Tailoring growth of MOF199 on hierarchical surface of bamboo and its antibacterial property

Minglei Su · Rong Zhang · Jingpeng Li · Xiaobei Jin · Xiaofeng Zhang · Daochun Qin

Received: 21 February 2021 / Accepted: 9 October 2021 / Published online: 22 October 2021
© The Author(s), under exclusive licence to Springer Nature B.V. 2021

Abstract Bamboo, as a fast-grown forest resource, can be functionalized by metal–organic frameworks (MOFs) with various potential applications. However, the stability of MOFs immobilized on bamboo surface remains to be improved. In this work, MOF199, as known as HKUST-1, was in situ anchoring on moso bamboo via regulating pretreatment of bamboo and a green two-step synthesis route. The two-step synthesis route was completed under room temperature and both precursor solutions can be reused. The results indicated that, with the collaboration of delignification and carboxymethylation pretreatment of bamboo, a dense and well-dispersed MOF coating was successfully synthesized, the adhesion between MOF199 and bamboo surface was also improved. Besides, the quantity and size of MOF199 on bamboo can be tailored by tunning the carboxyl groups of pretreated bamboo and the concentration of copper nitrate solution. More importantly, results show that the formation of carboxyl-copper (II) complex served as nucleation sites for the growth of MOF199 crystals, which was essential to prepare uniform MOF layers. The growth of MOF199 endowed bamboo with good antibacterial activity against Escherichia coli. This method provides a facile and practical strategy for designing MOF coated woody materials.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10570-021-04265-z.

M. Su · R. Zhang · X. Jin · X. Zhang · D. Qin
Key Laboratory of National Forestry and Grassland Administration/Beijing for Bamboo & Rattan Science and Technology, International Center for Bamboo and Rattan, Beijing 100102, China
E-mail: zhangrong@icbr.ac.cn

D. Qin
E-mail: qindc@icbr.ac.cn

J. Li
Key Laboratory of High Efficient Processing of Bamboo of Zhejiang Province, China National Bamboo Research Center, Hangzhou 310012, China
Introduction

Bamboo has been widely used as a raw material for interior decoration and necessities, such as flooring, furniture, fabrics, and paper, especially in Asia (Li et al. 2017). However, the main drawback of bamboo is its susceptibility to bacteria and fungi, owing to its rich nutrient content (Li et al. 2019; Zhang et al. 2020). Numerous chemicals, such as halogen compounds, metal salts, and metal complexes, have been used for antibacterial activity (Wang et al. 2015; Zhang et al. 2017). However, most of these compounds are toxic to humans and easily cause environmental hazards. Metal–organic frameworks (MOFs) have attracted considerable attention due to their high porosity and surface area, flexible tunability, and well-defined architecture (Duan et al. 2019a). It has been used in antibacterial systems, gas storage, heavy metal adsorption, and catalysis fields (Nasruddin et al. 2020). MOF199, which consist of Copper (II) ions and 1,3,5-benzenetricarboxylic acid (BTC), has been proven to impart antibacterial activity to textiles fabric (Ma et al. 2018; Wang et al. 2015). In our previous work, we successfully deposited MOF199 on the surface of Phyllostachys edulis, commonly known as moso bamboo, and the obtained materials exhibited good antibacterial activity against both Staphylococcus aureus (S. aureus) and Escherichia coli (E. coli) (Su et al. 2019). However, owing to the poor physical deposition of MOF199 on the bamboo, the MOF199 easily disengaged from the bamboo surface and thus its antibacterial performance deteriorated. Therefore, improving the bonding strength between the MOFs and bamboo is essential to ensure effective applications.

According to previous reports, MOFs have been successfully synthesized on different bio-based materials, such as cellulose fiber (Ma et al. 2018; Wang et al. 2015; Bunge et al. 2015), wool fabric (Lis et al. 2019), cotton fabric (Abdelhameed et al. 2016; Da Silva Pinto et al. 2012), and paper (Li et al. 2020), all of above have loose and porous structures which facilitate the attachment of MOFs (Duan et al. 2018). In cellulose materials, various efforts have been made to improve the attachment between MOFs and substrate by introducing carboxyl groups, such as carboxymethylation (Kim et al. 2019; Duan et al. 2019a), TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl radical)-mediated oxidation (Duan et al. 2019b), and hydrogen peroxide oxidation (Abdelhameed et al. 2016). However, in the cell wall of woody plants, such as bamboo, lignin tightly wraps the cellulose and hemicellulose. Since lignin does not have a sufficient number of active functional groups and distributed inconsistently on the cell wall, it is
difficult to achieve uniform surface modification of woody materials (Guo et al. 2016; Ma et al. 2020). Compared with lignin and hemicellulose, cellulose is easier to modify because of the active primary alcohol in its repeating glucose structure (Abdelhameed et al. 2016). Therefore, in this study, delignification was used to expose the cellulose of bamboo, which was conducive to the subsequent carboxymethylation treatment for improving MOFs attachment (Chen et al. 2020). In addition, the bonding mechanism between MOF199 and the components (cellulose, lignin and hemicellulose) of bamboo are discussed in this article. The size and quantity of MOF crystals significantly affected on the performance of the composites (Wyszogrodzka et al. 2016). Several methods have been used to control MOF loading on various matrix material composites (Laurila et al. 2015; Abdelhameed et al. 2016; Duan et al. 2018; Qiu et al. 2020). However, due to the variability of biomaterials, regulating the growth of MOFs on bamboo remains a challenge.

In this study, by regulating pretreatment and a green two-step synthesis route, in situ growth of MOF199 on the hierarchical surface of bamboo was successfully tailored, as shown in Scheme 1. To improve the attachment of MOFs on bamboo surface, pretreatment with carboxymethylation and delignification was carried out collaboratively. Notably, the two-step preparation process could be used industrially and is environmentally sustainable, particularly as both the copper nitrate solution and BTC solution can be reused. The size and quantity of MOF199 on the bamboo surface could be easily controlled and the crystal growth mechanism was studied. The antibacterial properties of MOFs coated bamboo were analyzed. This study provides a new strategy for the fabrication of MOF-functionalized woody materials.

**Experimental**

**Materials and chemicals**

*Moso* bamboo (*Phyllostachys edulis*) of four-year-old was obtained from Yongan, Fujian, China. The bamboo samples were cut into segments of 20 mm × 25 mm × 4 mm (L × T × R), ultrasonically cleaned with deionized water for 30 min, and then vacuum dried at 60 °C for 24 h before use.

Copper nitrate trihydrate [Cu(NO₃)₂·3H₂O], 1,3,5-benzentricarboxylic acid (BTC, C₆H₃(COOH)₃], and sodium chlorite (NaClO₂, 80%) were purchased from Aladdin Chemistry Co. Ltd (Shanghai, China). Sodium hydroxide (NaOH), chloroacetic acid sodium

---

**Scheme 1** Illustration of the two-step in situ growth of MOF199 on pretreated bamboo with antibacterial properties
salt (CICH2COONa), acetic acid (CH3COOH), anhy-
drous ethanol (C2H5OH), triethylamine ((C2H5)3 N),
and N, N-dimethylformamide (DMF, (CH3)2NCHO)
were purchased from Beijing Chemical Works (Beijing,
China). All chemicals were used as received
without further purification and deionized (DI) water
was throughout the process.

Pretreatment of bamboo

Three batches of pretreated bamboo were obtained by
delignification and carboxymethylation separately and
collaboratively, the experimental process is as
follows:

Delignification: Natural bamboo samples were
initially delignified by dipping in an aqueous solution
of 1 wt% sodium chlorite (pH = 4.6, acetic acid) at
100 °C for 1 h. Subsequently, the delignified bamboo
samples were rinsed with DI water, dried in a vacuum
oven for 24 h, and marked as DB.

Carboxymethylation: Carboxymethylation of bam-
boo was carried out through a condensation reaction
between cellulose and chloroacetate salt in the pres-
ence of sodium hydroxide (Laurila et al. 2015; Wang
et al. 2012). Natural bamboo and DB samples were
respectively submerged in sodium hydroxide solution
(1 M) for 30 min at room temperature, and the
samples were then soaked in 1 M aqua solution of
chloroacetate salt for 30 min and dried at 85 °C for
30 min. Later, the samples were acidified with 2 g/L
aqueous solution of acetic acid for 10 min at room
temperature. Finally, the pretreated samples were
washed with DI water to remove the excess precursor,
dried in a vacuum oven for 24 h, and marked as
carboxymethylated bamboo (CB), delignified and
carboxymethylated bamboo (DCB).

In situ growth of MOF199 on bamboo

The synthesis of MOF199 on bamboo was performed
using a two-step route according to the previous
literature, with some slight adjustments (Lange and
Obendorf 2015). In the typical synthesis reaction,
copper nitrate trihydrate (17.9 g) was dissolved in
250 mL mixed solvent DMF/ethanol/water (v/v/v = 1:1:1) as solution A, BTC (10.4 g) was dissolved in
250 mL of the same mixed solvent DMF/ethanol/
water (v/v/v = 1:1:1) and 1.25 mL of triethylamine
was added, as solution B. Four kinds of bamboo
samples (natural bamboo, DB, CB, and DCB) were
respectively submerged in solution A overnight at
room temperature. After that, the samples were
removed and the excess liquid was wiped off, and
the samples was then submerged in solution B for
another 24 h. Finally, the as-prepared four kinds of
MOF199 coated bamboo were washed with ethanol
and water and named as MOF199/B, MOF199/DB,
MOF199/CB, MOF199/DCB, respectively.

Tailoring crystal size of MOF199

4.48, 8.95, 17.9, and 35.8 g of copper nitrate trihydrate
were individually dissolved in 250 mL solvent solu-
tion of DMF/ethanol/water (v/v/v = 1:1:1). The DCB
samples were immersed in four concentrations of
copper nitrate solution overnight. After removing the
excess liquid, the samples were placed in solution B
for another 24 h, respectively. Finally, the obtained
samples were washed with ethanol and water and
named as MOF199/DCB-1, MOF199/DCB-2,
MOF199/DCB-3, and MOF199/DCB-4, respectively.

Alternative synthesis of MOF199 on bamboo

The DCB samples were first immersed overnight in
solution B. Subsequently, the samples were taken out
to remove the excess liquid attached and transferred
solution A for another 24 h. After that, the obtained
samples were washed with ethanol and water and
named rMOF199/DCB.

Characterization

Microstructure investigations were performed using
scanning electron microscopy (SEM, XL30ES-HFEG, PHILIPS, Netherlands) at 10 kV. Elemental
analysis was detected by an energy-dispersive X-ray
spectroscopy (EDS, quantax400, Bruker). FTIR spec-
tra were collected with a Thermo iS10 FT-IR
spectrometer (Nicolet, USA) using an attenuated total
reflection (ATR) module, at a scanning number of 64
and spectral resolution of 4 cm−1, ranging from 600 to
4000 cm−1. The crystalline structures of the samples
were identified by X-ray diffraction (XRD, X’ Pert
PRO MPD, Nalytical, Netherlands) using Cu Kα radi-
ation at a scan rate of 2°/min and generator voltage
of 40 kV, ranging from 5° to 80°. X-ray photoelectron
spectroscopy (XPS, Thermo ESCALAB 250Xi, USA)
was used to analyze the elemental valence, which was obtained using an ESCALab MKII X-ray photoelectron spectrometer with Al Kα radiation as the excitation source.

Antibacterial test

The antibacterial properties of MOF199 coated bamboo against *E. coli* (ATCC 25922) were evaluated according to the Japan Industry Standard JIS Z 2801-2000 and Chinese Industry Standard QB/T 2591-2003. On the surface of each sample, 0.2 mL bacterial suspension with a concentration of 5.0–10.0 × 10⁵ CFU/ml was added, and each sample was covered by polyethylene films (18 × 18 mm²). The inoculated samples were then incubated for 24 h (37 ± 1 °C, RH > 90%). After incubation, each sample and the polyethylene film were rinsed with 20 mL eluent (with 0.5% Tween 80), the dilutions of each sample were collected, and 20 μL of each dilution was inoculated in nutrient broth and cultured for another 24 h at 37 ± 1 °C. Finally, the number of bacterial colonies in each sample was calculated according to Chinese Standard GB 4789.2–2016, and the actual data was presented as the CFU/piece. The antibacterial test for each sample was repeated three times.

The antibacterial rate calculation formula is as follows:

\[
AR(\%) = \frac{B - C}{B} \times 100\%
\]

In which: AR—Antimicrobial rate (%). B—Average number of recovered bacteria in the blank control sample (CFU/piece). C—Average number of recovered bacteria in the antibacterial sample (CFU/piece).

Results and discussion

Morphology and chemical composition of pretreated bamboo

Bamboo principally consists of parenchyma and fiber, with a cell wall that is mainly composed of cellulose microfibrils embedded in a matrix composed of lignin and hemicellulose. Here, an efficient pretreatment method for bamboo was established by combining delignification with carboxymethylation, in which delignification could increase the porosity of bamboo templates and facilitate the permeation of the precursor solution, while carboxymethylation could improve the attachment of MOFs on the bamboo surface. As control, individual pretreatment with delignification or carboxymethylation were also performed. To investigate the influence of pretreatment on the morphology and chemical composition of bamboo, SEM images and FTIR spectra of natural and pretreated bamboo, DB, CB, and DCB, were obtained. As shown in Fig. 1f, g, and h, the hierarchically organized cell structures of DB, CB, and DCB were well preserved. However, images of the cell corner (Fig. 1j, k, l) revealed that delignification or carboxymethylation pretreatment removed the innermost surface layer of the parenchyma cell walls.

Delignification is effective to increasing the porosity of the bamboo. After delignification, nanoscale pores and multilayer cell wall structures appeared in the cell wall and middle lamellae (Fig. 1j, l), suggesting a higher porosity. The parenchyma cell surface of DB and DCB (Fig. 1b, d) is smoother than that of natural bamboo (Fig. 1a), because of the highly ordered cellulose of the microfibrils exposed after lignin removal (Chen et al. 2020). From the macroscopic view in Fig. 1m, the original yellowish bamboo became bleached (DB) after delignification, indicating successful removal of the dark-colored lignin with the colorless polysaccharides exposed (Guan et al. 2018). The delignification treatment was further identified by FTIR, and the characteristic peaks of lignin at 1655, 1600, 1512, 1458, and 834 cm⁻¹ disappeared in DB (Fig. 1n).

To enhance the bonding strength between MOF199 and bamboo, the carboxyl groups were introduced to the bamboo surface by carboxymethylation. Remarkably, the increase of bands at 1594 cm⁻¹ observed in CB indicated that the active carboxyl group was successfully introduced into the bamboo surface by carboxymethylation. Meanwhile, the hemicelluloses (mannan and xylan) and some lignin-like polyphenols in the innermost surface layer were removed by the alkali treatment (Kim et al. 2012), as the entire absence at 1729 cm⁻¹ (hemicellulose-related peaks) and a significant decrease at 1245 cm⁻¹ (hemicellulose and lignin-related peaks) were found in the FTIR spectra of CB. These results are in good agreement with those from research on carboxymethylation of European beech (*Fagus sylvatica*) (Tu et al. 2020).
According to previous research, alkali treatment of bamboo can also improve the surface roughness of bamboo (Costa et al. 2017), which is conducive to the attachment of MOFs onto the bamboo surface.

To facilitate the introduction of carboxyl groups, collaboration of delignification and carboxymethylation treatment of bamboo were performed. Delignification increases the surface porosity of the bamboo, and exposes the cellulose in the cell wall, thus facilitating carboxymethyl reactions. As noted, a new large wide peak at 1540–1650 cm\(^{-1}\) appeared in the DCB, which was attributed to the C=O stretching vibration in the introduced carboxyl groups (Duan et al. 2019b). Meanwhile, the characteristic peaks of lignin (1655, 1512, 1458, and 834 cm\(^{-1}\)) and hemicellulose (1729 and 1245 cm\(^{-1}\)) and in DCB disappeared in the FTIR spectra. SEM images showed that several folds appeared in the parenchyma cell wall of DCB, accompanied by the hollow of the cell wall corner (Fig. 1d, h, l), resulting from the loss of hemicellulose and lignin.

Tailoring growth of MOF199 on Bamboo

**In situ growth of MOF199 on pretreated bamboo**

SEM images of the MOF199 grown on the parenchyma and fiber cell surface of pretreated bamboo are

---

Fig. 1 SEM images of natural bamboo (a, e, i) and pretreated bamboo DB (b, f, j), CB (c, g, k), and DCB (d, h, l); Optical images (m) and ATR-FTIR spectra (n) of natural bamboo and pretreated bamboo DB, CB, and DCB.
shown in Fig. 2 and Fig. S1. For MOF199/B, only loose and small-sized MOF199 crystals were observed (Fig. 2a, e and Fig. S1a, e). For MOF199/DB, uniform crystals with octahedral shapes and relatively large sizes were observed (Fig. 2b, f and Fig. S1b, f), at approximately 0.9–2.4 nm (Fig. S2b). For MOF199/CB, large numbers of MOF199 with relatively small sizes (about 0.6–1.5 nm, Fig. S2c) were distributed uniformly (Fig. 2c, g and Fig. S1c, g). Furthermore, a much denser MOF199 layer was observed on MOF199/DCB (Fig. 2d and Fig. S1d) and magnified images (Fig. 2h and Fig. S1h) revealed that the crystal size on MOF199/DCB was the smallest among the three pretreated bamboo samples, around 0.3–1.2 nm (Fig. S2d).

It is important to determine the loading amount of MOF199 on bamboo surface, and thermogravimetric (TGA) analysis and BET surface area measurements were attempted (Bunge et al. 2020), but were not possible due to the MOF199 layer being thin relative to the entire bamboo substrate. Here, the EDS spectra of the four kinds of MOF199-coated bamboo and natural bamboo are presented in Fig. 2a, b, c, d, and Fig. S3, respectively. The elemental analysis results also demonstrated that the copper content of MOF199/DCB (11.1%) was higher than that of MOF199/CB (8.5%) and MOF199/DB (6.0%), while MOF199/B had a minimum copper content of 0.5%, which is consistent with the SEM results and our prediction. Figure 3 shows the X-ray diffractograms of natural bamboo and MOF199 coated bamboo. The three diffraction peaks at 20 = 16°, 22.5°, and 35° could be attributed to the (1–10)/(110), (200), and (004) crystal faces of cellulose, respectively. And the new peaks at 6.6°, 9.5°, and 11.5° correspond to the (200), (220), and (222) crystal faces of MOF199, respectively, consistent with other literature (Loera-Serna et al. 2012; Wang et al. 2015; Lis et al. 2019). XRD analysis indicated the successful synthesis of MOF199 on bamboo. It should be noted that, the MOF199/DCB sample displayed the sharpest characteristic peaks of all the samples, suggesting that combined delignification and carboxymethylation is conducive for the crystal growth of MOF199 on the surface of bamboo. These results indicate that pretreatment is essential for the in-situ growth of MOF199 on bamboo.
Tailoring crystal size of MOF199 on bamboo

The crystal size could also be controlled in our two-step synthesis process by adjusting the concentration of the copper nitrate solution. Four gradient concentrations of copper nitrate solutions with a unified concentration of BTC solution were used to perform the same procedure, and four different MOF199/DCB samples were subsequently obtained. SEM results and particle size measurements suggest that the crystal size of MOF199 increased with increasing Cu$^{2+}$ concentration (Fig. 4 and Fig. S4). Besides, the EDS analysis revealed that the Cu content of the MOF199/DCB samples increased with the addition of Cu$^{2+}$ ion in the prepared solution (Table S1). Similarly, the same increasing trend was observed in the XRD pattern (Fig. S5), and the FTIR spectra (Fig. S6) for the MOF199 characteristic peaks.

Interaction analysis between MOF199 and bamboo

FTIR was used to investigate the interaction between MOF199 and the bamboo cell wall after delignification/carboxymethylation, the spectra are shown in Fig. 5. The possible interaction between MOF199 and bamboo occurs through the coordination of Cu (II) and the carboxyl group. The peaks at 730, 762, 1375, and 1447 cm$^{-1}$ in the MOF coated bamboo were in strong consistency with MOF199 (Lange and Obendorf 2015; Song et al. 2011). Compared with natural bamboo, the new peak at 1648 cm$^{-1}$ in MOF199/B replaced the original peak at 1653 cm$^{-1}$ (C=O groups of lignin structure), which is attributed to the absorption band of the carboxyl group in MOF199 (Abdelhameed et al. 2016; Küsgens et al. 2009).

Compared with the DB samples, the C=O peak of carboxyl group in MOF199/DB shifted from 1635 cm$^{-1}$ (Fig. 1n) to 1643 cm$^{-1}$ (Fig. 5a, b), resulting from the interaction between MOF199 and bamboo through the coordination of carboxyl group from hemicellulose and Cu$^{2+}$ (Abdelhameed et al. 2016). Similarly, the bands at 1642, and 1640 cm$^{-1}$ in MOF199/CB and MOF199/DCB also exhibited a similar shifting trend (Fig. 5a, b), compared with the C=O peak of –COO$^-$ in the CB (1594 cm$^{-1}$) and DCB (1599 cm$^{-1}$) samples (Fig. 1n), respectively. This absorption band shift can be attributed to the changes in the metal–carboxylate interaction from COO$^-$–Na$^+$ to COO$^-$–Cu$^{2+}$ (Tu et al. 2020). With an increase in the carboxyl group (green boxed section in Fig. 1n) of the pretreated bamboo (DB, CB, DCB), the COO$^-$–Cu$^{2+}$ characteristic absorption band around 1648 cm$^{-1}$ in MOF199 shifted to a lower wavenumber in MOF199/DB, MOF199/CB, MOF199/DCB samples (Fig. 5b). This shift demonstrated that MOF199 anchors onto the pretreated bamboo by forming a carboxyl-copper (II) complex.

The strong interaction between MOF199 and the carboxyl groups introduced in the pretreated bamboo was verified by performing an ultrasonic desorption test. The results showed that after 20 min of sonication of the aqueous solution, only trace amounts of MOF199 remained on the surface of the bamboo prepared by the deposition method (Fig. S7a). In comparison, after treatment under the same ultrasonic conditions, a large amount of MOF199 remained on the surface of MOF199/DCB (Fig. S7b). In summary, the FTIR results and ultrasonic desorption test demonstrated strong interaction between the pretreated bamboo and MOF199, which is beneficial for the anchoring of MOFs on bamboo substrates. It is known that MOF199 is water unstable, but the crystals appear to maintain their integrity on the surface of the bamboo in air, which is important in practical applications. However, a full study of the stability of MOF199 on the surface of bamboo needs further research.
Growth mechanism of MOF199 on bamboo

In our synthesis route, the growth of MOF199 was a separate two-step process, including the adsorption of copper (II) ions and the desorption-nucleation process. In the first step, the adsorption of Cu$^{2+}$ was initiated after immersing bamboo in copper nitrate trihydrate, which is mainly divided into two forms: weak adsorption and strong adsorption. Weak adsorption refers to the physical adsorption of Cu$^{2+}$ on the hierarchical bamboo surface. Strong adsorption refers to the binding between Cu$^{2+}$ and the strong polar groups of cellulose units, carboxylic acid of hemicellulose or phenolic hydroxyl groups, and aromatic esters of lignin (Hoffmann et al. 2008; Rowell 1984).

In the second step, after placing the Cu-adsorbed bamboo in copper nitrate trihydrate solution, the Cu$^{2+}$ ions are desorbed from the bamboo surface and nucleate into MOF199 crystals. These crystals grow and attach to the bamboo surface, forming a MOF199 layer on the bamboo surface.

Fig. 4 SEM images of MOF199/DCB-1 (a), MOF199/DCB-2 (b), MOF199/DCB-3 (c), and MOF199/DCB-4 (d)

Fig. 5 a ATR-FTIR spectra of natural Bamboo, MOF199/B, MOF199/DB, MOF199/CB, MOF199/DCB, and MOF199. b Partial magnification of the green box portion of the ATR-FTIR spectrum in (a)
bamboo blocks in the BTC solution, the adsorbed Cu$^{2+}$ with weak interactions desorb in the solution. The polydentate ligand BTC captures the free Cu$^{2+}$ and forms molecule clusters. Meanwhile, the carboxyl-copper (II) complex on pretreated bamboo acts as a nucleation site and allows in situ MOF199 growth by attracting free ions and clusters in solution.

The cell wall of bamboo is mainly composed of lignin, cellulose and hemicellulose, and the formation mechanism of MOF199 on pretreated bamboo with different functional group fractions is shown in Scheme 2. The carbonyl or carboxylic functions of lignin may explain why natural bamboo shows a slight affinity toward MOF199 crystals (Küsgens et al. 2009). After delignification, the hemicellulose of DB was exposed, which facilitated the coordination with Cu$^{2+}$ for the subsequent MOFs growth, as most of the carboxyl groups in bamboo originate from hemicellulose components, such as glucuronic acid (Michell et al. 1965). Carboxymethylation of natural bamboo alone can also promote MOFs attachment by introducing active carboxyl groups in the phenolic hydroxyl of lignin and the alcohol of cellulose (Konduri et al. 2015). Collaboration of delignification and carboxymethylation would introduce large numbers of carboxyl groups in the cellulose of DCB, providing sufficient active sites for coordinating Cu$^{2+}$, thus forming a dense and evenly distributed MOF199 coating. However, the large number of carboxyl-copper (II) complexes would initiate the rapid nucleation of MOFs, which leads to quick precursor consumption and relatively small-sized MOF199 crystals on the bamboo surface (Fig. 2h) (Su et al. 2019).

The order of immersion in copper nitrate or BTC solution was found to be another critical factor for the growth of MOF199 on bamboo surface by the two-step manufacturing process. In our hypothesis, the initial absorption of Cu$^{2+}$ on pretreated bamboo is critical for the growth of MOF199. By exchanging the order of immersion of the two precursor solutions, the sample was prepared as rMOF/DCB. As expected, few crystals were found on the rMOF/DCB surface with a different truncated octahedral morphology (Fig. S8). XRD and FTIR results confirmed that these crystals exhibited the same characteristic peaks as MOF199 (Figs. S5 and S6). In the XPS data, the Cu 2p$_{3/2}$ spectrum of MOF199/DCB (Fig. 6a) shows three peaks at 935.2, 940.2, and 944.1, all corresponding to Cu–O in MOF199 (Li et al. 2014). While the asymmetrical Cu 2p$_{3/2}$ peak of rMOF/DCB split into two peaks, the emerging stronger characteristic peak at 932.6 eV was attributed to Cu–O in the carboxyl-copper (II) complex, and the weak characteristic peaks at 934.8 eV belong to MOF199 (Fig. 6b) (Lemaire et al. 2016; Chawla et al. 1992; Senthil Kumar et al. 2013; Zhong 1989). XPS results suggested that the rMOF/DCB sample adsorbed a large amount of Cu$^{2+}$ by carboxyl group, and only a small amount of them eventually formed MOF199 crystals. The results further demonstrated that the attachment of Cu$^{2+}$ on the modified bamboo could serve as nucleation sites for the formation of MOF199 crystals, which is the key to the preparation of uniform MOF layers.

Antibacterial properties of MOF199 coated bamboo

*Escherichia coli* is a common bacterium that endangers human health. The antibacterial activity test results of MOF199 coated bamboo for *E. coli* are shown in Fig. 7. Pristine bamboo showed very low antibacterial activity, as it contains only weak natural antibacterial substances (Afrin et al. 2012). In contrast, the number of surviving bacterial colonies on the plate significantly decreased in the MOF199 coated samples. The antibacterial property of MOF199 coated samples were ranked by antibacterial ratio (AR) in decreasing order as follows: MOF199/DCB (91.4%), MOF199/CB (69.8%), MOF199/DB (64.9%), and MOF199/B (55.6%). Particularly, the MOF199/DCB resulted in the lowest number of surviving colonies, suggesting that the uniform and well-dispersed dense MOF199 coatings on bamboo would lead to better antibacterial properties. Previous studies shown that the particle size and shape appear to be the most significant variables determining the antibacterial activity of solids. And decreasing the particle size might be beneficial as it can considerably enhance the surface area, as well as the increased density of edge and corner sites on the surface of nanoparticles (Wyszogrodzka et al. 2016). Therefore, tailoring growth of MOF199, including its crystal size and amount, is of great significance for the optimal antibacterial properties of woody materials.

To study the antibacterial mechanism of MOF199, the antibacterial performance of bamboo with only adsorption of Cu$^{2+}$ (named B-Cu and DCB-Cu
Scheme 2 sketches represent the growth mechanism of MOF199 on pretreated bamboo.
samples) or BTC (named B-BTC sample) were investigated as control. As shown in the Fig. S9, the control samples with only copper ions (B-Cu and DCB-Cu) show very weak bactericidal activity. And the even lower antibacterial rate of B-BTC further confirm that the antibacterial activity of MOF loaded bamboo is mainly derived from the MOF199.

According to the literature, the antibacterial activity of MOFs is achieved mainly through physical contact, metal ions and ligands, oxidative stress, and photothermal effects (Liu et al. 2021). MOF199 has an octahedral structure, therefore the physical contact resulting in damage to the bacterial cell membrane may be a reason for antibacterial activity. It is well known that the Copper (II) ions can denature proteins and fatty acids in the bacterial cell membrane or alter the transmembrane potential, leading to cell rupture and death (Wang et al. 2015; Wyszogrodzka et al. 2016). However, Rodríguez et al. (2014) and Jo et al. (2019) suggested that Cu-based active sites on surface primarily make Cu-MOF crystals responsible for the excellent bactericidal property over the chemical properties of the constituents, owing to Cu-MOFs cannot easily release Copper (II) ions on their surfaces. We believe that the antibacterial activity of MOF199 involves more than one mechanism, and the surface-active metal sites, metal ions and physical contact work synergistically to combat bacteria.

Conclusions

In this work, in situ growth of MOF199 on bamboo surface was tailored via pretreatment and a green two-step synthesis route. The results showed that the collaboration of delignification and carboxymethylation pretreatment of bamboo facilitated the formation of a dense and durable MOF199 layer, which exhibited excellent antibacterial activity against Escherichia coli (E. coli). In addition, the quantity of MOF199 increased with an increase in the number of introduced carboxyl groups, while the crystal size of MOF199...
increased with an increase in the concentration of copper solution. In particular, the formation of carboxyl-copper (II) complexes serving as nucleation sites was found to be a critical factor affecting the in-situ growth of MOF199 on bamboo surface. This study provides an optimized strategy for preparing MOF/woody composites with great potential for various applications.

Acknowledgments The work was financially supported by the National Natural Science Foundation of China (Grant No. 31901377) and the Fundamental Research Funds for International Center for Bamboo and Rattan (No. 1632019016).

Author contributions MS: Methodology, Investigation, Writing—Original Draft. RZ: Software, Formal analysis, Writing—Review & Editing, Project administration, Funding acquisition. JL: Software, Formal analysis. XJ: Resources. XZ: Data Curation. DQ: Supervision, Project administration.

Declarations

Conflict of interest The authors declare no conflicts of interest.

References

Abdelhameed RM, Abdel-Gawad H, Elshahat M, Emam HE (2016) Cu–BTC@cotton composite: design and removal of ethion insecticide from water. RSC Adv 6:42324–42333. https://doi.org/10.1039/c6ra04719j

Afrin T, Tsuzuki T, Kanwar RK, Wang X (2012) The origin of the antibacterial property of bamboo. J Text I 103:844–849. https://doi.org/10.1080/00405000.2011.614742

Bunge MA, Ruckart KN, Leavesley S, Peterson GW, Nguyen N, West KN, Glover TG (2015) Modification of fibers with nanostructures using reactive dye chemistry. Ind Eng Chem Res 54:3821–3827. https://doi.org/10.1021/acs.iecr.5b00089

Bunge MA, Pasciak E, Choi J, Haverhals L, Reichert WM, Glover TG (2020) Ionic liquid welding of the UIO-66-NH2 MOF to cotton textiles. Ind Eng Chem Res 59:19285–19298. https://doi.org/10.1021/acs.iecr.0c03763

Chawla SK, Sankaranarayanan N, Payer JH (1992) Diagnostic spectra for XPS analysis of Cu–O–S–H compounds. J Electron Spectrosc 56:1–18. https://doi.org/10.1016/0022-7050(92)80047-c

Chen C, Li Z, Mi R, Dai J, Xie H, Pei Y (2020) Rapid processing of whole bamboo with exposed, aligned nanofibrils toward a high-performance structural material. ACS Nano 14(5):5194–5202. https://doi.org/10.1021/acsnano.9b08747

Costa MME, Melo SLS, Araújo EA, Cunha GP, Deus EP, Schmitt N (2017) Influence of physical and chemical treatments on the mechanical properties of bamboo fibers. Procedia Eng 200:457–464. https://doi.org/10.1016/j.proeng.2017.07.064

Da Silva PM, Sierra-Avila CA, Hinerestroza JP (2012) In situ synthesis of a Cu-BTC metal–organic framework (MOF 199) onto cellulose fibrous substrates: cotton. Cellulose 19:1771–1779. https://doi.org/10.1007/s10570-012-9752-y

Duan C, Meng J, Wang X, Meng X, Sun X, Xu Y (2018) Synthesis of novel cellulose-based antibacterial composites of Ag nanoparticles@metal–organic frameworks@carboxymethylated fibers. Carbohydr Polym 193:82–88. https://doi.org/10.1016/j.carbpol.2018.03.089

Duan C, Liu C, Meng X, Lu W, Ni Y (2019a) Fabrication of carboxymethylated cellulose fibers supporting Ag NPs@MOF-199s nanocatalysts for catalytic reduction of 4-nitrophenol. Appl Organomet Chem 33:e4865. https://doi.org/10.1002/aoc.4865

Duan C, Meng X, Liu C, Lu W, Liu J, Dai L (2019b) Carbohydrates-rich corncobs supported metal–organic frameworks as versatile biosorbents for dye removal and microbial inactivation. Carbohydr Polym 222:115042. https://doi.org/10.1016/j.carbpol.2019.115042

Guan H, Cheng Z, Wang X (2018) Highly compressible wood sponges with a spring-like lamellar structure as effective and reusable oil absorbents. ACS Nano 12:10365–10373. https://doi.org/10.1021/acsnano.8b05763

Guo J, Rennhofer H, Yin Y, Lichtenegee HG (2016) The influence of thermo-hydro-mechanical treatment on the micro- and nanoscale architecture of wood cell walls using small- and wide-angle X-ray scattering. Cellulose 23:2325–2340. https://doi.org/10.1007/s10570-016-0982-2

Hoffmann SK, Goslar J, Ratajczak I, Mazela B (2008) Fixation of copper-protein formulation in wood: Part 2. molecular mechanism of fixation of copper(II) in cellulose, lignin and wood studied by EPR. Holzforschung 62:300–308. https://doi.org/10.1515/hf.2008.032

Jo JH, Kim H-C, Huh S, Kim Y, Lee DN (2019) Antibacterial activities of Cu–MOFs containing glutarates and bipyridyl ligands. Dalton Trans 48:8084–8093. https://doi.org/10.1039/c9dt00791a

Kim JS, Awano T, Yoshinaga A, Takabe K (2012) Ultrastructural observations and chemical treatments on the mechanical properties of whole bamboo with exposed, aligned nanofibrils toward a high-performance structural material. ACS Nano 14(5):5194–5202. https://doi.org/10.1021/acsnano.9b08747

Kim ML, Otal EH, Hinerestroza JP (2019) Cellulose meets reticular chemistry: interactions between cellulose substrates and metal–organic frameworks. Cellulose 26:123–137. https://doi.org/10.1007/s10570-018-2203-7

Konduri MK, Kong F, Fatehi P (2015) Production of carboxymethylated lignin and its application as a dispersant. Eur Polym J 70:371–383. https://doi.org/10.1016/j.eurpolymj.2015.07.028

Küsgens P, Siegle S, Kaskel S (2009) Crystal growth of the metal–organic framework Cu3(BTC)2 on the surface of cellulose.
Loera-Serna S, Oliver-Tolentino MA, de Lourdes L-Núñez M, Liu J, Wu D, Zhu N, Wu Y, Li G (2021) Antibacterial mechanisms and applications of metal–organic frameworks. ACS Appl Mater Interfaces 7:3974–3980. https://doi.org/10.1021/acsami.6b03104

Laurila E, Thunberg J, Argent SP, Champness NR, Zacharias S, Westman G, Ohrström L (2015) Enhanced synthesis of metal–organic frameworks on the surface of electrospun cellulose nanofibers. Adv Eng Mater 17:1282–1286. https://doi.org/10.1002/adem.201400565

Lemaire PC, Zhao J, Williams PS, Walls HJ, Shepherd SD, Losego MD (2016) Copper benzenetricarboxylate metal–organic framework nucleation mechanisms on metal oxide powders and thin films formed by atomic layer deposition. ACS Appl Mater Interfaces 8:9514–9522. https://doi.org/10.1021/acsami.6b01195

Li Y, Wang LJ, Fan HL, Changguan J, Wang H, Mi J (2014) Removal of sulfur compounds by a copper-based metal–organic framework under ambient conditions. Energy Fuel 29:298–304. https://doi.org/10.1021/ef501918f

Li J, Wu Z, Bao Y, Chen Y, Huang C, Li N (2017) Wet chemical synthesis of ZnO nanocoating on the surface of bamboo timber with improved mould-resistance. J Saudi Chem Soc 21:920–928. https://doi.org/10.1016/j.jscc.2015.12.008

Li J, Su M, Wang A, Wu Z, Chen Y, Qin D, Jiang Z (2019) In situ formation of Ag nanoparticles in mesoporous TiO₂ films decorated on bamboo via self-sacrificing reduction to synthesize nanocomposites with efficient antifungal activity. Int J Mol Sci 20:5497. https://doi.org/10.3390/ijms20215497

Li Z, Hori N, Takeamura A (2020) A comparative study of depositing Cu-BTC metal–organic framework onto cellulose filter paper via different procedures. Cellulose 27:6537–6547. https://doi.org/10.1007/s10570-020-03229-z

Lis MJ, Caruzi BB, Gil GA, Samulewski RB, Bail A, Scacchetti MJ, Caruzi BB, Gil GA, Samulewski RB, Bail A, Scacchetti

Löwe MD (2016) Copper benzenetricarboxylate metal–organic framework: the effect of the method of synthesis. J Appl Polym Sci 133:16839–16846. https://doi.org/10.1002/app.40815

Su M, Zhang R, Li H, Jin X, Li J, Yue X, Qin D (2019) In situ deposition of MOF199 onto hierarchical structures of bamboo and wood and their antibacterial properties. RSC Adv 9:40277–40285. https://doi.org/10.1039/c9ra07046f

Tu K, Puértolas B, Adobes-Vidal M, Wang Y, Sun J, Traber J (2020) Green synthesis of hierarchical metal–organic framework/wood functional composites with superior mechanical properties. Adv Sci. https://doi.org/10.1002/advs.201902897

Wang Z, Hauser PJ, Laine J, Rojas OJ (2012) Multilayers of low charge density polyelectrolytes on thin films of carboxymethylated and cationic cellulose. J Adhes Sci Technol 25:643–660. https://doi.org/10.1163/016942410x525876

Wang C, Qian X, An X (2015) In situ green preparation and antibacterial activity of copper-based metal–organic frameworks/cellulose fibers (HKUST-1/CF) composite. Cellulose 22:3789–3797. https://doi.org/10.1007/s10570-015-0754-4

Wyszogrodzka G, Marszalek B, Gil B, Dorozynski P (2016) Metal–organic frameworks: mechanisms of antibacterial action and potential applications. Drug Discov Today 21:1009–1018. https://doi.org/10.1016/j.drudis.2016.04.009

pulp fibers. Adv Eng Mater 11:93–95. https://doi.org/10.1002/adem.200800274

Lange LE, Obendorf SK (2015) Functionalization of cotton fiber by partial etherification and self-assembly of polyoxometalate encapsulated in Cu₃(BTC)₂ metal–organic framework. ACS Appl Mater Interfaces 7:3974–3980. https://doi.org/10.1021/am506510q

Nasruddin ZA, Yulita F, Buhori A, Muahdzib M, Ghiyats M, Saha BB (2020) Synthesis and characterization of a novel microporous lanthanide based metal–organic framework (MOF) using naphthalenedicarboxylic acid. J Mater Res Technol 9:7409–7417. https://doi.org/10.1016/j.jmrt.2020.05.015

Qiu L, Wang L, Zhang M, Zhang M, Wu G (2020) A facile strategy for fabrication of HKUST-1 on a flexible polyethylene nonwoven fabric with a high MOF loading. Microporous Mesoporous Mater 292:107923. https://doi.org/10.1016/j.micromeso.2019.109723

Rodríguez HS, Hinesroza JP, Ochoa-Puentes C, Sierra CA, Soto CY (2014) Antibacterial activity against Escherichia coli of Cu-BTC (MOF-199) metal–organic framework immobilized onto cellulose fibers. J Appl Polym Sci 131:1–5. https://doi.org/10.1002/app.40815

Rowell R (1984) The chemistry of solid wood. American Chemistry Society, Washington, DC

Senthil Kumar R, Senthil Kumar S, Anbu Kalandainathan M (2013) Efficient electrosynthesis of highly active Cu₃(BTC)₂-MOF and its catalytic application to chemical reduction. Microporous Mesoporous Mater 168:57–64. https://doi.org/10.1016/j.micromeso.2012.09.028

Song J, Luo Z, Britt DK, Furukawa H, Yaghi OM, Hardcastle KI, Hill CL (2011) A multiunit catalyst with synergistic stability and reactivity: a polyoxometalate-metal organic framework for aerobic decontamination. J Am Chem Soc 133:16839–16846. https://doi.org/10.1021/ja203695h

Ma K, Idrees KB, Son FA, Maldonado R, Wasson MC, Zhang X et al (2020) Fiber composites of metal–organic frameworks. Chem Mater 32:7120–7140. https://doi.org/10.1021/acs.chemmater.0c02379

Michell AJ, Watson AJ, Higgins HG (1965) An infrared spectroscopic study of delignification of eucalyptus regnans. Tappi 48:520–532

Wang Z, Rojas OJ (2012) Multilayers of low charge density polyelectrolytes on thin films of carboxymethylated and cationic cellulose. J Adhes Sci Technol 25:643–660. https://doi.org/10.1163/016942410x525876

Wang C, Qian X, An X (2015) In situ green preparation and antibacterial activity of copper-based metal–organic frameworks/cellulose fibers (HKUST-1/CF) composite. Cellulose 22:3789–3797. https://doi.org/10.1007/s10570-015-0754-4

Wyszogrodzka G, Marszalek B, Gil B, Dorozynski P (2016) Metal–organic frameworks: mechanisms of antibacterial action and potential applications. Drug Discov Today 21:1009–1018. https://doi.org/10.1016/j.drudis.2016.04.009
Zhang J, Zhang B, Chen X, Mi B, Wei P, Fei B, Mu X (2017) Antimicrobial bamboo materials functionalized with ZnO and graphene oxide nanocomposites. Materials (basel) 10:239. https://doi.org/10.3390/ma10030239

Zhang R, Li Y, He Y, Qin D (2020) Preparation of iodopropynyl butycarbamate loaded halloysite and its anti-mildew activity. J Mater Res Technol 9:10148–10156. https://doi.org/10.1016/j.jmrt.2020.07.019

Zhong ZL (1989) XPS study of coordination of Cu(II) with 2-mercaptobenzothiazole. J Struct Chem 8:301–304. https://doi.org/10.14102/j.cnki.0254-5861.1989.04.010

Publisher’s Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.