hyphae, which indicated that PMHS hydrophobic modification had a synergistic effect on the anti-mildew properties of bamboo with a ZnO coating.

**Keywords:** bamboo; anti-mildew; ZnO; poly(methylhydrogen)siloxane; synergistic effect

## 1. Introduction

Bamboo, the second most abundant natural resource, has a long history of utilization. It has many advantages, such as a short growth cycle, high strength, high toughness, recyclability, and simple processing. Moreover, products made from bamboo are environmentally friendly and biodegradable [1]. Bamboo is widely used for furniture [2], building materials [3], scaffolding [4] and handicraft [5]. Unfortunately, when used in outdoor environments, bamboo is easily infected by mildew due to its high sugar, starch and protein contents [6], which strongly reduces the durability of bamboo products. To overcome this drawback, physical and chemical modifications have been carried out [7,8]. The physical methods include microwave and high-temperature treatment [9,10]. However, these traditional physical methods are not completely effective. Chemical mold-resisting agents are also commonly used for bamboo preservation. The chemical compounds used include pentachlorophenol, alkaline copper quaternary compounds (ACQ), chromated copper arsenate (CCA), and so on [11–13]. However, pentachlorophenol is harmful to human health. As a result, it has been banned as a wood (and bamboo) preservative in some countries [14,15]. Also, the potential toxicity of chromium, arsenic, and halogens to ecosystems should be taken into account [16]. Therefore, it is desirable to investigate

novel efficient and non-toxic anti-mildew agents for bamboo materials. Recently, nano-metals and their oxides, such as $TiO_2$, CuO, ZnO, and Ag have been widely prepared by various methods and applied to improve anti-mildew properties [17–21]. These nano-metals and their oxides have been reported to be more active than the non-nano ones, which has been attributed to their higher surface area and ability to display unique physical and chemical properties. For instance, Devi et al. [22] demonstrated that a wood/polymer composite treated with $TiO_2$ had improved mechanical stability, UV stability, and antimicrobial properties. $TiO_2$ deposited onto the surface of bamboo at low temperatures by the sol-gel method has improved the anti-mildew properties of bamboo [19]. Xie et al. [23] also reported that nano copper particles imparted wood excellent mildew resistance to wood. It was shown that nano ZnO can be fabricated successfully on bamboo surfaces by the hydrothermal synthesis method, resulting in improved resistance of bamboo timber against mold [24]. Among the aforementioned nano materials, nano zinc oxide (ZnO) has received more and more attention due to its high chemical stability, non-toxicity, low cost, and good anti-mildew properties [25].

Another problem limiting the application of bamboo is its easy absorption of water from environment [26]. In recent years, research on hydrophobic surfaces has advanced considerably. For instance, bamboo or wood has been modified by stearic acid [27], 1H, 1H, 2H, 2H–perfluoroalkyltriethoxysilane (POTS) [28], and fluoroalkylsilane (FAS) [29], improving its hydrophobicity. However, most of the modifiers used were fluorine-containing, and therefore very expensive. The modification processes for the other compounds are complicated and time-consuming, which have limited their practical applications for the hydrophobic surface improvement of bamboo. It has been reported that hydrophobic surfaces can inhibit the adherence of bacteria, decreasing the incidence of infection [30,31]. It has been reported that hydrophobic wood can have improved water resistance and mildew inhibition, but the anti-mildew effect was not significant [32]. Although a hydrophobic surface can reduce the adherence of bacteria and water, it does not have the function of sterilization, leading to poor anti-mildew properties for hydrophobic modified bamboo [31,32]. It is interesting to investigate the synergistic effect of hydrophobic surface with antimicrobial agents, because it will afford bamboo good resistance to both water absorption and microbial degradation.

Our previous studies revealed that poly(methylhydrogen)siloxane (PMHS) is an excellent hydrophobic agent for wood [33]. This is due to the special chemical structure of PMHS. PMHS possesses hydrophobic methyl groups and abundant –Si–H groups. The former will significantly lower the surface energy of the modified surface, while the latter can react with –OH groups on the substrate surface through dehydrogenation reactions [34,35]. In this work, ZnO/PMHS coatings were fabricated on the surface of bamboo to improve its anti-mildew properties, and the synergistic effect of ZnO and PMHS was also investigated. The results indicated that the ZnO/PMHS coated bamboo possessed excellent anti-mildew properties against three mold fungi, *Trichoderma viride*, *Aspergillus niger*, and *Penicillium citrinum*.

## 2. Experimental Section

### *2.1. Materials*

Bamboo was produced by China Resources Bamboo Co., Ltd., Zhejiang, China. The bamboo specimens were processed into blocks with the dimensions of (50 ± 1) mm (length) × (20 ± 0.5) mm (width) × (5 ± 0.5) mm (thickness), then washed several times with deionized water and ethanol to remove surface contamination and dried at 80 °C for 24 h.

Anhydrous sodium hydroxide (NaOH) and zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$) were provided by Sinopharm Chemical Reagent Co. Ltd., Shanghai, China. Zinc acetate, n-hexane, and methanol were purchased from Tianjin Zhiyuan Chemical Reagent Co. Ltd., Tianjin, China. Sodium dodecyl sulfate (SDS) and hexamethylenetetramine (HMTA) were supplied by Aladdin, Shanghai, China. PMHS with a reactive hydrogen content of 1.5% and Kastredt catalyst (platinum-1,3-divinyl-1,1,3,3-tetramethyldisiloxane) with a Pt content of 2000 ppm were obtained

from Chenguang Research Institute of Chemical Industry (Chengdu, China). All agents were used as received, without further purification.

*Aspergillus niger*, *Penicillium citrinum*, and *Trichoderma viride* were provided by Academy of Sciences Quality Inspection Biotechnology Co. Ltd. (Beijing, China).

### 2.2. Preparation of ZnO-Coated Bamboo Timber

In a typical synthesis process [29,36], a methanol solution of sodium hydroxide (NaOH, 0.12 M) was added slowly to a methanol solution of $Zn(CH_3COO)_2{\cdot}2H_2O$ ($Zn(Ac)_2$, 0.04 M) with a volume ratio of 1:1. Subsequently, the resulting mixed solution was stirred for 30 min at 60 °C using a magnetic stirrer (DF-101S, Yuhua Instrument Co. Ltd., Gongyi, China), until a homogeneous and stable colloid solution formed. Bamboo specimens were coated by the ZnO colloid solution through a repeated dip-coating process. In detail, the bamboo slices were immersed in the ZnO colloid solution for 10 min. Next, the bamboo slices were dried at 150 °C for 10 min inside a drying oven. The dip-coating and drying procedures were repeated three times to obtain multilayer films. The reaction solution for hydrothermal treatment was then prepared by the following procedure: equimolar aqueous solutions (0.2 M) of zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$) and hexamethylenetetramine ($C_6H_{12}N_4$, HMTA) were prepared in a vessel under constant stirring, while a 0.16 M sodium dodecyl sulfonate ($NaC_{12}H_{25}SO_3$, SDS) solution was added. After stirring for 30 min to form a clear solution, the mixed solution was transferred into a Teflon-lined autoclave with the bamboo samples. The hydrothermal treatments were performed at 95 °C for 3 h. The samples were then washed several times with distilled water (DI water) and dried at 80 °C for 48 h in a vacuum oven. The ZnO/bamboo samples are denoted as zinc oxide modified samples.

### 2.3. Surface Modification of ZnO/Bamboo

The modifier solution was obtained by mixing 2.5 g PMHS, 47.5 g n-hexane and 2 drops of Kastredt catalyst. ZnO/bamboo samples were dipped into the modifier solution for 3 min. The modified bamboo samples were finally washed three times with n-hexane to remove the PMHS chains that were not covalently bonded onto the bamboo surface. Thereafter, the specimens were heated at 60 °C for 20 min. After PMHS modification, the samples were named PMHS-ZnO/bamboo.

### 2.4. Characterization

Scanning electron microscopy images of the bamboo samples were observed by Supra55 (scanning electron microscopr, SEM, Zeiss, Oberkochen, Germany) at an accelerating voltage of 20 kV, attached to an X-ray energy dispersive spectrometer (EDS, Genisis XM, Oxford, UK). EDS microanalysis was conducted to obtain information on the elemental compositions of the samples. Before scanning process, a thin layer of gold was sputtered onto sample surfaces to enhance their electron conductivity. The changes in the crystalline structures of bamboo surface before and after modification were characterized using X-ray diffraction (XRD, D/max-UItima III, Rigaku, Tokyo, Japan). The scattered radiation was detected in the range of 5°–80° at a scanning rate of 2° $s^{-1}$. The chemical composition of the modified and unmodified bamboo surfaces were determined by Fourier-transform infrared spectroscopy (FTIR, Bruker Tensor 27, Bruker Optik GmbH, Ettlingen, Germany). For each sample, the absorbance spectrum was measured from 4000 to 400 $cm^{-1}$ at a 4 $cm^{-1}$ resolution for 32 scans. The water contact angle of bamboo was measured using a goniometer (Krüss DSA100, Krüss GmbH, Hamburg, Germany) at room temperature, with average values taken from of five measurements.

### 2.5. Test of Anti-Mildew Properties

The test of anti-mildew properties for bamboo was carried out according to the standard of GB/T18261-2013 [37] (test method for anti-mildew agents in controlling wood mold and stain fungi). Six dimensioned bamboo samples were tested with each fungus. The bamboo samples were exposed to fungi growing on potato media, which allowed mildew growth under a controlled temperature of

28 °C and relative humidity of 95%–98%. Samples were evaluated daily for mildew growth. Mildew growth on bamboo surfaces was visually rated using grading standards of infection, shown in Table 1. The final grade was determined by taking the average infected area of six bamboo samples exposed to the same fungus. The lower the infection value, the better the efficiency of treatment.

**Table 1.** The grading standards for the infection vof bamboo samples by mold fungi.

| Grading | Description |
|---|---|
| 0 | No hypha or mold |
| 1 | The surface infection area of the sample is less than 1/4 |
| 2 | The surface infection area of the sample is between 1/4 and 1/2 |
| 3 | The surface infection area of the sample is between 1/2 and 3/4 |
| 4 | The surface infection area of the sample is greater than 3/4 |

## 3. Results and Discussion

### *3.1. Morphology of ZnO Coatings on Bamboo Surface*

Scanning electron microscopy (SEM) was used to observe the morphology of bamboo surfaces. The surface morphologies of bamboo samples before and after treatment are shown in Figure 1. There are numerous pits on the surface of the original bamboo samples, as revealed in Figure 1a. As shown in Figure 1b, the surface is covered with various layers of ZnO, in which the ZnO sheets formed flower-like aggregations constructed in a hierarchical manner [29]. In Figure 1c, the surface of the ZnO is less rough after treatment with PMHS. This may be due to the long chain molecule of the PMHS, which filled the gaps between ZnO sheets. In addition, the poor electrical conductivity of PMHS on ZnO surface probably contributed to the indistinct morphology of the PMHS-ZnO/bamboo samples. However, the surface of PMHS-ZnO/bamboo was still very rough compared to that of original bamboo.

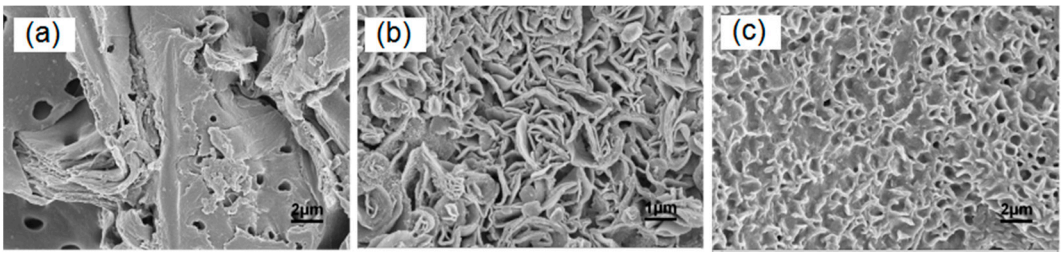


**Figure 1.** Scanning electron microscope images of untreated and treated bamboo surfaces: (**a**) original (untreated) bamboo; (**b**) ZnO/bamboo; (**c**) PMHS-ZnO/bamboo.

### *3.2. Chemical Structure of the Bamboo Surface*

The main chemical elements of the bamboo surface before and after modification were analyzed by EDS. EDS spectra of the original bamboo, ZnO/bamboo, and PMHS-ZnO/bamboo are presented in Figure 2A. As shown in Figure 2A(a), for the original bamboo, only the C and O elements could be observed, accounting for 58.37% and 41.63%, respectively. The ZnO/bamboo revealed the presence of Zn element in addition to the C and O elements, which confirmed the loading of the bamboo surface with ZnO (Figure 2A(b)). In addition, a small amount of sulfur was also found, which could be attributed to the addition of a surfactant (SDS). Finally, after the PMHS treatment, silicon was also observed in Figure 2A(c). This indicates the existence of PMHS on the surface of the coated bamboo.

The FTIR spectra for the original bamboo, ZnO/bamboo, and PMHS-ZnO/bamboo are shown in Figure 2B. The original bamboo (Figure 2B(a)), had an absorption peak at 1036 $cm^{-1}$, belonging to skeletal vibration of the C–O–C from the pyranose ring [38]. The absorption bands at 1742 $cm^{-1}$ and 1423 $cm^{-1}$ could be attributed to the C=O stretching vibration and C–H asymmetric stretching

vibration, respectively [36]. Compared with the original bamboo, the FTIR spectrum of ZnO/bamboo showed a distinct absorption peak at 460 $cm^{-1}$, as shown in Figure 2B(b), which could be assigned to the stretching vibration of the Zn–O groups [29]. In the FTIR spectrum of PMHS-ZnO/bamboo (Figure 2B(c)), there were three strong absorption peaks at 2851, 2921, and 2964 $cm^{-1}$, which could be attributed to the $–CH_2$ and $–CH_3$ stretching vibration respectively [34]. In addition, Si–O–Si and Si–C absorption bands were found for PMHS at 799 and 1255 $cm^{-1}$, respectively [39]. These results confirmed that the PMHS chains had been successfully grafted onto ZnO/bamboo surface.

To further ascertain the crystal structure and chemical composition of the bamboo surface before and after ZnO and PMHS modification, XRD was employed. The typical reflection planes of the crystalline domain of cellulose were found at 2θ angles of 22°, 16°, and 34°, respectively (Figure 2C(a)) [40]. For ZnO/bamboo, shown in Figure 2C(b), in addition to the characteristic peaks of cellulose, there were also characteristic ZnO diffraction peaks at 2θ = 31.8°, 34.4°, 36.2°, 34.4°, 56.6°, 62.8°, 66.4°, and 67.9°, attributed to (100), (002), (101), (102), (110), (103), (201), and (004) respectively, for the diffraction of ZnO crystals with a hexagonal structure. These characteristic peaks are in good agreement with the standard card (JCPDS card NO. 36-1451). These findings confirm the formation of ZnO on the bamboo surface. Furthermore, the structure was not changed, because there was only a thin PMHS layer on the surface of ZnO after PMHS modification (Figure 2C(c)).

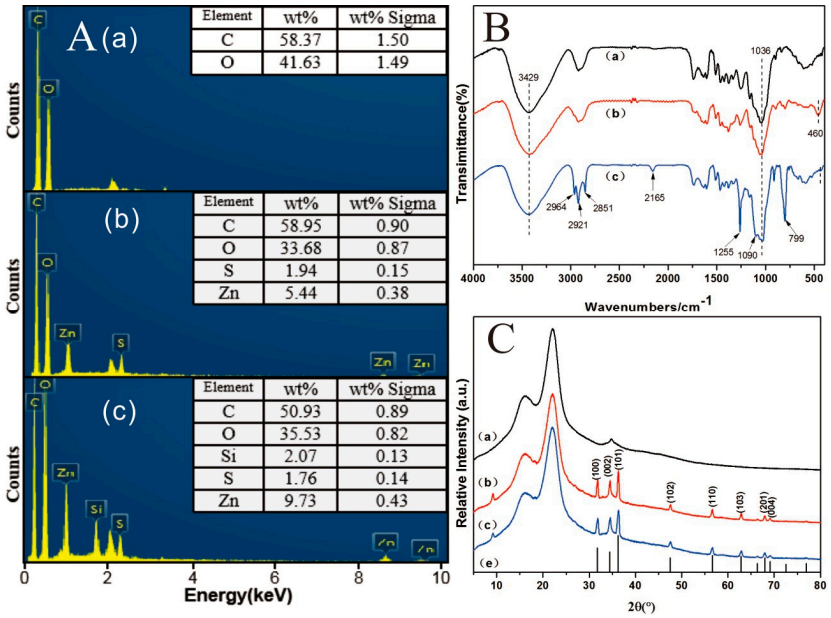


**Figure 2.** (**A**) The EDS spectra and element, (**B**) FTIR spectra, and (**C**) XRD patterns of (**a**) original bamboo, (**b**) ZnO/bamboo, and (**c**) PMHS-ZnO/bamboo.

### *3.3. Hydrophobicity of Modified Bamboo Surfaces*

Water contact angle (WCA) was used to characterize the hydrophobicity of treated bamboo surfaces. Figure 3 presents the WCA of original untreated bamboo, ZnO/bamboo, and PMHS-ZnO/bamboo samples. Figure 3a presents an image of water droplets on a radial section of original bamboo. The WCA of original bamboo was only 12°, which indicates that unmodified bamboo is very hydrophilic and therefore the water drop could spread over a large surface area. This is because unmodified bamboo contains large amounts of hydroxyl groups. Therefore, unmodified bamboo can easily absorb water from the environment, which aids the growth of mold on the bamboo surface. As shown in Figure 3b, after the deposition of ZnO, WCA of ZnO/bamboo was 65°, indicating an improvement in hydrophobicity. Most importantly, after modification with PMHS, the WCA of PMHS-ZnO/bamboo was dramatically increased to 142°, indicating that ZnO-PMHS/bamboo surfaces became very hydrophobic. It is well-known that good surface hydrophobicity can not only inhibit the

adhesion of bacteria, but also keep bamboo from absorbing water from the environment. Both of these effects are beneficial to the anti-mildew properties of bamboo.

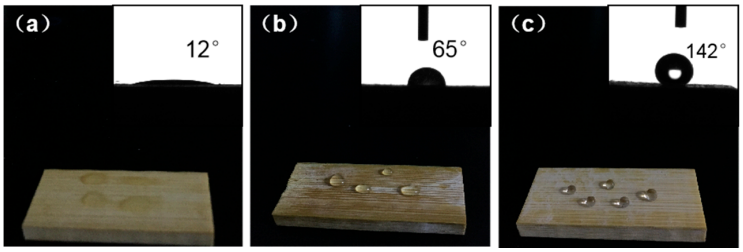


**Figure 3.** Water contact angle of (**a**) original bamboo, (**b**) ZnO/bamboo, and (**c**) PMHS-ZnO/bamboo.

### *3.4. Schematic Representation of Surface Modification*

Based on the above experimental results, a schematic diagram of the proposed mechanism of deposition of ZnO and PMHS modification of the bamboo surface is shown in Figure 4. The surface of bamboo has many hydroxyl groups. ZnO seeds were loaded on the surface of the bamboo by soaking the bamboo in the ZnO colloid solution (Figure 4a). The ZnO seeds were bonded onto the surface of the bamboo by hydrogen bonds. Thereafter, the bamboo was soaked three times to create a dense ZnO seed layer on the bamboo surface. Then, as is shown in Figure 4b, the hierarchically structured ZnO coating was fabricated on the surface of the bamboo by the hydrothermal method. As shown in Figure 4d, the PMHS chain contains hydrophobic $–CH_3$ groups and a large quantity of reactive –Si–H bonds. The reactive –Si–H bonds can participate in a variety of chemical reactions, especially with vinyl- and hydroxyl-containing materials. The $–CH_3$ groups provide the PMHS with very low surface energy. As shown in Figure 4e, the surface of ZnO prepared by the hydrothermal method contains a large amount of hydroxyl groups. Karstedt catalyst is the complex compound of platinum and 1,3-divinyl-1,1,3,3-tetramethyldisiloxane, which has very high catalytic activity for dehydrogenation between –Si–H bands of PMHS and hydroxyl groups of ZnO at room temperature. Therefore, it was inferred that the bamboo surface would be grafted with numerous hydrophobic PMHS chains by this simple method (Figure 4f). As a result the hydrophobicity of ZnO/bamboo could be significantly improved by PMHS modification.

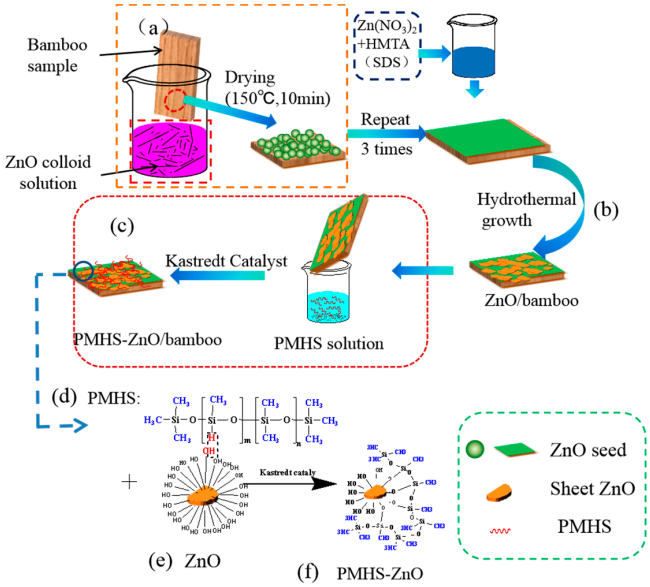


**Figure 4.** Schematic of (**a**) deposited ZnO seed; (**b**) the hydrothermal reaction generates ZnO; and (**c**) reaction of ZnO and PMHS; (**d**) the PMHS chain; (**e**) the ZnO; and (**f**) the PMHS-ZnO.

### 3.5. Anti-Mildew Properties

Poor anti-mildew properties limit bamboo's application, as mentioned above. Therefore, it is very important to develop mildew-resistant bamboo. The mildew-resistances of the original bamboo, ZnO/bamboo, and PMHS-ZnO/bamboo during a 4 weeks incubation trial are presented in Figure 5. The original bamboo samples were infected by *Trichoderma viride* on the 3rd day (Figure 5a). On the 8th day, the area of original bamboo infected by *Trichoderma viride* was more than 75%, and the infection was rated as 4 on the grading scale (Table 1). After 4 weeks of testing, original bamboo samples were totally covered by *Trichoderma viride* (Figure 6a), suggesting that the original bamboo had very poor resistance against *Trichoderma viride*. This is because bamboo is rich in nutrients and easily absorbs water from the environment. These factors provide the growth conditions for mold. ZnO/bamboo was not infected by *Trichoderma viride* over the first 19 days, but hyphae appeared on the surface on the 20th day. After 4 weeks of testing, the infection grading value was 1 and only 5% of the bamboo area was infected (Figure 6d). This means that ZnO/bamboo had an anti-mildew effect, and growth of *Trichoderma viride* was obviously inhibited on the bamboo surface. The reason for delayed mold growth of ZnO modified bamboo has been suggested by previous scholars [17,30]. ZnO nanoparticles destroy the membrane wall of the mold, which may be due in part to the direct interaction between ZnO nanoparticles and the surface of the bacterial membrane. During 28 days of observation, there was no *Trichoderma viride* on the surface of bamboo samples coated with PMHS-ZnO (Figure 6g). This indicates that the PMHS modification had a synergistic or additive effect on the anti-mildew properties of bamboo with ZnO deposition. This is because PMHS chains on the ZnO/bamboo surface greatly reduce its surface energy, which inhibits the bamboo from absorbing water from the environment and gives the bamboo better anti-mildew properties. In addition, the hydrophobic surface may also reduce the adhesion of mold. Similarly, as shown in Figure 5b,c, original bamboo also showed no resistance to *Aspergillus niger* and *Penicillium citrinum*. The ZnO/bamboo had improved anti-mildew resistance to *Aspergillus niger* and *Penicillium citrinum*, while PMHS-ZnO/bamboo possessed excellent anti-mildew resistance to *Aspergillus niger* and *Penicillium citrinum*. Therefore, it can be concluded that the ZnO/PMHS coated bamboo possessed excellent anti-mildew resistance to various molds, including *Trichoderma viride*, *Aspergillus niger*, and *Penicillium citrinum*.

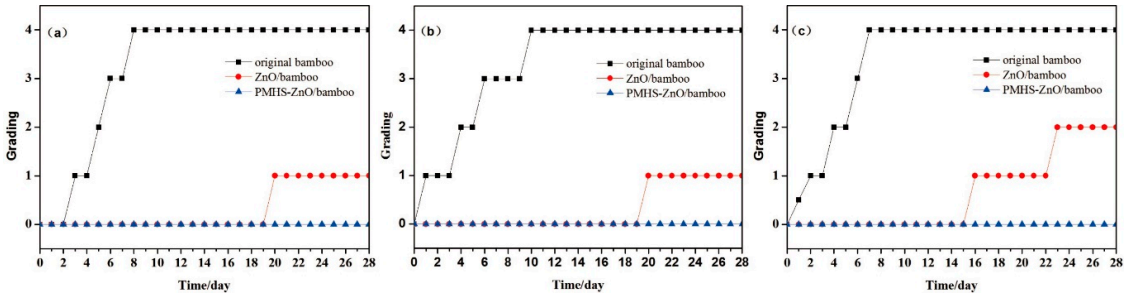


**Figure 5.** Infection values over 28 days of bamboo samples with different surface treatment against (**a**) *Trichoderma viride*, (**b**) *Aspergillus niger*, and (**c**) *Penicillium citrinum*.

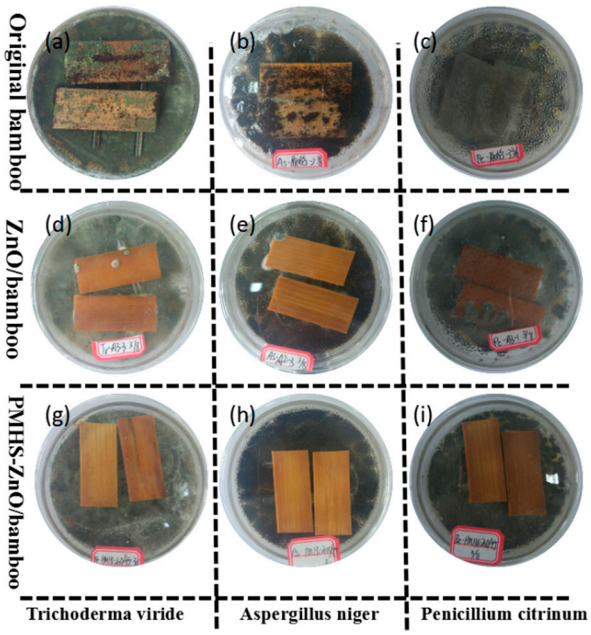


**Figure 6.** The physical images of anti-mildew properties in (**a**–**c**) original bamboo, (**d**–**f**) ZnO/bamboo, and (**g**–**i**) PMHS-ZnO/bamboo stain over 28 days of cultivation with different fungi types.

## 4. Conclusions

In this study, an easy approach was developed for fabrication of hydrophobic ZnO/PMHS coatings on bamboo surfaces, based on a hydrothermal process and hydrophobic treatment. The nano ZnO sheets were successfully grown on the surface of bamboo, where they formed a hierarchical flower-like structure. Further PMHS modification greatly improved the hydrophobicity of bamboo by dramatically increasing the WCA to 142°. Deposition of ZnO onto bamboo surfaces could significantly improve the anti-mildew properties of the bamboo. A further PMHS modification of ZnO coated bamboo gave the bamboo excellent anti-mildew properties, indicating a good synergistic or additive effect of nano-ZnO and PMHS on the anti-mildew properties of bamboo. The innovative fabrication of the ZnO/PMHS coating directly on the surface of the material can be used not only for bamboo, but also for wood, etc. Due to its synergistic effect against mildew, it can effectively extend the service life of bamboo products.

**Author Contributions:** Conceived and designed the experiments, Y.M., J.C. and R.L.; Performed the experiments, H.L., Q.Z. and J.C.; Formal Analysis, Y.M., J.C.; Contributed analysis tools, X.Z., W.Y.; Writing-Original Draft Preparation, J.C.; Critically revised the article, J.C., Y.M., H.L., Q.Z., X.Z., W.Y. and R.L.; Writing-Review & Editing, W.Y., X.Z.; Supervision, W.Y., R.L.

**Funding:** This work was supported by Major Scientific and Technological Projects for University in Fujian Province (No. 2016H61010036), Science and Technology Extension Project of Fujian Forestry Department (No. 2018TG13-2), the National Natural Science Foundation of China (Grant No. 31700498), Natural Science Foundation of Fujian Province (No. 2017J05072), Fujian Agriculture and Forestry University Fund for Distinguished Young Scholars (No. xjq201726).

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Scurlock, J.M.O.; Dayton, D.C.; Hames, B. Bamboo: An overlooked biomass resource? *Biomass Bioenergy* **2000**, *19*, 229–244. [CrossRef]
2. Ma, W.S.A.; Wang, M.J.J.; Chou, F.S. Evaluating the mechanical injury problem in the wood-bamboo furniture manufacturing industry. *Int. J. Ind. Ergon.* **1991**, *7*, 347–355. [CrossRef]

3. Dang, M.N.; Grillet, A.C.; Diep, T.M.H.; Do, T.V.V.; Chi, N.H.T.; Woloszyn, M. Hygric and thermal insulation properties of building materials based on bamboo fibers. In Proceedings of the 4th Congrès International de Géotechnique-Ouvrages-Structures, Ho Chi Minh City, Vietnam, 26–27 October 2017; pp. 508–522.
4. Chung, K.F.; Yu, W.K. Mechanical properties of structural bamboo for bamboo scaffoldings. *Eng. Struct.* **2002**, *24*, 429–442. [CrossRef]
5. Wang, Y.; Ge, W.; Tian, G.; Zheng, L.; Xiao, Q.F.; Zhou, X.; Han, X.; Gao, X. Structures of bamboo fiber for textiles. *Text. Res. J.* **2010**, *80*, 334–343. [CrossRef]
6. Sun, F.; Bao, B.; Ma, L.; Chen, A.; Duan, X. Mould-resistance of bamboo treated with the compound of chitosan-copper complex and organic fungicides. *J. Wood Sci.* **2012**, *58*, 51–56. [CrossRef]
7. Yu, H.; Du, C.; Liu, H.; Wei, J.; Zhou, Z. Advance in anti-mildew research of bamboo. *J. Bamboo Res.* **2016**, *35*, 46–51. (In Chinese)
8. Liu, Y.D. Bamboo timber mildew and anti-mold technology. *Adv. Eng. Forum* **2012**, *4*, 139–144. [CrossRef]
9. Kang, F.; Cheng, Y.; Huang, Q.; Wei, Y.; Zhang, R.; Yang, F. Advances in application of microwave technology to pest quarantine. *Plant Prot.* **2009**, *35*, 36–39. (In Chinese)
10. Cheng, D.; Jiang, S.; Zhang, Q. Mould resistance of moso bamboo treated by two step heat treatment with different aqueous solutions. *Eur. J. Wood Wood Prod.* **2013**, *71*, 143–145. [CrossRef]
11. Ullah, M.A. Biotreatment of Pentachlorophenol Using Wood Rotting Fungi. Ph.D. Thesis, The University of Westminster, London, UK, 2000.
12. Bolin, C.A.; Smith, S. Life cycle assessment of ACQ-treated lumber with comparison to wood plastic composite decking. *J. Clean. Prod.* **2011**, *19*, 620–629. [CrossRef]
13. Janin, A.; Coudert, L.; Blais, J.F.; Mercier, G.; Cooper, P.; Gastonguay, L.; Morris, P. Design and performance of a pilot-scale equipment for CCA-treated wood remediation. *Sep. Purif. Technol.* **2012**, *85*, 90–95. [CrossRef]
14. Peper, M.; Ertl, M.; Gerhard, I. Long-term exposure to wood-preserving chemicals containing pentachlorophenol and lindane is related to neurobehavioral performance in women. *Am. J. Ind. Med.* **1999**, *35*, 632–641. [CrossRef]
15. Zheng, R.-Z.; Zhang, Q.-H.; He, Y.-X.; Zhang, Q.; Yang, L.-S.; Zhang, Z.-H.; Zhang, X.-J.; Hu, J.-T.; Huang, F. Historical long-term exposure to pentachlorophenol causing risk of cancer-a community study. *Asian Pac. J. Cancer Prev.* **2013**, *14*, 811–816. [CrossRef] [PubMed]
16. Mercer, T.G.; Frostick, L.E. Evaluating the potential for environmental pollution from chromated copper arsenate (CCA)-treated wood waste: A new mass balance approach. *J. Hazard. Mater.* **2014**, *276*, 10–18. [CrossRef] [PubMed]
17. Laohhasurayotin, K.; Pookboonmee, S. Multifunctional properties of Ag/$TiO_2$/bamboo charcoal composites: Preparation and examination through several characterization methods. *Appl. Surf. Sci.* **2013**, *282*, 236–244. [CrossRef]
18. Ren, D.; Li, J.; Xu, J.; Wu, Z.; Bao, Y.; Li, N.; Chen, Y. Efficient antifungal and flame-retardant properties of ZnO-$TiO_2$-layered double-nanostructures coated on bamboo substrate. *Coatings* **2018**, *8*, 341. [CrossRef]
19. Sun, F.B.; Yu, Y.; Jiang, Z.H.; Ren, H.Q.; Wang, G.; Liu, X.E. Nano $TiO_2$ modification of bamboo and its antibacterial and mildew resistance performance. *Spectrosc. Spectr. Anal.* **2010**, *30*, 1056–1060. (In Chinese)
20. Teli, M.D.; Sheikh, J. Modified bamboo rayon-copper nanoparticle composites as antibacterial textiles. *Int. J. Biol. Macromol.* **2013**, *61*, 302–307. [CrossRef] [PubMed]
21. Wang, J.; Li, J.; Zhuang, X.; Pan, X.; Yu, H.; Sun, F.; Song, J.; Jin, C.; Jiang, Y. Improved mould resistance and antibacterial activity of bamboo coated with ZnO/graphene. *R. Soc. Open Sci.* **2018**, *5*, 180173. [CrossRef] [PubMed]
22. Devi, R.R.; Gogoi, K.; Konwar, B.K.; Maji, T.K. Synergistic effect of nano $TiO_2$ and nanoclay on mechanical, flame retardancy, UV stability, and antibacterial properties of wood polymer composites. *Polym. Bull.* **2013**, *70*, 1397–1413. [CrossRef]
23. Xie, G.; Zhou, Y.; Cao, Y.; Li, L. Anti-mildew properties of copper cured heat-treated wood. *Bioresources* **2018**, *13*, 5643–5655.
24. Li, J.; Wu, Z.; Bao, Y.; Chen, Y.; Huang, C.; Li, N.; He, S.; Chen, Z. Wet chemical synthesis of ZnO nanocoating on the surface of bamboo timber with improved mould-resistance. *J. Saudi Chem. Soc.* **2016**, *21*, 920–928. [CrossRef]

25. Khan, M.F.; Hameedullah, M.; Ansari, A.H.; Ahmad, E.; Lohani, M.B.; Khan, R.H.; Alam, M.M.; Khan, W.; Husain, F.M.; Ahmad, I. Flower-shapedZnO nanoparticles synthesized by a novel approach at near-room temperatures with antibacterial and antifungal properties. *Int. J. Nanomed.* **2014**, *9*, 853–864. [CrossRef] [PubMed]
26. Godbole, V.S.; Lakkad, S.C. Effect of water absorption on the mechanical properties of bamboo. *J. Mater. Sci. Lett.* **1986**, *5*, 303–304. [CrossRef]
27. Wang, C.; Piao, C.; Lucas, C. Synthesis and characterization of superhydrophobic wood surfaces. *J. Appl. Polym. Sci.* **2011**, *119*, 1667–1672. [CrossRef]
28. Wang, F.; Li, S.; Wang, L. Fabrication of artificial super-hydrophobic lotus-leaf-like bamboo surfaces through soft lithography. *Colloids Surf. A Physicochem. Eng. Asp.* **2017**, *513*, 389–395. [CrossRef]
29. Jin, C.; Li, J.; Han, S.; Wang, J.; Sun, Q. A durable, superhydrophobic, superoleophobic and corrosion-resistant coating with rose-like ZnO nanoflowers on a bamboo surface. *Appl. Surf. Sci.* **2014**, *320*, 322–327. [CrossRef]
30. Fadeeva, E.; Truong, V.K.; Stiesch, M.; Chichkov, B.N.; Crawford, R.J.; Wang, J.; Ivanova, E.P. Bacterial retention on superhydrophobic titanium surfaces fabricated by femtosecond laser ablation. *Langmuir* **2011**, *27*, 3012–3019. [CrossRef] [PubMed]
31. Tang, P.; Zhang, W.; Wang, Y.; Zhang, B.; Wang, H.; Lin, C.; Zhang, L. Effect of superhydrophobic surface of titanium onstaphylococcus aureusadhesion. *J. Nanomater.* **2011**, *20*, 3385. [CrossRef]
32. Shen, Y.; Wu, Y.; Shen, Z.; Chen, H. Fabrication of self-healing superhydrophobic surfaces from water-soluble polymer suspensions free of inorganic particles through polymer thermal reconstruction. *Coatings* **2018**, *8*, 144. [CrossRef]
33. Lin, W.; Huang, Y.; Li, J.; Liu, Z.; Yang, W.; Li, R.; Chen, H.; Zhang, X. Preparation of highly hydrophobic and anti-fouling wood using poly (methylhydrogen) siloxane. *Cellulose* **2018**, *25*, 7341–7353. [CrossRef]
34. Liu, Z.Q.; Yu, J.W.; Lin, W.S.; Yang, W.B.; Li, R.; Chen, H.X.; Zhang, X.X. Facile method for the hydrophobic modification of filter paper for applications in water-oil separation. *Surf. Coat. Technol.* **2018**, *352*, 313–319. [CrossRef]
35. Sun, Y.Y.; Lin, H.; Hu, X.Y.; Chen, C.X.; Xie, X.Z.; Yang, W.B.; Zhang, X.X.; Chen, H.X. Refractive-tunable and hydrophobic antireflective coatings by PMHS-modification assisted sol-gel method. *Mater. Lett.* **2017**, *186*, 123–126. [CrossRef]
36. Jin, C.; Li, J.; Han, S.; Wang, J.; Yao, Q.; Sun, Q. Silver mirror reaction as an approach to construct a durable, robust superhydrophobic surface of bamboo timber with high conductivity. *J. Alloy Compd.* **2015**, *635*, 300–306. [CrossRef]
37. *GB/T 18261-2013 Test Method for Anti-Mildew Agents in Controlling Wood Mould and Stain Fungi*; Standardization Administration of China: Beijing, China, 2013. (In Chinese)
38. Meng, F.D.; Yu, Y.L.; Zhang, Y.M.; Yu, W.J.; Gao, J.M. Surface chemical composition analysis of heat-treated bamboo. *Appl. Surf. Sci.* **2016**, *371*, 383–390. [CrossRef]
39. Vinogradov, I.; Lunk, A. Film deposition in the dielectric barrier discharge at atmospheric pressure in $He/O_2$/HMDSO and $He/N_2O$/HMDSO mixtures. *Plasma Proc. Polym.* **2010**, *6*, 514–518. [CrossRef]
40. Jie, C.; Zhang, J.H.; Li, M.A.; Lu, H.D. Study of crystallinity performance of pretreated bamboo fibers based on X-ray diffraction and NMR. *Spectrosc. Spectr. Anal.* **2017**, *37*, 256–261. (In Chinese)