Preparation and Properties of Nano-TiO_2-Chinese Herbal Medicine Composite Wood

Xiaoqi Zhao,[1] Jie Wang,[1] Lei Wang, Shiming Ren, Zheng Hu, and Yamei Wang *

The sol-gel method was used to make nano-TiO_2 and five Chinese herbal medicines of *Sophora flavescens* Alt., *Hypericum perforatum* L., *Cnidium monnieri* (L.) Cuss., *Kochia scoparia* (L.), and *Zanthoxylum bungeanum* Maxim. to prepare five kinds of nano-TiO_2-Chinese herbal medicine composite anti-degradative wood. *Populus tomentosa* Carr was chosen as the wood sample. Indoor decay resistance test results showed that the resistance to weight gain and decay of nano-TiO_2-Chinese herbal medicine composite anti-degradative wood noticeably increased compared with either Chinese herbal medicine modified wood or nano-TiO_2 modified wood, reaching a strong decay resistance level. The results of the anti-loss test showed that the magnitude of loss of wood samples treated with nano-TiO_2 and Chinese herbal medicine was noticeably reduced compared with that with just Chinese herbal medicine. It was found by scanning electron microscopy that the nano-TiO_2 particles and the Chinese herbal medicine enter the wood cell cavity, and the wood vessels and pits were the main permeation channels. Fourier transform infrared analysis results showed that nano-TiO_2 could not only enter the wood interior, and associate with wood components through physical adsorption to form hydrogen bonds, but also through the carboxyl groups in cellulose and hemicellulose, or the phenolic hydroxyl group in lignin, forming a coordinated chemical bond to fix it in the wood component.

Keywords: *Sol-gel method*; *Nano-TiO_2; Chinese herbal medicines*; *Mechanism*; *Anti-loss test*

Contact informational: College of Materials Science and Art Design, Inner Mongolia Key Laboratory of Sandy Shrubs Fibrosis and Energy Development and Utilization, Inner Mongolia Agricultural University, Hohhot 010018 China; [1]: These two authors contributed to this work equally;
** Corresponding author: wangym80@126.com*

INTRODUCTION

In recent years, nanotechnology has become an active research direction in the field of wood. Combining nanotechnology with wood science will bring broad prospects for wood preservation. In the next few years, new material preparation technologies developed based on nanotechnology, such as wood modification technology, wood anti-degradative technology, wood composite preparation, *etc.*, will greatly influence the development direction of the wood industry (Usmani *et al*. 2018, 2020). TiO_2 is a type of inorganic antimicrobial agent with photo-catalytic activity with strong antimicrobial activity, high safety, good heat resistance, and weatherability (Kathavate and Deshpande 2020; Yang *et al*. 2020). TiO_2 will generate -OH, O^{2-}, H_2O_2, and other substances with strong oxidation property when TiO_2 is exposed to light (Yang *et al*. 2018). These substances enter into the cell membrane and degrade the cell membrane after the metabolism is out of balance by changing the concentration of each component. The photo-catalytic and strong oxidation of TiO_2 is used to act on substances in the cell and gradually promote cell death as TiO_2

enters the cell (Kathavate and Deshpande 2020). Moreover, the strongly oxidizing -OH can rapidly and effectively decompose nutrients needed for the growth and survival of bacteria and play a bactericidal and bacteriostasis role (Gherardi *et al*. 2018). The durability of TiO_2 as an antibacterial agent is better than other common antibacterial agents (Yu *et al*. 2020).

The sol-gel method is currently one of the most widely used methods for preparing nanometer titanium dioxide in the laboratory. The principle is that ester compounds or metal alkoxides form a uniform solution in an organic solvent after adding other components. The hydrolysis reaction and polycondensation reaction will occur in a certain temperature environment, and a sol is gradually formed. Nanometer titanium dioxide with high purity and small particle size is obtained after high-temperature calcination (Priyanka *et al*. 2016). Vicente Hernandez *et al.* (2020) treated wood samples with different TiO_2 nanoparticles and evaluated the generation of free radicals and color changes after UV irradiation. The experimental results showed that the use of TiO_2 whose photosensitivity was suppressed could increase the content of phenoxy groups. The color change also achieved similar results. These results indicated that the photocatalysis of TiO_2 may be crucial to the performance of nanoparticles as a photoprotective treatment on the surface of wood (Hernandez *et al*. 2020). Iran Gomes da Rocha Segundo *et al.* (2018) proposed a cost-effective solution for the first time based on a low percentage of the combination of two semiconductors, TiO_2 and ZnO, using two photocatalytic techniques-spray deposition and asphalt modification. The results showed that TiO_2 nanoparticles and ZnO particles could make asphalt softer and have better anti-short-term aging effect, and will not cause any deterioration of asphalt before or after short-term or long-term aging (Segundo *et al*. 2018). Gholam Ali Shafabakhsh *et al.* (2020) studied the effects of nano SiO_2 and nano TiO_2 on the rheological behavior of asphalt. The results showed that adding different percentages of nanomaterials to asphalt could improve the asphalt's aging resistance and resistance to rutting and fatigue damage and improve the rheology of asphalt. The results showed that the use of 1.2% nano SiO_2 and 0.9% Nano TiO_2 had the best performance.

The main components of wood cell walls are cellulose, hemicellulose, and lignin, which contain a large number of hydroxyl groups. The main component of cellulose is β-D-glucose, each unit of which contains three active hydroxyl groups, which is the structural basis for condensation polymerization (Fernandez-Costas *et al*. 2017; Valette *et al*. 2017; Wang *et al*. 2018). Therefore, the prepared TiO_2 precursor sol can enter wood cells and intercellular spaces under the action of capillary tension, concentration gradient, and internal and external pressure difference (Ermeydan 2018). The wood is impregnated with inorganic nanoparticles. The hydroxyl groups on the surface of the particles are chemically bonded to the active hydroxyl groups in the wood cell wall, or they are deposited in the gap between the microfibrils in the amorphous region through physical adsorption (Antonelli *et al*. 2020). The hardness and density of wood cell walls can improve the physical properties of wood, such as improving mechanical properties, wear resistance, dimensional stability, bacteriostasis, flame retardancy, *etc.* Therefore, the durability of TiO_2 as an antibacterial agent is better than other ordinary antibacterial properties (Moongraksathum and Chen 2018; Iwatsu *et al*. 2020; Rokicka-Konieczna *et al*. 2020).

Poplar is a fast-growing wood widely planted in China, but it is susceptible to rot, mildew, and moth infestation, which seriously restricts its use. The antidegradation treatment of poplar is an effective way to improve its performance and value. As people pay more attention to environmental protection, more plant-derived wood preservatives are used in wood protection, such as Chinese herbal medicine extracts, vegetable oil, and konjac powder, *etc.* (Ahn *et al*. 2010; Bae *et al*. 2019; Bi *et al*. 2019; Ahmed *et al*. 2020).

However, due to the weathering resistance and easy loss of Chinese herbal medicine preservatives, the antifungal active ingredients in the Chinese herbal medicine extract are inactivated or lost, which affects the antiseptic effect (Tian *et al*. 2020). Therefore, the study uses the good weather resistance and antibacterial ability of nano-TiO_2. The Chinese herbal medicine extracts and nano-TiO_2 are effectively combined through the sol-gel method, so that the antibacterial properties of the two are complementary (Maness *et al*. 1999).

EXPERIMENTAL

Materials

Tetrabutyl titanate, ethanol, ice acetic acid, and nitric acid were purchased from Sinopharm Chemical Reagent Co., Ltd. (Hohhot, Inner Mongolia, China). *Sophora flavescens*, *Hypericum perforatum*, *Cnidium monnieri*, *Kochia scoparia*, and *Zanthoxylum bungeanum* were purchased from an Inner Mongolia Hohhot city pharmacy. *Matrine*, *Forsythin*, and *Osthol* standard were provided by Shanghai Pure Excellent Biotechnology Co., Ltd. (Shanghai, China).

Populus tomentosa Carr. (mature wood and sapwood) was produced in Hohhot (Inner Mongolia, China). The tree belongs to Salicaceae, which is widely used in urban greening. The sample size was 20 mm (R) × 20 mm (T) × 10 mm (L). The experimental strain *Trametes versicolor* (L.) Lloyd was selected and purchased from the Institute of Forest Ecology and Environment and Protection, Chinese Academy of Forestry (Beijing, China), and then cultivated and activated in the laboratory.

Instruments Analyze

The wood samples were cleaned with an ultrasonic cleaner ((KS-300EI; Ningbo Haishu Kesheng Co., Ltd., Ningbo, China). The drying oven was used for drying wood (DHG-9245A; Shanghai Qixin Co., Ltd., Shanghai, China). A hydrothermal reaction kettle was used for compounding of Chinese herbal medicine and TiO_2 sol (YZHR-250; Shanghai Yanzheng Co., Ltd., Shanghai, China). A vertical autoclave sterilizer was used for sterilization of culture medium and wood samples (SHENAN DSX-280; Shanghai Shen'an Medical Equipment Factory, Shanghai, China). The incubator with constant temperature and humidity is used to culture the strains and test the decay resistance of wood ((BSC-250; Shanghai Boxun Industry & Commerce Co., Ltd., Shanghai, China). Scanning electron microscopy (SEM) was used to observe the micromorphology of wood (FEI Quanta 200; Thermo Fisher Scientific, Waltham, MA, USA). A Fourier infrared spectroscopy analyzer was used to characterize specific tensile vibrations of chemical bonds (Dhg-9245a; Shanghai Qixin Scientific Instrument Co., Ltd., Shanghai, China). The chemical structures of *Matrine*, *Forsythin*, and *Osthol* were determined by nuclear magnetic resonance (NMR) (Bruker, Billerica, MA).

Test Specimens

The specimen diameter of 20 mm (R) × 20 mm (T) × 10 mm (L) was used of nature poplar wood, TiO_2-sol modified wood (TSMW), *Sophora flavescens*-treated wood (SFTW), nano-TiO_2-*Sophora flavescens* composite wood (NTSW), nano-TiO_2-*Hypericum perforatum* composite wood (NTHW), nano-TiO_2-*Cnidium monnieri* composite wood

(NTCW), nano-TiO_2-*Kochia scoparia* composite wood (NTFW), and nano-TiO_2-*Zanthoxylum bungeanum* composite wood (NTZW).

Experimental Methods

The poplar sample was immersed in distilled water and cleaned by ultrasonic vibrations for 20 min to remove impurities and contaminants on the wood surface. Then, the wood was pretreated by drying to constant weight in an oven at 80 ℃. The purpose of pretreatment was to improve the permeability of the poplar sample. This test, which has been used to show antibacterial property and decay resistance in research related to Chinese herbal medicine, showed that white-rot fungus had a bacteriostatic effect. However, the effect was not obvious. Five low-price Chinese herbal medicines were considered: *Sophora flavescens*, *Hypericum perforatum*, *Cnidium monnieri*, *Kochia scoparia*, and *Zanthoxylum bungeanum*. The ratio of 1:8 Chinese herbal medicine and distilled water was used, and the specimens were soaked for 30 min; then the mixture was heated and boiled (Zhang *et al*. 2020). Then the TiO_2 sol and the 0.6% *Sophora flavescens* water extract were added to the hydrothermal reactor at a ratio of 1:1.2, and the specimens were subjected to composite modification treatment by the hydrothermal method.

The five selected Chinese herbal medicines were prepared into 0.2 g/mL, 0.4 g/mL, 0.6 g/mL, 0.8 g/mL, and 1 g/mL water extract by water extraction method.

Next, nano-TiO_2-Chinese herbal compound anti-degradative agents were prepared for five kinds of Chinese herbal medicine in five concentrations under the conditions of adding 10 mL of titanium source, 4 h of soaking time, pH of 1, and temperature at 90 ℃ using the sol-gel method.

Preparation of nano-TiO_2-chinese herbal medicine composite preservative wood

The samples of poplar wood were placed in a drying oven at 103 ℃ to reach a constant weight, and then taken out for weighing. Five concentrations of *Sophora flavescens*, *Hypericum perforatum*, *Cnidium monnieri*, *Kochia scoparia*, and *Zanthoxylum bungeanum* were combined with nano-TiO_2 sol and then placed in the hydrothermal reaction kettle. The samples were modified and treated with nano-TiO_2 treatment materials and five kinds of Chinese herbal medicine treatment materials as the control group. Each group contained 20 samples. The processed samples were placed in the drying oven at 40 ℃ and baked to constant weight, denoted as WT. The weight gain (WPG) was calculated according to Eq. 1,

$$WPG = \frac{W_{\mathbf{C}} - W_{\mathbf{T}}}{W_T} \times 100\% \tag{1}$$

where WPG (%) is the percentage of weight gain, W_C (g) is the total dry mass of the poplar sample after impregnation, and W_T (g) is the total dry mass of untreated poplar samples.

Anti-loss test

The purpose of anti-loss test was to investigate the leaching effect of antibacterial ingredients in compound antidegradation wood. This experiment referred to the national standard in accordance to Chinese standard GB/T 29905 (2013) and the American AWPA E11-06 (2006) standard. Six specimens from each group with concentrations of 0.2 g/mL, 0.6 g/mL, and 1 g/mL were placed in a 500-mL beaker, and 180 mL distilled water was added to make the specimens immersed below the liquid level. The distilled water was replaced every 6 h, 24 h, and 48 h, and then every 48 h for a total of 14 d. The filtrate was collected after each change and combined for content analysis. After the test, the samples were taken out and wiped clean, and put in the drying oven at 103 ℃ for drying to the constant weight, and the weight was recorded. The loss of preservative components to be measured was calculated according to the Eq. 2,

$$L = \frac{m_A}{m} \times 100\% \tag{2}$$

where L (%) is the component loss of preservatives to be tested, m_A (mg) is the mass of preservative to be measured in the filtrate, and m (mg) is the total mass of preservative to be measured in wood sample.

All the test samples were calculated by weight changes before and after the anti-loss test, and the content of active components in the filtrate was determined by high performance liquid chromatography (HPLC, LC3010002; Fairborn Industrial Development Co. Ltd., Shanghai, China). Due to the limited experimental research on the effective ingredients of Chinese herbal medicine to inhibit wood decay fungi, only *Matrine*, *Forsythin*, and *Osthol* were found to be the effective antibacterial components of *Sophora flavescens*, *Hypericum perforatum*, and *Kochia scoparia* in Fig. 1. Therefore, the specific method for analyzing the anti-loss performance of this test was carried out as follows:

The samples treated with three Chinese herbs of *Sophora flavescens*, *Hypericum perforatum*, and *Cnidium monnieri* were tested for the concentration of the components in the filtrate by HPLC.

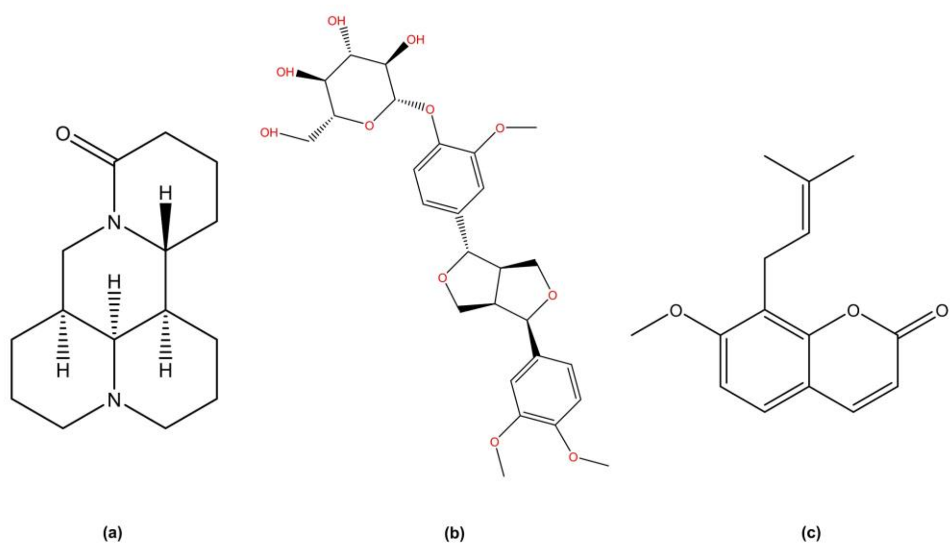


Fig. 1. Structure of the bacteriostatic components: the structure of *Matrine* (a); the structure of *Forsythin* (b); and the structure of *Osthol* (c)

The mobile phase of *S. flavescens* was acetonitrile-anhydrous ethanol-3% phosphoric acid solution (80:10:10). The mobile phase of *H. perforatum* was acetonitrile-water (25:75). The mobile phase of *C. monnieri* was acetonitrile-water (65:30). The filling agent was amino bonded silica gel and octadecylsilane bonded silica gel. The detection wavelength were 220 nm, 277 nm, and 322 nm.

The control substance of *Matrine*, *Forsythin*, and *Osthole* were precisely weighed and prepared. The control products were 0.05 mg/mL *Matrine* solution, 0.2 mg/mL

Forsythin solution, and 45 μg/mL *Osthole* solution. In accordance with the specific methods in the Chinese pharmacopoeia, the sample solutions were prepared, and 5 μL of each control sample solution and 5 to 10 μL of each test sample solution were precisely absorbed and injected into the liquid chromatograph for determination.

Through the regression equation, the concentration was calculated according to the peak area measured by the chromatogram, and then the percentage of the effective component was calculated according to the Eq. 3,

$$X = \frac{C \times V}{m} \times n \times 10^{-4} \tag{3}$$

where X (g/100 g) is the content of effective components of the filtrate, C (μg/mL) is the concentration calculated by the regression equation, V (mL) is the constant volume, m (g) is the sample quantity, n is the dilution multiple.

Indoor decay resistance test

This experiment was conducted with reference to China's forestry industry standard LY/T 1283 (2011). The river sand sawdust medium was prepared with a screw-capped wide-mouth flask to which 75 g of washed dry river sand (20- to 30-mesh), 7.5 g of Masson pine edge sawdust (20- to 30-mesh), 4.3 g of corn flour, and 0.5 g of brown sugar were added. Three pieces of wood were put on the surface, 50 mL maltose solution was slowly added into the bottle and the bottle cap tightened, and then it was put in the steam autoclave for sterilization for 1 h. Then it was removed and put on a clean table to cool down and become inoculated.

Activation and inoculation of strains-activation of strains for testing

The 5 mm diameter potato agar medium block was inoculated into the middle part of the river sand sawdust medium under aseptic operation conditions, and it was placed in a temperature of 28 ± 2 °C and humidity of 75 to 85%, cultivating for 10 d in a constant temperature and humidity incubator.

Sterilization and inoculation of the sample

The modified and absolutely dry samples were wrapped with multi-layer gauze and put in a triangular flask. Then, a little distilled water was added, and it was placed in a steam sterilization pot sterilize for 30 min under the conditions of pressure of 0.01 MPa and temperature of 121 ± 2 °C. The samples were taken out and quickly placed in the ultra-clean workbench after cooling, and the UV lamp was turned on to continue sterilization for 30 min. The sample was brought into contact with the forage wood that had been overgrown with hyphae in the culture bottle with a wide surface under aseptic operating conditions. A sample was placed on each piece of forage wood, and 3 samples were placed in each culture bottle.

Sample decay test

The sterilized samples were placed directly above the feeding wood in the culture bottle, and the culture bottle were placed in a constant temperature and humidity incubator with a temperature of 28 ± 2 °C and a humidity of 75 to 85% for 12 weeks after the mycelium in the sawdust culture medium was overgrown.

All light was cut off during the decay period except for the use of light during inspection. Water was added regularly and checked the temperature and humidity of the constant temperature and humidity box. The samples were removed from the culture bottle, and the surface of the samples was carefully scraped clean of mycelium and other impurities after 12 weeks. The samples were placed in the drying oven, and then dried at 40 ℃ to the constant weight. The recorded weights were accurate to 0.01 g.

The mass loss L after each sample was infected by bacteria was calculated according to the Eq. 4. There were 6 samples for each group, and the average value was taken. Finally, the mass loss was used as the evaluation index of the decay resistance of different samples, as in Eq. 4.

$$L = \frac{m_A}{m} \times 100\% \tag{4}$$

In Eq. 4, L (%) is the component loss of preservatives to be tested, m_A (mg) is the mass of preservative to be measured in the filtrate, and m (mg) is the total mass of preservative to be measured in wood sample.

The samples treated by different methods were decayed by wood decaying fungi, as shown in Fig. 2.

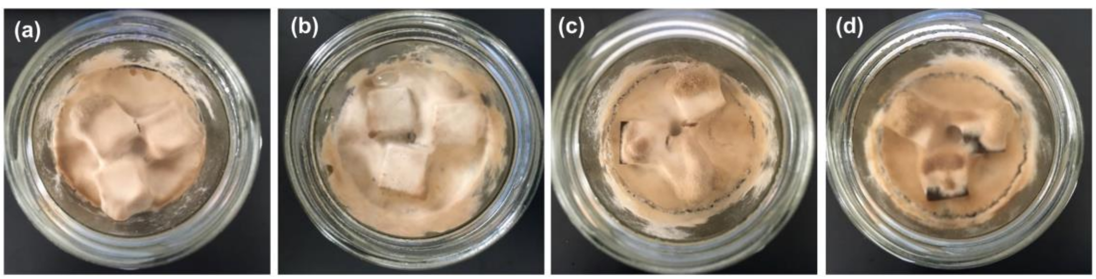


Fig. 2. Decay resistance of wood samples treated by different methods. Blank (a); Chinese herbal treatment wood (b); TiO_2 sol treatment wood (c); Nano-TiO_2-Chinese herbal compound antidegradation wood (d)

Structural Characterization

Scanning electron microscopy (SEM) and SEM-energy dispersive X-ray (EDX)

A blade was used to cut a thin slice of 10 mm × 10 mm × 1 mm, and it was placed on a clean sample table at the same position of each sample, and the surface was sprayed gold by Ion sputtering apparatus (GVC-1000; Beijing Zhongke Instrument Co. Ltd., Beijing, China) after vacuuming, and it was placed in an electron microscope for observation, and pictures of different positions were taken at different magnifications.

Fourier transform infrared (FTIR) analysis

The samples were placed in a constant temperature drying oven to be dried to absolute dryness. The samples were broken by a high-speed multifunctional crusher, sieved through a 200-mesh sieve and dried, and an appropriate amount of the dried samples were pressed with potassium bromide. The slice method was used to prepare the samples, and they were placed on the attenuated total reflectance (ATR) attachment (spectrum 100; Perkin-Elmer, Waltham, MA, USA) of the instrument sample stage for observation. The resolution was 4 cm^{-1}, and the number of scans was 32 times.

RESULTS AND DISCUSSION

Weight Gain and Decay Resistance Analysis

Table 1 shows the variance analysis of the weight gain data (P=0.25, P=0.1, P=0.1) of nano-TiO_2-Chinese herbal medicine composite antidegradative wood. Based on the F values obtained ($F_{0.25}(2, 2)=3$, $F_{0.1}(2, 2)=9$, $F_{0.05}(2, 4)=6.94$), it can be seen that $FA>F_{0.05}(2, 2)=6.94$, indicating that the influence of factor A on weight gain had a significant effect. $FB>F_{0.05}(2, 2)=6.94$, indicating that the influence of factor B on weight gain also had a significant effect. $FC=F_{0.25}(2, 2)=3$, indicating that factor C also had a certain effect on weight gain, but the effect was not significant. $FD<F_{0.25}(2, 2)=3$, indicating that factor D had no significant effect on weight gain (A: Immersion time, B: Titanium source addition amount, C: Immersion temperature, D: pH value).

Table 1. Analysis of Variance of Weight

Source of difference	SS	df	MS	F	P
total	0.0156	8			
A	0.0115	2	0.00575	57.5	*
B	0.0033	2	0.00165	16.5	
C	0.0006	2	0.0003	3	*
D	0.0001	1	0.0001	1	
error	0.0001	1	0.0001		
Note: * indicates a significant impact					

Table 2 shows the analysis of variance of the weight gain data (P=0.25, P=0.1, P=0.1) of nano-TiO_2-Chinese herbal medicine composite anticorrosive wood. It was found that $F_{0.25}(2, 2)=3$, $F_{0.1}(2, 2)=9$, $F_{0.05}(2, 4)=6.94$. It can be seen that $FA>F_{0.25}(2, 2)=3$, indicating that factor A has an influence on the weight gain. FB, FC, $FD<F_{0.25}(2, 2)=3$, indicating that factors B, C, D have no effect on the weight gain.

Table 2. Analysis of Variance of Weight Gain

Source of difference	SS	df	MS	F	P
total	28.2860	8			
A	14.6747	2	7.3374	3.5938	*
B	9.7564	2	4.8782	2.3892	
C	1.7222	2	0.8611	0.4217	
D	0.09103	1	0.0910	0.0446	
error	2.0417	1	2.0417		
Note: * indicates a significant impact					

Table 3 shows the analysis of variance of the weight loss data (P=0.25, P=0.1, P=0.1) of nano-TiO_2-Chinese herbal medicine composite anticorrosive wood. Because $F_{0.25}(2, 2)=3$, $F_{0.1}(2, 2)=9$, and $F_{0.05}(2, 4)=6.94$, it can be seen from the table that FA, $FB>F_{0.05}(2, 2)=6.94$, indicating that factors A and B had a significant effect on the weight loss. The comparison FC, FD<$F_{0.25}$(2, 2)=3, indicates that factors C and D had no significant effect on the weight loss.

Table 3. Analysis of Variance of Weight Loss

Source of difference	SS	df	MS	F	P
total	2.4936	8			
A	1.5403	2	0.7702	12.4426	*
B	0.6763	2	0.3382	5.4637	
C	0.1197	2	0.0599	0.9677	*
D	0.0954	1	0.0954	1.5412	
error	0.0619	1	0.0619		
Note: * indicates a significant impact					

The concentration of *Sophora flavescens*, *Hypericum perforatum*, *Zanthoxylum bungeanum*, *Cnidium monnieri*, and *Kochia scoparia*, five kinds of Chinese medicinal water extracts, was 0.6 g/mL. The concentrations of nano-TiO_2-*Sophora flavescens*, nano-TiO_2-*Hypericum perforatum*, nano-TiO_2-*Zanthoxylum bungeanum*, nano-TiO_2-*Cnidium monnieri*, nano-TiO_2- *Kochia scoparia* complex, and TiO_2 sol were 0.2 g/mL, 0.4 g/mL, 0.6 g/mL, 0.8 g/ mL, and 1 g/mL, respectively. Chinese medicinal water extracts and different concentrations of nano-TiO_2-Chinese herbal medicine were used to treated wood samples with white-rot.

Table 4 shows the weight loss after 12 weeks of bacterial decay. The weight loss of poplar wood without any treatment reached 51.0%, and the weight loss of poplar wood without treatment was greater than 45% after 12 weeks of indoor decay resistance test, and the test results were valid, as could be seen from Table 4. The weight loss values of the samples were 13.9%, 14.6%, 12.2%, 13.2%, and 15.3% after treatment with the concentration of 0.6 g/mL of *S. flavescens*, *H. perforatum*, *Z. bungeanum*, *C. monnieri*, and *K. scoparia*, respectively. All belonged to the II level of decay resistance, which indicated that the five-flavored Chinese herbal medicine had a certain decay resistance effect on the wood. It could also be seen that the decay resistance of the samples from strong to weak were *Z. bungeanum*, *C. monnieri*, *S. flavescens*, *H. perforatum*, and *K. scoparia*, and the range of weight gain was 6.67% to 7.02%. There was no noticeable difference in the drug loading of the test pieces after being treated with different Chinese herbal extracts. The weight loss of the sample treated with TiO_2 sol alone was 21.6%, which belonged to the II level of decay resistance, indicating that TiO_2 itself imparted certain decay resistance. The weight gain of the sample was 10.0%, which was greater than the wood test after the water extract treatment of Chinese medicine.

The weight loss of the wood samples treated with TiO_2 sol and five kinds of Chinese herbal medicines was considerably lower than that of the samples treated with Chinese medicine alone and the samples treated with TiO_2 sol alone, and the decay resistance level reached the I level. The results showed that the decay resistance of Chinese herbal medicines and TiO_2 sol improved after compounding.

Table 4. Results of Laboratory Tests

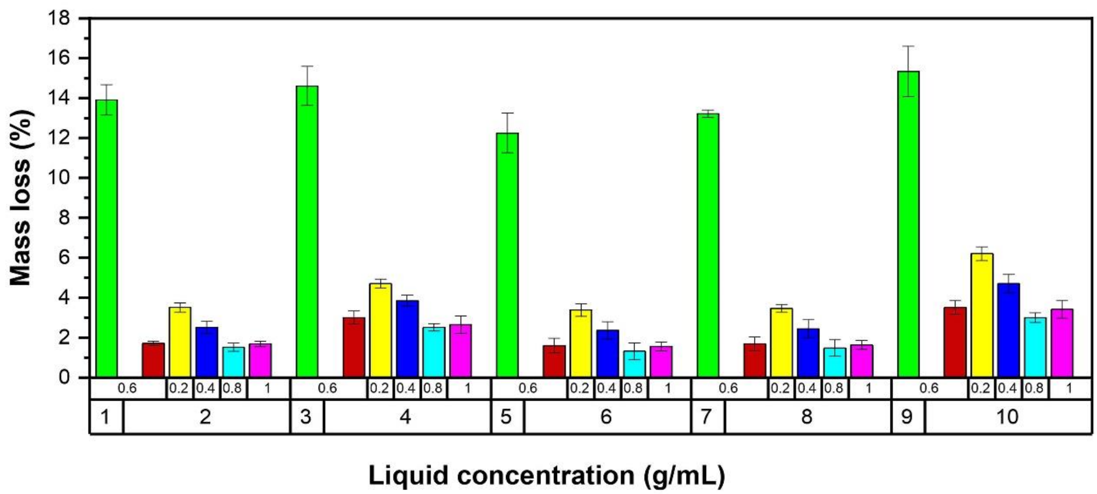
Preservatives	Solution Concentration (g/mL)	Average Weight Gain (%)	Mean Weight Loss (%)	Decay
Sophora flavescens Alt.	0.6	6.83	13.92	II
Nano-TiO_2-*Sophora flavescens* Alt.	0.2	18.32	3.52	I
	0.4	19.67	2.53	I
	0.6	21.21	1.71	I
	0.8	22.91	1.52	I
	1.0	22.44	1.69	I
Hypericum perforatum L.	0.6	6.92	14.61	II
Nano-TiO_2-*Hypericum perforatum* L.	0.2	18.41	4.71	I
	0.4	19.62	3.86	I
	0.6	20.98	3.01	I
	0.8	22.42	2.52	I
	1.0	23.75	2.66	I
Zanthoxylum bungeanum Maxim.	0.6	6.67	12.25	II
Nano-TiO_2-*Zanthoxylum bungeanum* Maxim.	0.2	18.47	3.39	I
	0.4	20.05	2.37	I
	0.6	21.71	1.61	I
	0.8	23.54	1.32	I
	1.0	24.68	1.57	I
Cnidium monnieri (L.) Cuss.	0.6	7.02	13.22	II
Nano-TiO_2-*Cnidium monnieri* (L.) Cuss.	0.2	18.52	3.47	I
	0.4	20.01	2.44	I
	0.6	21.63	1.69	I
	0.8	23.30	1.48	I
	1.0	24.79	1.63	I
Kochia scoparia (L.)	0.6	6.78	15.33	II
Nano-TiO_2- *Kochia scoparia* (L.)	0.2	17.99	6.21	I
	0.4	19.18	4.71	I
	0.6	20.51	3.52	I
	0.8	22.23	3.01	I
	1.0	23.72	3.42	I
TiO_2 sol	—	10.01	21.59	II
Raw material	—	—	50.96	—
Note: I (0%-10%): Strong decay resistance; II (11%-24%): decay resistance; III (25%-44%): Slight decay resistance; and IV (>45%): No decay resistance				

Note: Set five groups of parallel tests for each concentrations, repeat five times for each group of data, and take the average.

At the same time, TiO_2 can act as a carrier to load more Chinese herbal medicines into the wood, and this may be a contributing reason for the enhanced decay resistance of the samples. It can be seen from the weight gain and weight loss of the wood samples after five kinds of nano-TiO_2-Chinese herbal medicine composite treatment that there was no noticeable difference in the weight gain of the wood samples after the composite agent impregnation. It can be judged by the weight loss of the wood samples that the decay resistance of the composite agents from strong to weak were: nano-TiO_2-*Zanthoxylum bungeanum*, nano-TiO_2-*Cnidium monnieri*, nano-TiO_2-*Sophora flavescens*, nano-TiO_2-

Hypericum perforatum, and nano-TiO_2- *Kochia scoparia*. The order of decay resistance was the same as that of the five kinds of Chinese herbal medicine water extracts separately processing wood.

It can be seen from Fig. 3 that the weight loss of the wood samples after the five kinds of nano-TiO_2-Chinese herbal medicine composite treatments all showed a trend of first decreasing and then increasing with the increase of the concentration of the drug solution. When the concentration of the drug solution was 0.8 g/mL, and the weight loss was the smallest, the weight loss was 2, 4, 6, 8, and 10 was 1.71%, 2.52%, 1.32%, 1.48%, and 3.01%, respectively.



Note: Set five groups of parallel tests for each concentration, repeat five times for each group of data, and take the average.

Fig. 3. The weight loss of the wood samples: 1. *S ophora flavescens* Alt.; 2. Nano-TiO_2-*Sophora flavescens*; 3. *Hypericum perforatum* L.; 4. Nano-TiO_2-*Hypericum perforatum* L.; 5. *Zanthoxylum bungeanum* Maxim.; 6. Nano-TiO_2-*Zanthoxylum bungeanum* Maxim.; 7. *Cnidium monnieri* (L.) Cuss.; 8. Nano-TiO_2-*Cnidium monnieri* (L.) Cuss.; 9. *Kochia scoparia* (L.); and 10 Nano-TiO_2-*Kochia scoparia* (L.)

Table 5. Results of Anti-loss Performance

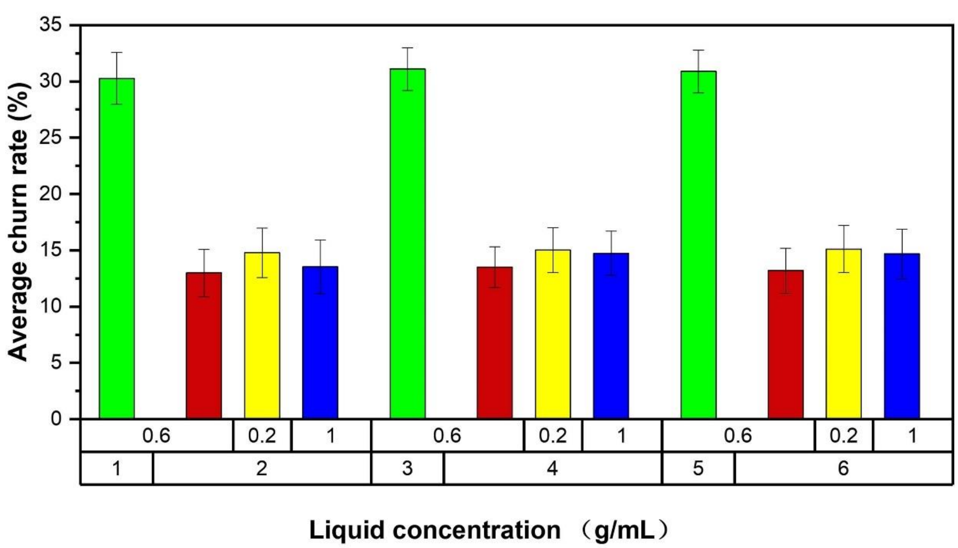
Preservatives	Solution Concentration (g/mL)	Average Weight Gain (%)	Average Leaching (%)
Sophora flavescens Alt.	0.6	6.79	30.26
Nano-TiO_2-*Sophora flavescens* Alt.	0.2	18.32	14.78
	0.6	21.21	12.99
	1.0	22.44	13.53
Hypericum perforatum L.	0.6	6.92	31.09
Nano-TiO_2-*Hypericum perforatum* L.	0.2	18.41	15.02
	0.6	20.98	13.51
	1.0	23.75	14.73
Cnidium monnieri (L.) Cuss.	0.6	7.02	30.89
Nano-TiO_2-*Cnidium monnieri* (L.) Cuss.	0.2	18.52	15.11
	0.6	21.63	13.20
	1.0	24.79	14.69

Note: Set five groups of parallel tests for each concentrations, repeat five times for each group of data, and take the average.

The weight gain of the wood sample increased with the increase of the concentration of the chemical solution, which showed that with the concentration of the chemical solution, the absorption of the wood sample gradually increased, and thus the decay resistance increased. When the concentration of the chemical solution increased from 0.8 g/mL to 1 g/mL, the decay resistance of the wood decreased. This may be because the concentration was too large. The decay resistance decreased as the loss increased. It could be seen from the test results that the TiO_2 sol promoted the absorption of the Chinese herbal medicine liquid by the wood sample and increased its decay resistance.

Analysis of Anti-loss Performance

Results for the anti-loss test of the samples treated with *Sophora flavescens*, *Hypericum* perforatum, and *Cnidium monnieri* by HPLC are shown in Table 5. It can be seen that the loss of wood samples after nano-TiO_2 and Chinese herbal medicine composite treatment was noticeably lower than that of wood samples treated only by Chinese herbal medicine combining Table 5 and Fig. 4. The loss of nano-TiO_2-*Sophora flavescens* composite anti-degradative wood in the treated samples was 57.1% less than that of *S. flavescens* treated material after the same concentration of liquid medicine (0.6 g/mL), and the loss of nano-TiO_2-*Hypericum perforatum* composite anti-degradative wood was 56.6% less than that of *H. perforatum* treated material. The loss of nano-TiO_2-*Cnidium monnieri* composite anti-degradative wood was 57.3% lower than that of *Cnidium monnieri* treated material. At the same time, it could be seen that the weight gain of the sample increases with the increase of the concentration of the drug solution, but the loss first decreased and then increased. When the concentration of the chemical solution was 0.6 g/mL, the loss of the three composite anti-degradative kinds of wood all reached the minimum. The losses of 0.6 g/mL Nano-TiO_2-*Sophora flavescens*, 0.6 g/mL Nano-TiO_2-*Hypericum perforatum*, and 0.6 g/mL Nano-TiO_2-*Cnidium monnieri* were 13.0%, 13.5%, and 13.2%.



Note: Set five groups of parallel tests for each concentrations, repeat five times for each group of data, and take the average.

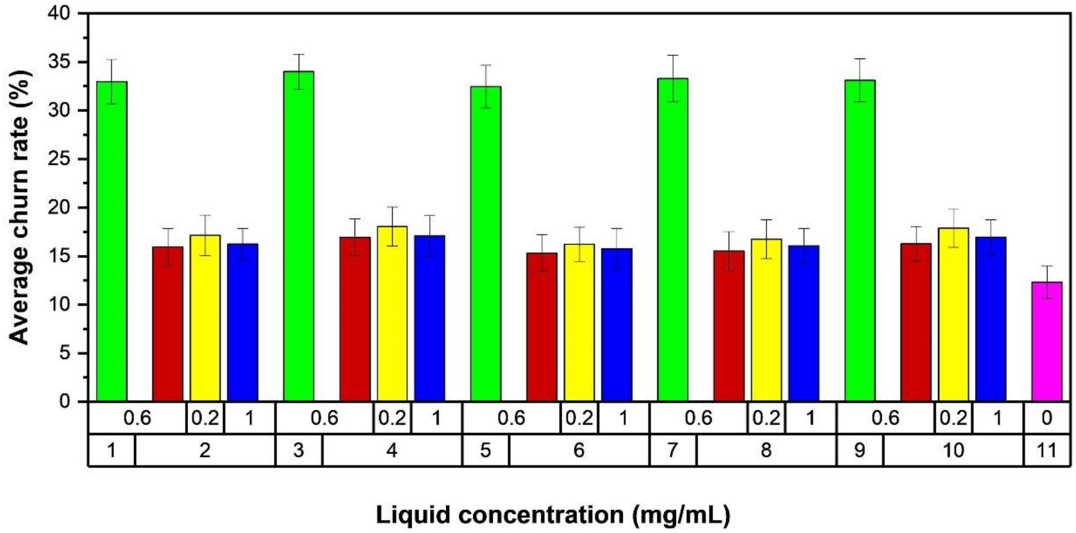
Fig. 4. Results of anti-loss performance: 1. *Sophora flavescens*; 2. Nano-TiO_2-*Sophora flavescens*; 3. *Hypericum perforatum* L.; 4. Nano-TiO_2-*Hypericum perforatum* L.; 5. *Cnidium monnieri* (L.) Cuss.; 6. Nano-TiO_2-*Cnidium monnieri* (L.) Cuss.

It could be seen that the loss of wood samples after nano-TiO_2 and Chinese herbal medicine composite treatment was noticeably lower than that of wood samples treated only with Chinese herbal medicine, combining Table 6 and Fig. 5. After the same concentration of liquid medicine (0.6 g/mL) the loss of nano-TiO_2-*Sophora flavescens* composite anti-degradative wood in the treated samples was 51.6% less than that of *Sophora flavescens*-treated material, and the loss of nano-TiO_2-*Hypericum perforatum* composite anti-degradative wood was 50.2% less than that of *Hypericum perforatum* treated material, the loss of nano-TiO_2-*Cnidium monnieri* composite anti-degradative wood was 53.4% less than that of *Cnidium monnieri* treated material, and the loss of nano-TiO_2- *Kochia scoparia* composite anti-degradative wood was 50.9% less than that of *K. scoparia* treatment. The loss of nano-TiO_2-*Zanthoxylum bungeanum* composite anti-degradative wood was 52.8% lower than that of *Z. bungeanum* treatment material. At the same time, it could be seen that the weight gain of the sample increased with the increase of the concentration of the drug solution, but the loss first decreased and then increased. When the concentration of the chemical solution was 0.6 g/mL, the average leaching of the five composite anti-degradative kinds of wood all reached the minimum. The average leaching of 0.6 g/mL Nano-TiO_2-*Sophora flavescens*, 0.6 g/mL Nano-TiO_2-*Hypericum perforatum*, 0.6 g/mL Nano-TiO_2-*Zanthoxylum bungeanum*, 0.6 g/mL Nano-TiO_2-*Cnidium monnieri*, and 0.6 g/mL Nano-TiO_2- *Kochia scoparia* were 15.96%, 16.93%, 15.31%, 15.53%, and 16.26%.

Table 6. Results of Anti-loss Performance

Antiseptic agent	Solution Concentration (g/mL)	Average Weight Gain (%)	Average Leaching (%)
Sophora flavescens Alt.	0.6	6.79	32.98
Nano-TiO_2-*Sophora flavescens* Alt.	0.2	18.32	17.14
	0.6	21.21	15.96
	1.0	22.44	16.25
Hypericum perforatum L.	0.6	6.92	34.01
Nano-TiO_2-*Hypericum perforatum* L.	0.2	18.41	18.05
	0.6	20.98	16.93
	1.0	23.75	17.08
Zanthoxylum bungeanum Maxim.	0.6	6.67	32.45
Nano-TiO_2-*Zanthoxylum bungeanum* Maxim.	0.2	18.47	16.22
	0.6	21.71	15.31
	1.0	24.68	15.77
Cnidium monnieri (L.)	0.6	7.02	33.29
Nano-TiO_2-*Cnidium monnieri* (L.) Cuss.	0.2	18.52	16.74
	0.6	21.63	15.53
	1.0	24.79	16.07
Kochia scoparia (L.)	0.6	6.78	33.11
Nano-TiO_2- *Kochia scoparia* (L.)	0.2	17.99	17.88
	0.6	20.51	16.26
	1.0	23.72	16.94
TiO_2 sol	—	10.01	12.31

Note: Set five groups of parallel tests for each concentrations, repeat five times for each group of data, and take the average.



Note: Set five groups of parallel tests for each concentration, repeat five times for each group of data, and take the average.

Fig. 5. Results of anti-loss performance: 1. *Sophora flavescens*; 2. Nano-TiO_2-*Sophora flavescens*; 3. *Hypericum perforatum*; 4. Nano-TiO_2-*Hypericum perforatum*; 5. *Zanthoxylum bungeanum*; 6. Nano-TiO_2-*Zanthoxylum bungeanum*; 7. *Cnidium monnieri* ; 8. Nano-TiO_2-*Cnidium monnieri*; 9. *Kochia scoparia*; 10. Nano-TiO_2- *Kochia scoparia*; 11. Blank

As can be seen in Tables 5 and 6, the loss trend of Chinese herbal medicine was consistent when detected by the two methods. The loss of the drug was noticeably reduced after adding nano-TiO_2, indicating that nano-TiO_2 can improve the anti-loss performance of the agent (Barbero-Lopez *et al*. 2021). However, it could be seen in Table 6 that the loss results in Table 5 were lower than the corresponding results. This might be due to the limited conditions when using HPLC to detect that the Chinese herbal medicines in the filtrate were effective. The concentration of bacteriostatic components could not be measured against the loss of nano-TiO_2 and other components in Chinese herbal medicine, so the results obtained were less than those obtained in Table 6.

The change trend of sample loss with the concentration and weight gain of the sample might be due to the fact that the concentration of preservatives must meet a certain value when the wood was treated with preservatives, and the main components of preservatives and wood components need to be combined. When the concentration was too small, the distance between molecules exceeded the range required to produce enough interaction, and it was unable to form precipitation of insoluble substances in the wood or chemical combination with wood, so as to achieve good anti-loss effect (Brischke 2020). When the concentration was too high, too many Chinese herbal medicine particles adhere to the surface of nano-TiO_2, making nano-TiO_2 easy to agglomerate to form particles with a larger particle size and deposit in the cell cavity, and cannot physically adsorb or chemically react with wood components, which was easy to drain (Sadeghnejad and Shafabakhsh 2017).

EDX Analysis of Surface Composition

The energy spectrum analysis of the surface composition of nano-TiO_2-Chinese herbal medicine composite anti-degradative wood sample by EDX is shown in Figs. 6 to 12. Figure 6 shows the analysis diagram of the main components of poplar wood, Fig. 7

illustrates the analysis diagram of the main components of TiO_2 modified wood, and Figs. 8 through 12 are the nanometer prepared by *Z. bungeanum*, *K. scoparia*, *S. flavescens*, *H. perforatum*, and *C. monnieri* of TiO_2-Chinese herbal medicine composite anti-degradative wood main component analysis diagram.

Figure 6 shows that the composition of poplar wood was mainly composed of two elements, C and O. The weight percentage (wt%) was 53.5% and 45.8%, and the atomic number percentages (At%) were 60.7% and 39.0%. The remaining elements Ca, P, K, Al, *etc.*, were trace elements present in wood, and the sum of weight percentage was 0.64 wt%, and the sum of atomic number percentage was 0.27 at%. The higher carbon content indicates that the wood mainly consists of lignin, cellulose, and hemicellulose.

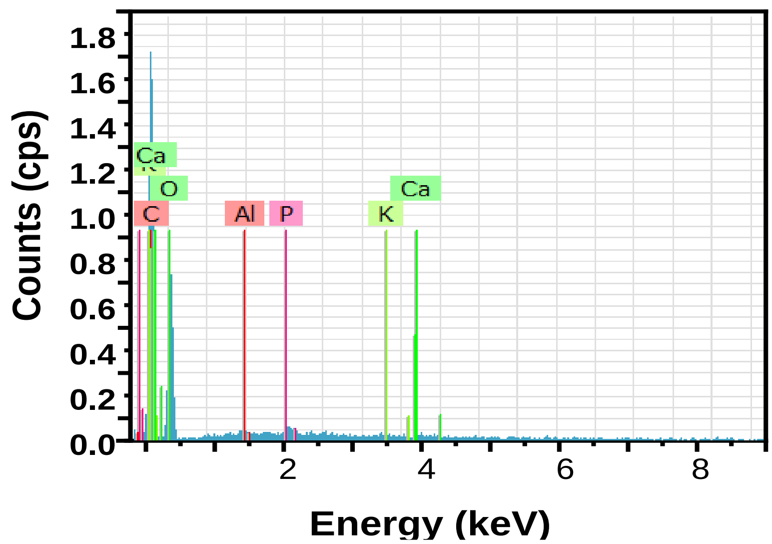


Fig. 6. The poplar wood

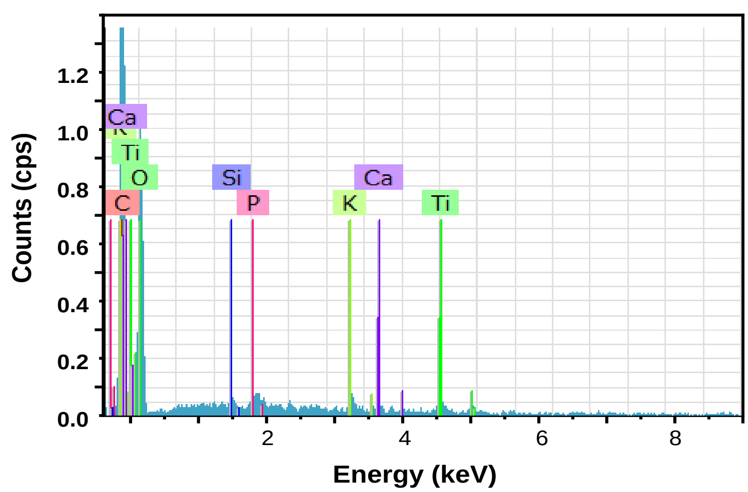


Fig. 7. TiO_2 sol modified wood

Figure 7 shows that the TiO_2 sol modified wood sample mainly contained three elements: C, O, and Ti, and the weight percentages were 52.1 wt%, 46.4 wt%, and 0.71 wt%, respectively. The atomic percentages were 59.6 At%, 39.8 At%, and 0.2 At%, respectively. Among them, C came from wood, Ti came from TiO_2 grains, and O came from wood and TiO_2 grains. The remaining elements Ca, P, K, Si, *etc.*, were trace elements present in wood, and the sum of weight percentage was 0.83 wt%, and the sum of atomic percentage was 0.31 At%. The results of EDX showed that TiO_2 grains successfully entered the wood body.

Figures 8 to 12 show that the main components of the preservative wood samples of nano-TiO_2 compounded with *Z. bungeanum, K. scoparia*, *S. flavescens*, *H. perforatum* and *C. monnieri* were C, O, and Ti, of which C and O were mainly from Chinese herbal medicine and wood, and the weight percentage of C element wt% and atomic number percentage At% were the highest. Among them, the abundant carbon compounds were contained in Chinese herbal medicine.

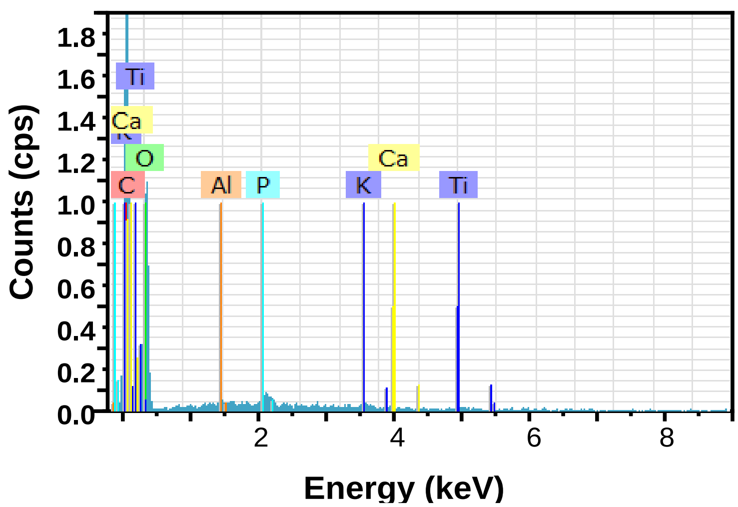


Fig. 8. Nano TiO_2-*Zanthoxylum bungeanum* composite anti-degradative wood

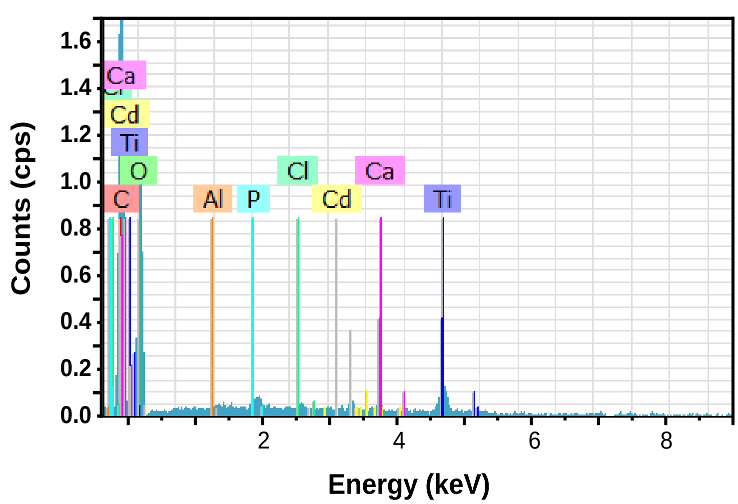


Fig. 9. Nano TiO_2- *Kochia scoparia* composite anti-degradative wood

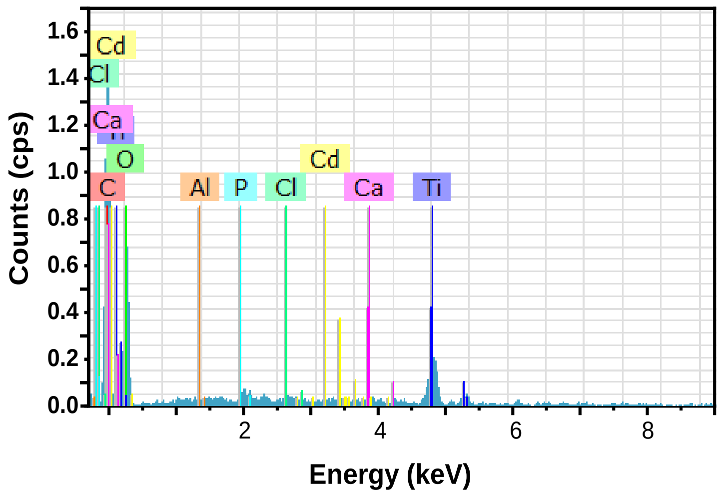


Fig. 10. Nano TiO_2-*Sophora flavescens* composite anti-degradative wood

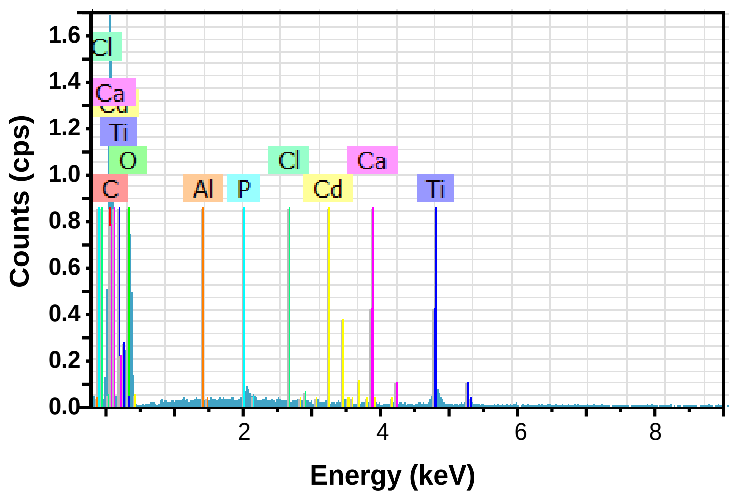


Fig. 11. Nano TiO_2 -*Hypericum perforatum* composite anti- degradative wood

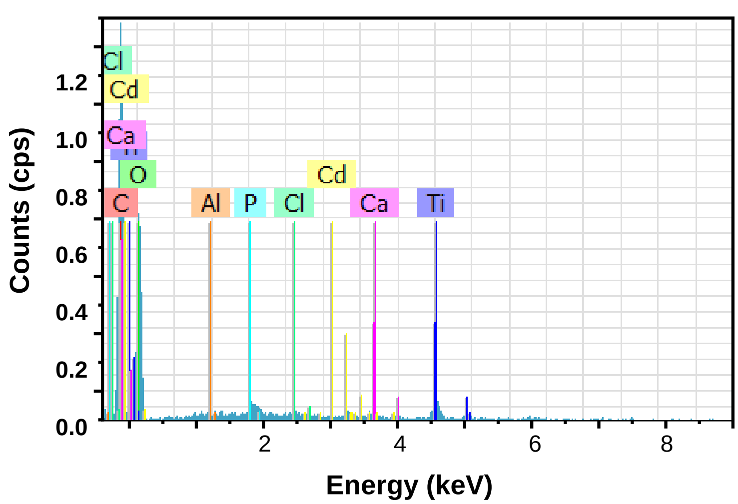


Fig. 12. Nano TiO_2-*Cnidium monnieri* composite anti- degradative wood

From the results of EDX, it can be seen that the main components of poplar wood were C, O, Ca, and the main components of wood treated with TiO_2 are C, O, Ca, Ti. It can be seen that there were TiO_2 crystal grains on the surface of the modified wood, and Chinese herbal medicine and nano-TiO_2 chemically combined. Moreover, nano-TiO_2 can act as a carrier to transport more Chinese herbal medicine into wood.

SEM Analysis of Surface Morphology

The SEM diagram is shown in Fig. 13, which shows the surface morphology of the original wood and the wood after anti-degradative treatment. Figure 13 (a, b) shows the original pictures of untreated wood. The orderly arrangement of conduits and pore structures on the surface of the untreated wood through SEM can be clearly observed. Figure 13 (c, d) shows the wood after antiseptic treatment with Chinese herbal medicine. It can be seen from the figure that the morphology of the wood changed after the Chinese herbal medicine was impregnated. In addition, the Chinese herbal medicine was evenly distributed in wood vessels and fiber-tracheids.

It could be seen from Fig. 13 (d) that there were trace deposits in the wood, and the wood had a small amount of Chinese herbal medicine after treatment that will enter its interior which are consistent with the results of EDX.

Figure 13 (e, f) shows the morphology of wood after TiO_2 sol treatment. It could be seen from Fig. 13 (e) that there were obvious particles in the lumen. It could be seen that TiO_2 particles entered the wood through the pipes and pits between the pipes after TiO_2 sol treatment combined with EDX analysis. Figure 13 (g, h) shows the topography of wood after nano-TiO_2-Chinese herbal medicine composite treatment. It could be seen from the figure that the tracheids and pores inside the wood were filled with a large amount of TiO_2 particles and a small amount of Chinese herbal medicine deposits. According to the enlarged image Fig. 13 (h), there were a large number of particles in the pores of the wood, which indicated that the TiO_2 particles could enter the pores inside the wood. Comparing Fig. 13 (h and f), the internal filling of wood after nano-TiO_2-Chinese herbal medicine composite treatment was noticeably greater than that of wood only after TiO_2 sol treatment. It showed that TiO_2 particles entered the wood and also served as a carrier with loading more Chinese herbal medicines.

From Fig. 13(e, g), it can be seen that the TiO_2 particles were attached to the vessel cell wall in a granular form, which made the inner wall of the vessel appear uneven compared to untreated wood, and it could be seen that the TiO_2 particles were agglomerated after entering the wood from Fig. 13 (h). The above analysis showed that the TiO_2 particles were mainly distributed in the lumens and pits of the wood. It could be inferred that the vessels and pits of the wood were the main channels through which nano-TiO_2 penetrates the wood. At the same time, the TiO_2 provided a suitable high-surface-area support that allowed the herbal extract compounds to fixed to be effective against microbial species. Nano-TiO_2 would serve as a carrier to allow more Chinese herbal medicines to enter the wood to produce a synergistic bactericidal effect. After the wood was impregnated with the preservative solution, it will not significantly change the color, because the concentration of the preservative solution is very low, and the color itself is also very natural, so there is no obvious change in the color, gloss, *etc.* of the wood (Wu *et al*. 2020). At present, the combination of TiO_2 particles and Chinese herbal medicine and wood had not yet been explained, and further research was needed.

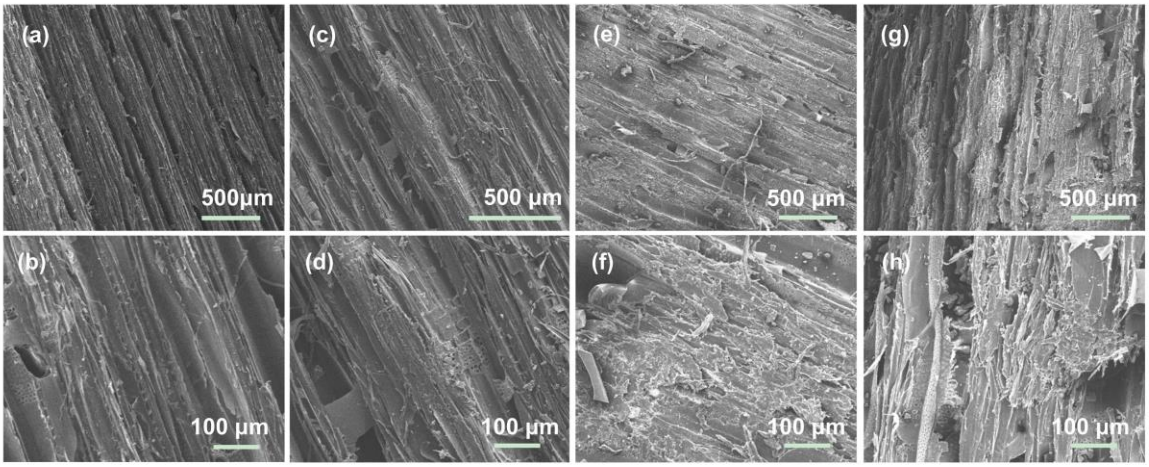


Fig. 13. SEM images of poplar wood and composite materials prepared by different methods: Untreated wood (a, b); Chinese herbal medicine treatment wood (c, d); TiO_2 sol treatment wood (e, f); Nano-TiO_2-Chinese herbal medicine compound treatment wood (g, h)

FTIR Analysis

The infrared spectra of poplar material, TiO_2 sol treatment material, Chinese herbal medicine treatment material, and nano-TiO_2-Chinese herbal medicine composite treatment material are shown in Fig. 14 (a to d), respectively. It can be seen from Fig. 14 that the characteristic hydroxyl peaks at 3200 to 3500 cm^{-1} of the poplar spectra b, c, and d after three different conditions were weakened to different degrees than the poplar spectra a, and the intensity became lower. Among them, the spectrum c of the TiO_2 sol treatment material showed the largest change, the spectrum b of the Chinese herbal medicine treatment material was extremely small, and the change of the spectrum d of the nano-TiO_2-Chinese herbal medicine composite treatment material was between b and c. It showed that a large number of hydroxyl groups on poplar cellulose and TiO_2 particles were chemically combined and deposited in the wood after treatment. It would not be noticeably weakened with only physical adsorption while the Chinese herbal medicine and wood were only weakly combined. The weakening degree of c was less than that of d, indicating that the TiO_2 sol had acted as a carrier and successfully loaded Chinese herbal medicine into the wood. Compared with poplar wood material, in the TiO_2 sol-treated material and the nano-TiO_2-Chinese herbal medicine composite treatment material, the absorption band of the characteristic peak of 1700 to 1725 cm^{-1} disappeared. The characteristic peak was the C=O stretching vibration peak, which mainly came from the acetyl group in wood hemicellulose and the ester group in lignin. The disappearance of this peak indicated that the hemicellulose and lignin of the wood were hydrolyzed under acidic conditions. They formed a coordination chemical bond with Ti^{4+} on the surface of the TiO_2 particles to combine with the wood components. The peak value of Chinese herbal medicine treatment material here was the same as that of poplar wood material. This showed that TiO_2 particles were successfully introduced into the wood and formed a chemical bond with the components in the wood. Compared with poplar wood, the characteristic peak of 500 to 800 cm^{-1} in TiO_2 sol-treated material and nano-TiO_2-Chinese herbal medicine composite treatment material was clearly enhanced. This characteristic peak was the stretching vibration peak of Ti-O-Ti in TiO_2, which indicated that TiO_2 particles enter up the wood interior.

From the above analysis, it could be seen that after TSMW and nano-TiO_2-Chinese herbal medicine composite-treated wood, nano-TiO_2 particles entered the wood, some of which were combined with wood components through hydrogen bonding through physical adsorption, and the other was chemically combined with wood cell walls. The carboxyl groups of the cellulose and hemicellulose in the lignin chemically associated with the phenolic hydroxyl groups in the lignin and were fixed in the wood. The above conclusions were consistent with the conclusions of the wood indoor decay resistance test and anti-loss test.

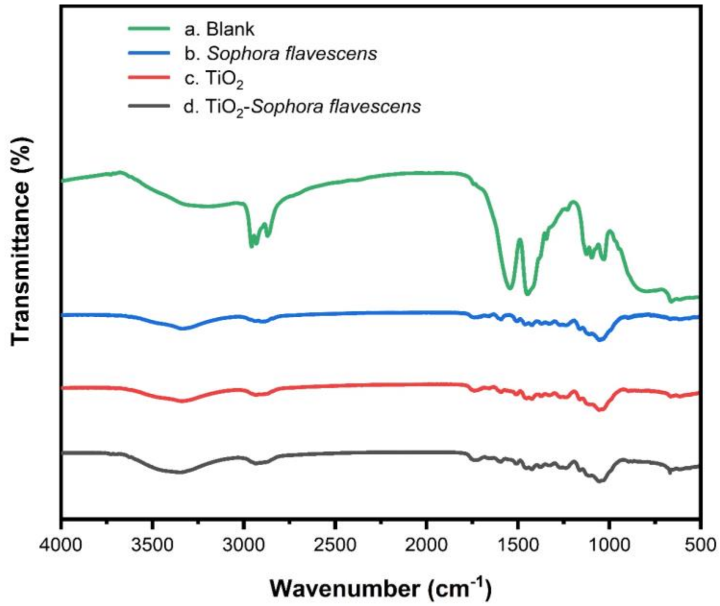


Fig. 14. FTIR spectra of poplar wood and composites fabricated by different methods

CONCLUSIONS

1. The anti-degradative test results of the wood treated with nano-TiO_2 and Chinese herbal medicine composite showed that the wood treated with the Chinese herbal medicine and nano-TiO_2 composite had noticeably enhanced the anti-degradative effect in comparison to the wood treated with either the Chinese herbal medicine itself or the TiO_2 sol alone. The combined treatment provided strong resistance relative to the original level of decay, indicating the successful combination of Chinese herbal medicine and nano-TiO_2 through the sol-gel method, so that the antibacterial properties of the two complement each other. In addition to anti-fungal effects, Chinese herbal medicines can also prevent termites. After termites eat Chinese herbal medicine, the Chinese herbal medicine can inhibit the symbiotic bacteria in the termite body and achieve the purpose of killing termites. Therefore, Chinese herbal medicine is also an agent for killing termites.
2. The anti-degradative effect of nano-TiO_2-*Zanthoxylum bungeanum* treatment material was the best, and the anti-degradative effect of nano-TiO_2-*Kochia scoparia* was relatively poor. The treated materials after nano-TiO_2 combined with Chinese herbal medicines, such as *Cnidium monnieri*, *Sophora flavescens*, and *Hypericum perforatum*, also showed different anti-degradative effects, and the weight loss rate of the treated

specimens gradually increased with the increase of the concentration of the agent reduced.

3. The test results of anti-loss resistance showed that the anti-loss resistance of the Chinese herbal medicine and nano-TiO_2 composite post-treatment material was noticeably higher than that of the Chinese herbal medicine itself. This might be caused by the adhesion of the nanomaterial itself, and the loss of preservatives increased with the concentration of the compound agent. The increase of TiO_2 showed a trend of first decreasing and then increasing, indicating that the composite of nano-TiO_2 and Chinese herbal medicines could help increase the fixation between Chinese herbal medicines and wood.

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