Antibacterial performance of Ag-doped TiO$_2$/wood surface under visible light irradiation and its superior mould-resistance

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Abstract. The TiO$_2$/wood (TW) based on fast-growing poplar wood was in situ synthesized through one-step solvothermal method and then Ag-doped TiO$_2$/wood (ATW) was also prepared via the solvothermal method. The morphologies, crystal structure, and chemical characteristics of the composites were carried out by SEM, XRD, XPS and FTIR. The results of XPS and FTIR showed that the nanoparticles (TiO$_2$ and Ag) were chemically bonded to the wood surface through the combination of hydrogen groups. Spherical-like Ag nanoparticles (Ag-NPs) was about 66 nm diameter. What’s more, the TW and ATW showed excellent antibacterial against Gram positive and negative bacterium under visible light irradiation and mould-resistance properties, which illustrated a significance and practical value in high added-value of wood.

1. Introduction

As one of four building materials (plastic, cement, steel, wood), wood is the only sustainable one and wood possesses the advantages of high specific gravity, low production cost, beautiful structure and texture, good thermal insulation performance, small energy consumption, renewable and recycle, wide range of application, no poison, environment friendly, and so on [1, 2]. However, wood is easily attacked by microorganisms like bacteria and mould [3, 4]. There are multiple of researches in antibacterial species such as various natural and inorganic templates [5]. With a high specific surface area and a fraction of surface atoms, metal nanoparticles such as Ag, Cu, and Nd, have been explored widely due to their unique physicochemical performances such as optical or electronic properties, catalytic activity, and antibacterial activity [6, 7]. Among these metal nanoparticles, Ag-NPs are well known because of inhibitory and bactericidal effects. Resistance to antibacterial agents by pathogenic bacteria has developed in recent years, which is also a major sustainable development issue [8]. It can be expected that the high specific surface area and high fraction of surface atoms of Ag-NPs will lead to high antibacterial activity as compared with bulk silver metal. Unfortunately, it is limited due to high-cost for its applications especially as large-area antibacterial coatings. Therefore, the combination the advantages of Ag with economic nanoparticles of metal oxides such as TiO$_2$, ZnO, and WO$_3$ could design an economical antimicrobial coating [9, 10]. Among these nanoparticles, TiO$_2$, a wide band gap and nontoxic semiconductor metal oxides, has attracted considerable research interest owing to its unique optical, electronic, and atalytic properties. The nanostructured synthesis of TiO$_2$ consisted of the nano-particles, nano-rods or nanotubes, which were applied to various fields such as catalysts, dye sensitized solar cells, pigments, and self-cleaning surfaces [11, 12]. However, there were only several researches on the antimicrobial activity of TiO$_2$. Furthermore, the synergy of Ag-NPs with the antimould and antibacterial performances of TiO$_2$ on surface of wood under visible light irradiation have not been
In this study, the prepared Ag-doped TiO$_2$ on wood surface were evaluated against two types of bacterias. Furthermore, mould-resistance activity was evaluated against three different kinds of moulds.

2. Experiments

2.1 Materials
The size of wood, which was sampled from the sap wood sections of poplar wood (Populusussuriensis Kom) in Hangzhou City, Zhejiang Province, is 10mm (length) × 10mm (width) × 10mm (thickness). The material was marked as OW. All the reagents were provided by Shanghai Boyle Chemical Co., Ltd. All the reagents were all nalytically pure grade and could be used directly without secondary purification.

2.2 Preparation of TiO$_2$/wood (TW) and Ag-doped TiO$_2$/Wood (ATW) by solvothermal method
First, wood was ultrasonically rinsing in ethanol, acetone and deionized water for 30 min, respectively, and dried in a vacuum oven at 45 °C for 48h. The humidity of the wood was measured by drying the wood until the weight was constant. The resulting humidity was 7%. The wood was immersed in of tetrabutyl titanate [Ti(OC$_4$H$_9$)$_4$] (4 mL) in 50 mL absolute ethanol and then hydrochloric acid (1 mL) was dropped dropwise into the solution with stirring for 30 min. After that, the solution with the wood was transferred into a 100 mL Teflon container in an oven at 95 °C for 5h. Finally, the specimen was taken out, cleaned with acetone and ethanol for 30 min, respectively. Then dried in a vacuum oven at 45 °C for 48 h. The prepared specimen was marked TW.

The TW was placed in an Teflon container with 4 mL tetrabutyl titanate solution, 50 mL acetic acid and1.0 g of AgNO$_3$. The solvothermal reaction was carried out at 160 °C for 3 h. After the solvothermal process, the specimens were washed by deionized water and then dried at 60 °C. The prepared specimen was marked ATW.

2.3 Characterizations
The Characterizations of the samples were shown in Text S1

2.4 The tests of antibacterial and mould-resistance performances

2.4.1 Antibacterial performance
According to the bacterial inhibition ring method (a gar plate diffusion test/CEN/TC248WG 13) and the reduction of bacterial growth test (ENISO 20743:2007 Transfer Method), antimicrobial performance were carried out carefully[13]. Antibacterial properties of the specimens were evaluated against was evaluated against two different types of bacteria--- *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*, ATCC 25922, Gram-positive bacterium). In detail, the nutrient broth and nutrient agar 1L distilled water at pH 7.2 as well as the empty Petri plates were mixed and autoclaved. The agar medium was then cast into the Petri plates and cooled in laminar airflow. Approximately 105 colony-forming units of each bacterium were inoculated on plates, and then specimens were grown onto the agar plates. All the plates were incubated at 37°C for 24h with a visible lamp (λm (mean)= 525 nm, 18 K lux), following which the zone of inhibition was measured. Three parallel specimens were tested. The number of living bacteria was counted. Remove (R %) is considered as antimicrobial efficiency, which is as follows:

\[
R (\%) = \frac{(B - M)}{B} \times 100\%
\]

B is the average bacteria counts on blank specimen. In contrast, M is the average bacteria counts on modified specimen.

2.4.2 Mould resistance test
Mould-resistance performance of OW, TW, and ATW was evaluated against three different kinds of mould------*Aspergillus niger* (*A. niger*), *Aspergillus terreus* (*A. terreus*), and *Paecilomyces variotii* (*P.
The specimens were exposed in an environment chamber to allow fungal growth under controlled conditions (95% relative humidity, 25 °C). Mould resistance test was conducted referenced to AWPA Standard EN24-06. Samples were tested after three weeks. Mould growth on each specimen was visually rated using the following criteria (complete description of visual rating scheme given in the AWPA Standard) (Table S1). The lower the infection value means the better the efficiency of treatment.

3. Results and discussion

Fig. 1 showed the SEM images and EDS spectra of the specimens. Fig. 1a exhibited that the OW showed typical wood structure and smooth surface. After a solvothermal process, the surface showed a coat of TiO$_2$ microparticles, (Fig. 1b). Then the TW was covered with a compact coat of Ag-NPs through the solvothermal synthesis to form the ATW shown in Fig. 1c and d. Further, the mean diameter of Ag nanoparticles was about 66 nm learned from Fig. 1d. Fig. 1e displayed that there were only C, Ti, Au, and O elements in TW. The element of Au derived from the coating layer used for SEM observation. The C and O elements were from the wood substrate and Ti element derived from TiO$_2$. From the EDS spectrum of ATW in Fig. 1f, obvious peak of Ag element was presented except for the signals of C, Ti, Au, and O element, indicating there was Ag loaded onto the surface of TW.

![Fig. 1 SEM images and EDS spectra of OW (a), TW (b) and ATW (c and d); EDS of TW (e) and ATW (f)](image-url)
Fig. S1 presented the XRD patterns of ATW and TW. The peaks at 22° and 16° were referred to the typical planes (002) and (101) in wood cellulose [14], while sharp peaks at 2θ of centered at 25.2°, 38.0°, 47.8°, 54.2°, 62.5°, 68.8°, and 74.9°, which could be ascribed to (101), (004), (200), (211), (204), (116) and (215) planes, which can be attributed to TiO$_2$ in the anatase form (PDF card 21-1272, JCPDS) [15]. Furthermore, for ATW, new sharp peaks at 2θ of centered at 38.1°, 44.2°, 64.4°, and 77.4° could be ascribed to (111), (200), (220) and (311) planes of cubic phase of Ag (PDF card 04-0783, JCPDS) [16]. These results confirmed that the TiO$_2$-doped (TW) and Ag-doped TiO$_2$ (ATW) on the surface of wood were successfully synthesized.

In Fig. 2a, the fully spectra showed that the Ti, O, and C elements in both of the ATW and TW while a new binding energy of around 370 eV assigned to Ag on the ATW. The C element could be attributed to the wood. These results were well consistent with that of XRD and EDS. In Fig. 2b, the Ti 2p XPS peak of the ATW could be fitted into two components Ti$^{4+}$ species (459.3 eV) and Ti$^{3+}$ species(458.9 eV). In addition, in the Ti 2p XPS spectra of the TW, the two peaks at 459.0 eV and 464.8 eV were attributed to the Ti 2p$_{3/2}$ and Ti2p$_{1/2}$, respectively. The existence of Ti$^{4+}$ was illustrated due to the gap of 5.7 eV between the two peaks. However, the red shift of the peak of Ti2p in the ATW compared with that of the TW confirmed a lower electron density of the Ti atom in the ATW, illustrating a strong interaction between metallic Ag and TiO$_2$ (the insert in Fig. 3b). From Fig. 2c, O1s XPS spectra with three peaks at binding energies of 530.4 eV, 532.9 eV, and 533.2 eV, attributing to O (Ti-O), O(O-H), and adsorbed O (O2 or C-O). As shown in Fig. 2d, the Ag3d XPS spectra with two peaks at 367.6 eV and 373.6 eV were corresponded to the Ag3d$_{3/2}$ and Ag 3d$_{3/2}$ peaks, respectively. The gap of 6.0 eV between the two peaks was also existing form of metallic Ag instead of Ag$^+$. Moreover, the peaks of Ag3d showed the blue shift to the lower position, illustrated that the electrons migrated to metallic Ag from the TiO$_2$ particles in the interface of ATW heterostructures.

Fig. 2 XPS spectra of TW and ATW: (a) survey spectra; (b) Ti 2p; (c) O1s; (d) Ag 3d.

Fig. S2 showed the FTIR spectra of OW, TW and ATW. For OW, the absorption peak at the 3400 cm$^{-1}$ derived from the wood surface due to the stretching vibrations of –OH. The intensity of hydroxyl
absorption peak at 3420-3400 cm⁻¹ band of TW was weakened, while the hydroxyl absorption peak intensity of ATW prepared by solvothermal synthesis significantly reduced, indicating that the Ag-TiO₂ may be combined with the surface of the wood through hydroxyl bond to a composite. The absorption peaks at 1423 cm⁻¹, 1261 cm⁻¹ and 1114 cm⁻¹ were the deformation vibration of Ti and the stretching vibration of Ti-OC [17]. The absorption peaks at 619 cm⁻¹ and 597 cm⁻¹ belonged to O-Ti [18]. However, both of the TW and ATW showed strong interaction of titanium dioxide at the 700-600 cm⁻¹ [19], which further showed that titanium dioxide is generated on the wood surface by the solvothermal method.

Antibacterial and mould-resistance properties analysis: More importantly, the both of TW and ATW exhibited superior antimicrobial and mould-resistance activities in the dark shown in Fig. 3. The R% of TW reached 94.9% and 96.4% toward E. coli and S. aureus, respectively. Simultaneously, the R% of ATW reached 99.0% and 90.5% toward E. coli and S. aureus, respectively. The ATW exhibited better antibacterial performance than TW as for gram-negative bacterium while the TW showed better antibacterial property than ATW for gram-positive bacterium. The rating of OW reached four toward A. niger, A. terreus, and P. variotii (Table 1). However, both of the TW and ATW illustrated grade zero toward A. niger, A. terreus, and P. variotii, further indicating that TW and ATW were better mould-resistance ability. As well known, silver was proved to possess antibacterial performance [20]. Ag-NPs in the ATW played a metal antibacterial agent role and a kind of doping metal in TW. It was reported that tetravalent Ti ions in TiO₂ would be substituted by monovalent Ag ions, resulting in various defects like oxygen vacancies [21], which might be benefit for the strengthen of antibacterial property of the ATW. Hence, both of the TiO₂/wood and Ag-doped TiO₂/wood possessed superior antibacterial and mould-resistance properties and Ag-doped TiO₂/wood was better than TiO₂/wood in antibacterial performance as for gram-negative bacterium.

Fig. 3. Antibacterial activity of TW and ATW toward E. coli (a) and S. aureus (b); Mould-resistance performance of OW, TW, and ATW toward A. niger, A. terreus, and P. variotii, respectively.
Table 1 Antibacterial rate and mould-resistance Rating

| Specimen | R (%) against E. coli | R (%) against S. aureus | Rating |
|----------|----------------------|------------------------|--------|
| OW       | 4                    | 0                      |        |
| TW       | 94.9                 | 96.4                   | 0      |
| ATW      | 99.0                 | 90.5                   | 0      |

4. Conclusion

In summary, the Ag-doped TiO₂ on wood surface was fabricated successfully through the solvothermal synthesis method. Furthermore, TiO₂ and Ag nanoparticles were connected on wood surface in situ by hydrogen bond. The results exhibited that the average particle size of Ag-NPs was about 66 nm and they were well dispersion. The antibacterial tests against S. aureus, E. coli and mould-resistance tests against A. niger, A. terreus, and P. variotii showed that Ag-doped TiO₂/wood had good antibacterial and mould-resistance performance, which illustrated that the Ag-doped TiO₂/wood could be applied in fields such as for the low-cost materials for antibacterial floor, nano-antibacterial furniture. Furthermore, the methods may be regarded as a candidate for the profitable antibacterial biomass-based composite materials in the home decoration, public places, as well as work office.

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