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Bamboo surface coated with polymethylsilsesquioxane/Cu-containing nanoparticles (PMS/CuNP) xerogel for superhydrophobic and anti-mildew performance

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Abstract

In this study, a colloidal suspension, composed of polymethylsilsesquioxane (PMS) and Cu-containing nanoparticles (CuNP), was prepared through simple neutralization reaction using sodium methyl siliconate (SMS) and $CuCl_2$ solutions. The nano-structure of CuNP was investigated by TEM and the results showed that lamellar crystal $Cu(OH)_2$ with size of around 10 nm was imbedded in PMS nano-particle. The FTIR also confirmed the presence of small amount of PMS in CuNP. The specific nano-structure of CuNP resulted in excellent thermal stability based on TG analysis. After dip-coating in optimized conditions and drying, a PMS/CuNP xerogel coating layer was generated at the bamboo surface, endowing superhydrophobic and excellent anti-mildew performance according to ASTM D3273-16. The water contact angle (WCA) reached up to $151.3 \pm 1.9°$ and the mildew resistance grade was marked as 10 where no mold was found at the surface after 4 weeks incubation.

Keywords: Bamboo, Coating, Anti-mildew, Superhydrophobic

Introduction

Bamboo is a promising wood substitute because of two chief reasons [1, 2]. Firstly it possesses excellent physical properties, such as high strength and good toughness. Secondly it grows so fast that usable bamboo timber can be harvested within 3–5 years. However, due to the presence of rich nutrients like starch and protein, bamboo is susceptible to mold fungi, decay fungi, and insects. Especially, mildew at bamboo surface has a deleterious impact on its appearance for furnishing. In severe case, it would threaten human health, causing skin allergy and respiratory tract infection [3].

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Although organic mildew preventives, such as 2-decyl dimethyl ammonium chloride (DDAC), propiconazole, and tebuconazole 3-iodo-2-propyl-butyl carbamate (IPBC), are very effective against several kinds of mold, they are always toxic and harmful to humans and livestock [4]. In contrast, nano-sized metal and metal oxides are regarded as novel and non-toxic mold-resistant agents. Li and Wu et al. [5] fabricated nano-ZnO-coated bamboo timber through wet chemical synthesis, which showed a better resistance against *Aspergillus niger* V. Tiegh and *Penicillium citrinum* Thom, but poor against *Trichoderma viride* Pers. ex Fr. Yu et al. [6, 7] investigated the influence of ZnO film morphology on the photostability and antifungal performance of coated bamboo. The results indicated that almost no visible mold growth was observed at the surface of bamboo samples coated with nanostructured networks. Xie et al. [8] found that wood samples of *Pinus massoniana* Lamb, modified through impregnating with copper-containing solutions followed by heat-treating at high temperature to generate in situ nano-copper particles, suppressed the growth of *Botryodiplodia theobromae* Pat. and *Aspergillus niger* van Tieghem with 100% efficiency, and *Penicillium citrinum* Thom with 75% suppression. Li and Jin et al. [9, 10] developed a facile method for preparation of TiO_2 nanocrystals on bamboo timber surface at room temperature which presented much superior antifungal capability under natural weather conditions [11].

Water is indispensable for the growth of mold. Thus hydrophobic modification is also an effective strategy to prevent fungal growth. Guillemot et al. [12] reported that surface hydrophobicity resulted in decreased microbial adhesion. Rowell et al. [13] found that the low cell wall moisture content in acetylated wood suppressed fungal attack, so that initial enzymatic attack starting the colonization did not occur. Wood panels treated with methylated 1,3-dimethylol-4,5-dihydroxyethyleneurea (mDMDHEU) improved hydrophobicity and dimensional stability during 18 months weathering, leading to reduced internal stresses and fewer cracks on the surface. As a result, panels treated with mDMDHEU exhibited improved resistance to wood decay and staining fungi by precluding the access of fungal spores to the interior parts of the wood substrate [14]. Yao and Zhang et al. reported that fungi could still be found inside hydrophobic wood after antifungal test while superhydrophobic wood could thoroughly prevent fungal attachment to wood surface [15]. However, the result was not representative.

As a cheap and environment friendly industry product, water-soluble sodium methyl siliconate (SMS) or potassium methyl siliconate is usually used as building waterproof material. Zhang et al. [16] firstly used potassium methyl siliconate to fabricate superhydrophobic surface on cellulose-based materials in order to eliminate acidic by-product from organic silicon halides. Carbon dioxide was bubbled into the potassium methyl siliconate solution to reduce the pH value, so that methyl siliconate formed silanol and assembled onto cellulose molecule surface via hydrogen bond interactions. Similar work was carried out to prepare a superhydrophobic wood surface [17].

Considering that metal oxides are always produced in alkaline condition while the sol–gel process of SMS takes place with reduced pH value, a coupled reaction is designed in this study. Acid $CuCl_2$ is used as the pH-controlling agent to neutralize alkaline SMS with the aim to obtain a hydrophobic colloidal suspension containing $Cu(OH)_2$ crystals which could act as mold inhibitor. Then difunctional coating layer at bamboo surface is prepared using one-step dip-coating method conveniently. Hydrophobicity from silica gel is expected to enhance the mold resistance efficiency of metal oxides.

Materials and methods

Materials

Moso bamboo (*Phyllostachys heterocycle*, Shaoguan, Guangdong, China) samples with the dimension of 50 mm × 20 mm × 5 mm were ultrasonically cleaned in 50% ethanol, deionized water and then dried at 103 ± 2 °C over night. Sodium methyl siliconate (SMS, Tech, Shandong Xingchi Chemical Co., Ltd., China), copper chloride ($CuCl_2$, AR, Tianjin Fuchen Chemical Reagent Co., Ltd., China), sodium hydroxide (NaOH, AR, Tianjin Hongyan Reagent Plant, China) were used without further purification.

Bamboo surface modification

The colloidal suspension was prepared through neutralization reaction between alkaline SMS and acidic $CuCl_2$ solution. Typically, 2% $CuCl_2$ solution was added into 2% SMS dropwise under stirring until the pH reached the target value of 11. The bamboo samples were immersed into the colloidal mixture suspension for 2 h under stirring and then dried in air for 10 min. This process was repeated for 5 times. The treated samples were finally dried at 103 °C for 2 h. For comparison, a one-component colloidal suspension was prepared by replacing $CuCl_2$ with hydrochloric acid (HCl) or SMS with sodium hydroxide (NaOH) to adjust the pH of the mixture to be 11.

Characterization

Polymethylsilsesquioxane/Cu-containing nanoparticles (PMS/CuNP) xerogel sample for characterization was prepared by dropping the colloidal suspension at pH 11 with 2% SMS at glass surface for complete gelation. CuNP was separated from the same colloidal suspension through centrifugation at 5000 rpm for 10 min. Pure PMS xerogel was prepared in the same way as PMS/CuNP xerogel except that 2% $CuCl_2$ was replaced with 2% HCl. These three samples were dried at 105 °C for 2 h and further ground into powder. CuNP and PMS/CuNP powders were ultrasonic dispersed in alcohol in a concentration of 3 wt % and then 10 μL drop of the supernatant was deposited onto carbon-coated transmission electron microscope (TEM) grids (300 mesh copper, formvar–carbon, Ted Oella Inc.). The excess liquid was blotted with filter paper after 5 min. High-resolution TEM (Talos F200S, ThermoFisher, Massachusetts, US) was used to observe the nano-structure of CuNP and PMS/CuNP. Fourier transform infrared analysis (FTIR) was carried out in a Fourier transform infrared spectrometer (Vertex 70, Bruker, Ettlingen, Germany). Each sample was scanned 64 times in transmittance mode, at 4 cm^{-1} resolution in the wave range from 4000 to 400 cm^{-1}. Thermogravimetric analysis was used to characterize the thermal stability with a TG 209 Instrument (Bruker Netzsch, Selb, Germany) at a heat rate of 10 °C/min from room temperature to 600 °C with air.

The wettability of modified bamboo samples was characterized by water contact angle (WCA) using Contact Angle System (OCA20, Dataphysics, Germany). Graphs of 5 μL water droplet on three different areas at bamboo surface were recorded and their WCAs were calculated by Young–Laplace fitting to obtain the average values. Six replicates were tested to obtain the average WCA values and their standard deviations. The morphology and microstructure of the sample surface were observed with a scanning electron microscope (SEM) (SU-70, Hitachi, Japan) at an accelerating voltage of 20 kV. All samples were sputter-coated with gold before SEM observation.

Anti-mildew test

The mildew resistance level was determined according to ASTM D3273-16 with minor modification. Mixed mold spores were obtained by exposing the malt extract agar medium in air until it was fully covered by mycelium. Next, the mycelium was carefully transferred into a spray bottle using 20-mL sterile water with 1–2 drop of Tween 80. Six replicates of bamboo samples, pre-conditioned at 23 °C and 65% relative humidity (RH) for 3 days, were sprayed with the above mold suspension and incubated at 28 °C and 90% RH for 4 weeks. Anti-mildew levels were divided into 0 to 10 according to the area of mold infection. Level 10 represented no defacement, and level 0 represented block that is completely defaced.

Results and discussion

SMS and potassium methyl siliconate are water-soluble and their pH value are larger than 12. When the pH value is reduced by acids or CO_2, the methyl siliconate forms silanol and slowly condenses to form oligomeric and polymeric siloxane [16]. In this study, $CuCl_2$ was used as the pH-controlling agent. Once it was added into SMS solution dropwise, the solution became blue turbid immediately. In this neutralization reaction, $Cu(OH)_2$ was probably formed as a by-product (Fig. 1), similar to the potassium carbonate and potassium bicarbonate in the previous study.

The blue turbidity was further collaborated through centrifugation and its nano-structure was characterized using TEM. Surprisingly it was observed that lamellar crystal $Cu(OH)_2$ with size of around 10 nm was imbedded in polymethylsiloxane (PMS) particle as seen in Fig. 2a. It was speculated that the wrapping structure was formed by self-assembly since the $Cu(OH)_2$ precipitation and silanol condensation took place simultaneously during the preparation of silanol solution. Herein the particular nano-structure of $Cu(OH)_2$ and PMS was named as Cu-containing nanoparticles (CuNP). As a contrast, for sample prepared in total blue colloidal suspension, parts of PMS particles contained nothing inside and they were connected with CuNP as well, seen in Fig. 2b. In other words, the obtained xerogel was a mixture of pure PMS particles and CuNP, as named PMS/CuNP. It is known that $Cu(OH)_2$ is a metastable phase which easily transforms into CuO [18]. However, CuNP and PMS/CuNP prepared in this study were still light blue after drying in oven at 105 °C for 2 h. From the results of TEM, their good thermal stability might be attributed to the specific nano-sized wrapping structure.

As seen in the FTIR spectra in Fig. 3, three characteristic IR absorption bands of Si–O–Si bonds, including the rocking mode at around 450 cm^{-1}, bending mode at 800 cm^{-1} and asymmetrical stretching mode at 1075 cm^{-1} [19], were clearly observed in PMS. The symmetric deformation of $-CH_3$ in PMS was also well identified at 1275 cm^{-1}. For CuNP, the absorption band around 510 cm^{-1} was assigned to the stretching vibration mode of Cu–O bonds and the broad bands at around 3450^{-1} might be attributed to the stretching vibration mode of –OH in crystalline $Cu(OH)_2$. The characteristic absorption bands of Si–O–Si and $-CH_3$ was also found in CuNP, although the intensity of these bands was low. The result was consistent with TEM

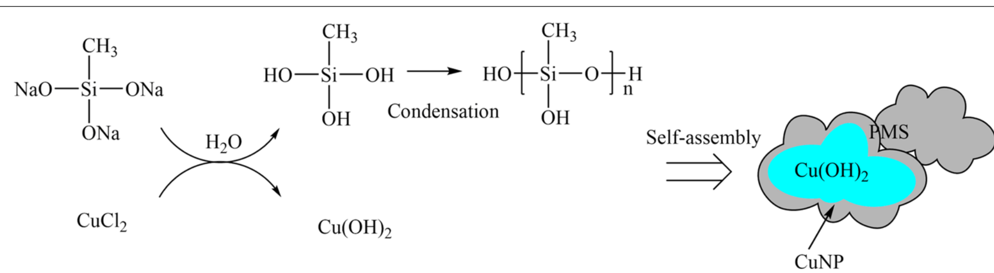

Fig. 1 Schematic diagram of PMS/CuNP formation

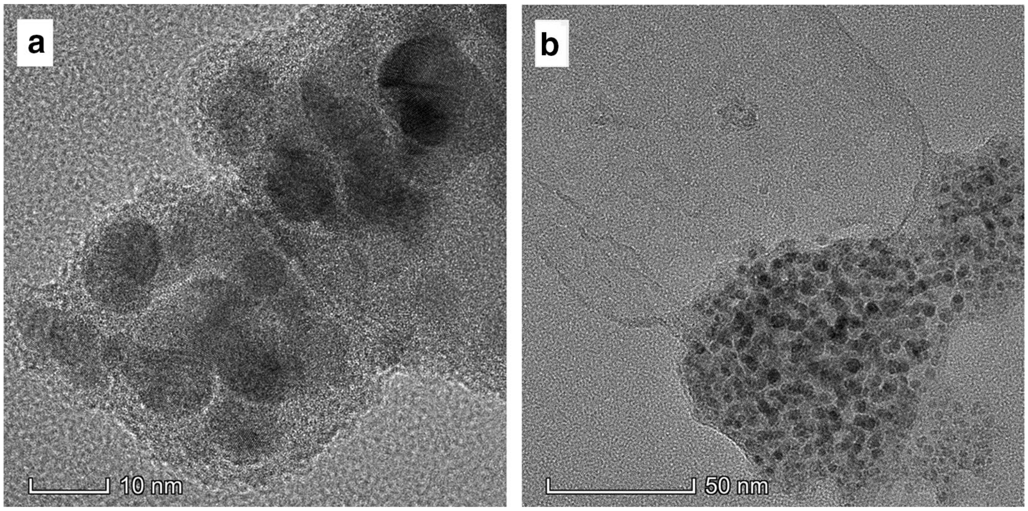

Fig. 2 TEM graphs of CuNP (**a**) and PMS/CuNP (**b**)

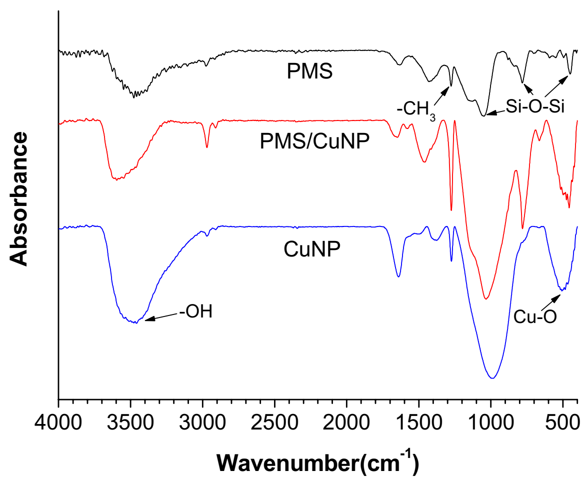

Fig. 3 FTIR spectra of PMS, PMS/CuNP and CuNP

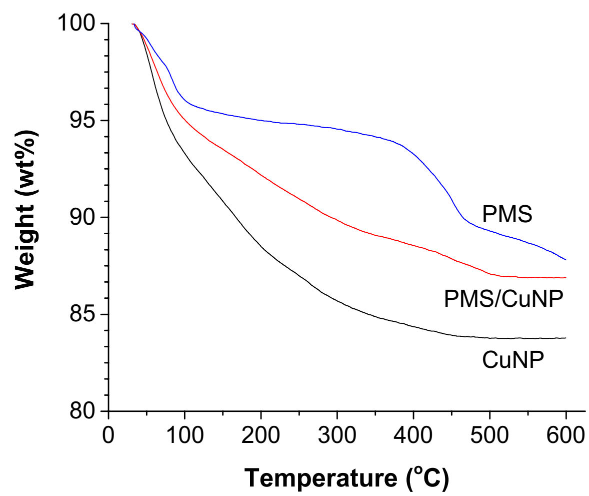

Fig. 4 TG spectra of PMS, PMS/CuNP and CuNP

observations that small amount of PMS was present in CuNP. For PMS/CuNP, the above characteristic bands were all observed, confirming that the PMS/CuNP xerogel was a mixture of PMS and CuNP.

The thermal stability of PMS, PMS/CuNP and CuNP was characterized by TGA with air as carrier gas. As shown in Fig. 4, water content in PMS was around 4% and the second stage of mass loss occurred at around 400 °C, which corresponded to the oxidation of $-CH_3$ in PMS. In contrast, a sustained weight loss was found until 500 °C for PMS/CuNP and CuNP and they changed to light black after TG analysis, indicating that crystalline $Cu(OH)_2$ imbedded in PMS in nano-size showed excellent thermal stability. Note that a slight mass loss was also found at 450–500 °C in PMS/CuNP, which belonged to the oxidation of $-CH_3$ in PMS.

After dip-coating in the colloidal suspension and drying, a compound membrane layer composed of PMS/CuNP xerogel formed at bamboo surface. Hydrophobicity of modified bamboo was influenced by several factors, including pH value, SMS concentration, immersion time and dip-coating times.

The hydrophobicity of modified bamboo through dip-coating in SMS solution was unsatisfied, since the WCA was only 118.2 ± 1.3°. Besides, the modified bamboo probably suffered from degradation under high alkaline conditions from SMS solution [20]. With the addition of $CuCl_2$, the pH value decreased gradually. The pH

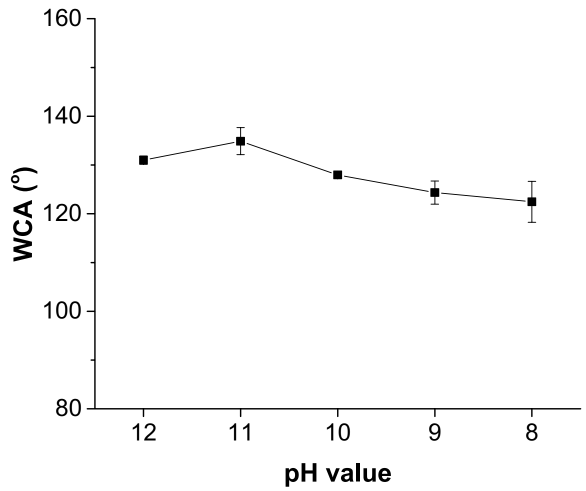

Fig. 5 The effect of pH value on WCA of modified bamboo

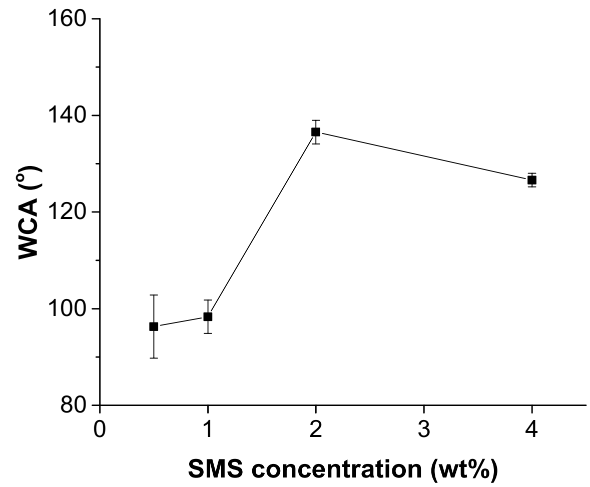

Fig. 6 The effect of SMS concentration on WCA of modified bamboo

value was an important parameter during the neutralization titration process. The effect of pH value on the contact angle of modified bamboo is shown in Fig. 5. Compared to immersion in the pH = 12 suspension, the bamboo modified in pH = 11 showed a higher WCA of 134.9 ± 2.8° due to more CuNP and PMS produced in the suspension of pH = 11. However, as the pH continued to decrease, the WCA decreased gradually. It is known that lower pH value enhanced the dehydration condensation among methysilanols, leading to flocculent PMS with larger colloidal particle size. In the meantime some crystalline $Cu(OH)_2$ was produced, but not inside PMS, which increased the hydrophilicity of the composite coating layer.

The effect of SMS concentration on hydrophobicity of bamboo was investigated and the final pH value was set at 11, as shown in Fig. 6. When the SMS concentration was lower than 1%, WCA of modified bamboo was less than 100° due to incomplete coverage of the coating layer at bamboo surface. For 2% SMS solution, the WCA increased to 136.3 ± 2.4°. However, WCA dropped slightly to 126 ± 1.4° when 4% SMS was used. Considering that original bamboo had micro-roughness derived from fibrous cell wall, the excess amount of PMS/CuNP adsorbed would diminish the micro-roughness and generate relatively flat surface, thus decreasing the final WCA of modified bamboo.

The effect of immersion time and dip-coating times on hydrophobicity of modified bamboo was investigated under the condition of 2% SMS and pH 11. As shown in Fig. 7, when the immersion time increased from 10 to 120 min, the WCA increased from 115.3° to 136.5°. After one dip-coating for 120 min, the coating layer was dried in air for 10 min and then a second dip-coating was carried out. As shown in Fig. 7, with the increase of dip-coating times, hydrophobicity of modified bamboo enhanced gradually and the WCA reached up to 151.3 ± 1.9° at the fifth dip-coating, which could be called superhydrophobic surface.

Bamboo was dip-coated in the colloidal suspension under optimized conditions and samples prepared in $Cu(OH)_2$ suspension and pure PMS colloidal suspension were prepared at pH = 11 and 2% concentration for comparison. The mildew resistance of original bamboo and bamboo coated with $Cu(OH)_2$, PMS and PMS/CuNP was evaluated according to ASTM D3273-16 [21]. The photographs of mold growth on bamboo surface after 4 weeks of incubation are presented in Fig. 8. Mold started to grow on the untreated bamboo surface within 2 days after inoculation and at least three kinds of mold were observed to cover fully the surface due to the rich content of sugars and starch inside bamboo. For bamboo coated with $Cu(OH)_2$, only Cu-tolerant fungal spores could germinate and grow on the surface, which probably belonged to *Trichoderma* [8]. PMS-modified bamboo surface showed limited mildew resistance as mold began to grow at the 7th day which might be attributed to a relatively dry surface environment generated by PMS layer. However, at the end of 4th week, its surface was still fully covered with several kinds of fungi, with less distribution density as compared to the unmodified bamboo. In contrast, the mildew resistance grade of the PMS/CuNP-modified bamboo was marked as 10 as no mold was found at the surface. The synergistic effect of hydrophobic surface with antimicrobial agents was also reported by Chen and Li et al. [22]. They found that after polymethylhydrogensiloxane (PMHS) hydrophobic modification, ZnO/bamboo had excellent anti-mildew properties

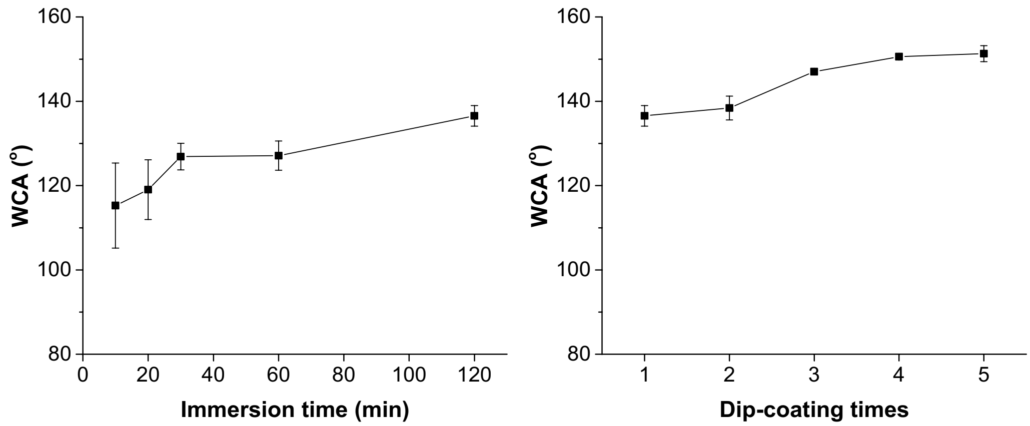

Fig. 7 The effect of immersion time and dip-coating times on WCA

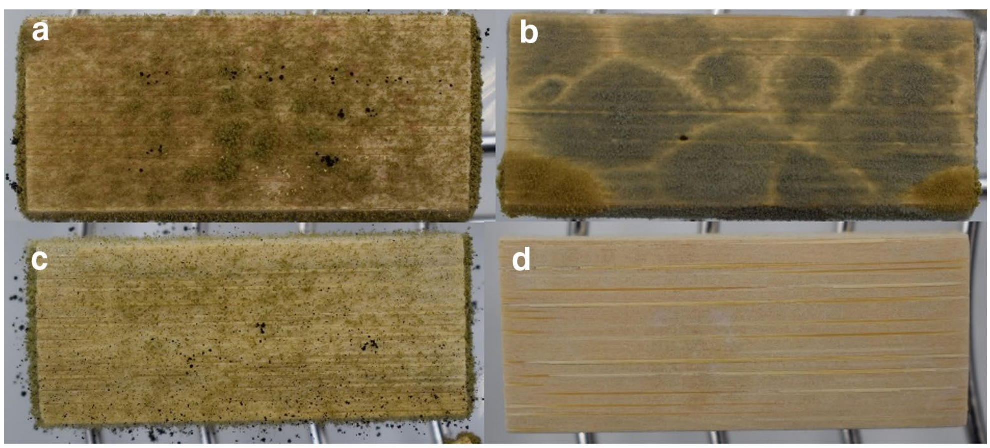

Fig. 8 Typical pictures of unmodified bamboo (**a**) and modified bamboo with $Cu(OH)_2$ (**b**), PMS (**c**) and PMS/CuNP (**d**) in anti-mildew test after 4 weeks

when exposed to *Trichoderma viride*, *Aspergillus niger*, and *Penicillium citrinum.*

The surface morphologies of unmodified bamboo and modified bamboo samples, containing parenchymal cells and vascular bundles are shown in Fig. 9. Unmodified bamboo surface was highly hydrophilic, with WCA 0°. For bamboo modified with $Cu(OH)_2$, nanoparticles evenly covered bamboo surface as shown in Fig. 9b. Since $Cu(OH)_2$ was hydrophilic, WCA of the modified bamboo was still 0°. After dip-coating in pure PMS sol and drying, bamboo surface was covered with cracked PMS layer, which was caused by the shrinkage of PMS gel during drying process. PMS was hydrophobic due to the presence of methyl groups and the original concave–convex cell structure of bamboo provided additional roughness, leading to an improved hydrophobicity with a WCA of 131.7°. It was conjectured that mold hypha could still grow through these cracked PMS layer with a slower growth rate due to the lack of water. With the addition of CuNP inside, the cracks of PMS layer almost disappeared, indicating that the possibilities of mold hypha contacting the bamboo surface were greatly reduced. Besides, SEM image suggested that PMS/CuNP was rougher than the pure PMS layer. The additional nano-size roughness on PMS layer further increased the WCA of modified bamboo.

Conclusion

In this study, PMS/CuNP colloidal suspension, containing pure PMS and CuNP, was prepared through simple neutralization reaction. The nano-structure of CuNP was that $Cu(OH)_2$ crystals imbedded by PMS

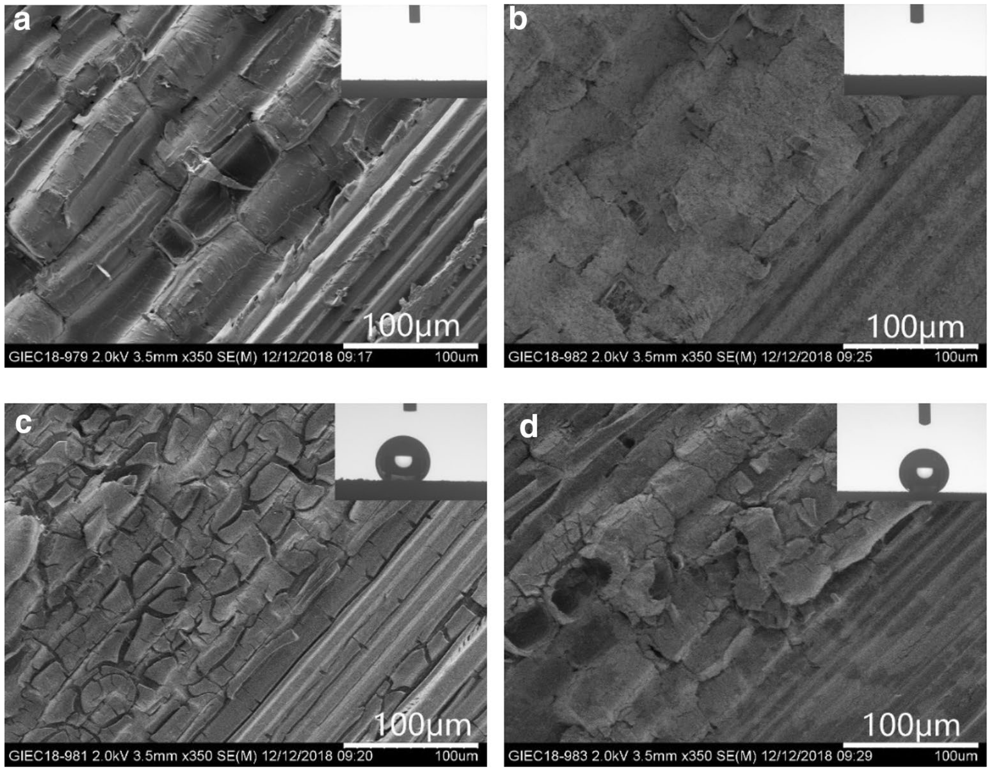

Fig. 9 SEM images of unmodified bamboo (**a**) and modified bamboo with $Cu(OH)_2$ (**b**), PMS (**c**) and PMS/CuNP (**d**) with corresponding WCA images inset

nanoparticles, which greatly improved its thermal stability. After dip-coating and drying, a PMS/CuNP coating layer was generated at bamboo surface, endowing superhydrophobic and excellent anti-mildew performance. The mildew resistance grade of the PMS/CuNP-modified bamboo was marked as 10 as no mold was found at the surface after 4 weeks of incubation. SEM results demonstrated that the presence of CuNP not only eliminated the cracks of PMS layer, but also provided additional nano-size roughness. Therefore, even Cu-tolerant mold could not survive at the PMS/CuNP coating layer. Further work would be focused on improving the weather resistance of the coating layer, so that the PMS/CuNP-coated bamboo could be applied for outdoor use.

Abbreviations
PMS: Polymethylsilsesquioxane; CuNP: Cu-containing nanoparticles; PMS/CuNP: Polymethylsilsesquioxane/Cu-containing nanoparticles; SMS: Sodium methyl siliconate; DDAC: 2-Decyl dimethyl ammonium chloride; IPBC: 3-Iodo-2-propyl-butyl carbamate; mDMDHEU: Methylated 1,3-dimethylol-4,5-dihydroxyethyleneurea; WCA: Water contact angle; RH: Relative humidity.

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Authors' contributions
DW carried out the preparation of polymethylsilsesquioxane/Cu-containing nanoparticles (PMS/CuNP) xerogel and characterized their wettability and anti-mildew performance. GW and MJ proposed the plans for improving the experiments and suggestions for theoretical analysis. JG and DT characterized the microstructure of PMS/CuNP and its thermal stability. CH and WZ finished the manuscript writing and analysis. All authors read and approved the final manuscript.

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Ethics approval and consent to participate
Not applicable.

Consent for publication
Not applicable.

Competing interests
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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