SOL-GEL DEPOSITION OF TiO₂ NANOCOATINGS ON WOOD SURFACES WITH ENHANCED HYDROPHOBICITY AND PHOTOSTABILITY

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Abstract. To enhance the resistance of wood against weathering, Chinese fir (Cunninghamia lanceolata) wood was modified via a two-step process by first growing titanium dioxide (TiO₂) nanocoatings on the wood substrate using a sol-gel process followed by low-surface free-energy treatment with hydrolyzed hexadecyltrimethoxysilane (HDTMS). The morphology and chemical composition of the formed coatings were examined by field-emission scanning electron microscopy, energy dispersive X-ray analysis, and Fourier transform IR spectroscopy. Water contact angle (WCA) was used to characterize hydrophobicity. UV-Vis spectroscopy and accelerated weathering were used to evaluate the UV-shielding properties of the coatings and the photostability of the treated wood, respectively. The results showed that the introduction of TiO₂ nanoparticles facilitated the generation of a dual-size roughness on the wood substrate, and the long-chain alkyl groups of HDTMS were covalently linked to the surface of the particles. The WCA of the treated wood was improved remarkably up to 138° displaying high hydrophobicity. The TiO₂ coatings also exhibited strong absorption of UV radiation and imparted the underlying wood substrate with enhanced photostability, which was highly dependent on the TiO₂ loadings in the coatings.

Keywords: TiO₂, nanocoatings, hydrophobicity, photostability, wood.

INTRODUCTION

Wood is a natural, renewable, sustainable material widely used for building and construction because of its specific strength, aesthetic appeal, and environmental friendliness. However, when wood is exposed to the outdoors, a variety of weathering factors, such as UV radiation, water, and extreme temperatures, are known to have a deteriorating effect on wood resulting in changes...

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in its surface characteristics such as discoloration, loss of gloss, roughening, checking, and even extensive loss of mechanical properties. Among the weathering factors, UV radiation is believed to have the most damaging effect, contributing considerably to the degradation of wood by inducing photochemical reactions that eventually lead to depolymerization of lignin and some polysaccharides in the cell walls (Müller et al 2003). Water plays an important role in weathering deterioration of wood by accelerating degradation of cell wall components and washing away the degradation products, resulting in surface erosion (Sudiyani et al 1999). In most cases, wood must have proper protection to avoid weathering-induced deterioration during its outdoor service.

Many attempts have been made to inhibit weathering deterioration of wood, including impregnation with preservatives (Temiz et al 2007; Zhang et al 2009), acetylation (Chang and Chang 2001; Prakash et al 2006), surface treatment with inorganic metal salts (Evans et al 1994; Pandey and Pitman 2002), heat treatment (Ayadi et al 2003; Nuopponen et al 2004), and finishing (George et al 2005). However, these methods are often not satisfactory because of possible leaching of the reactants and changes in color and appearance of the treated wood. Also, some chemicals used in these processes may negatively impact the environment. Recently, functionalization of wood surfaces using inorganic nanomaterials such as SiO$_2$, titanium dioxide (TiO$_2$), and ZnO have received extensive attention because of their excellent mechanical, thermal, and optical properties as well as their low toxicity (Mahltig et al 2008). These inorganic particles can be readily introduced on wood surfaces that are rich in hydroxyl groups by using common methods such as hydrothermal and sol-gel processes. It has been suggested that inorganic particles such as TiO$_2$ and ZnO have great potential to be used as protective agents for stabilizing wood against photodegradation because of their ability to scatter and absorb UV light (Yu et al 2010; Sun et al 2012). Additionally, deposition of these inorganic particles on the surfaces of woody materials can provide protection against fungal decay and termite attack (Yu et al 2011; Shupe et al 2012).

However, the deposited inorganic coatings are intrinsically hydrophilic because of the presence of abundant hydroxyl groups on the surface of the particles and thus show a strong affinity for water, causing damage to the underlying wood substrate associated with water absorption. For practical applications, it is necessary to develop hydrophobic nanocoatings on wood surfaces that are not only capable of providing protection against photochemical degradation, but are also water-repellent. In fact, the reactive hydroxyl groups on the particle surface have great potential to be further functionalized with hydrophobic groups to provide water repellency. Recently, inspired by the self-cleaning behavior of lotus leaves, highly hydrophobic coatings have been developed on solid wood substrates by roughening the wood surface with inorganic nanoparticles in combination with low-surface energy treatments (Hsieh et al 2011; Sun et al 2011; Wang et al 2011, 2013). Therefore, if properly designed, it is possible to functionalize wood surfaces with hydrophobic nanoparticles resulting in high water repellency and efficient UV-shielding properties simultaneously.

TiO$_2$ is one of the most promising functional materials. It has been widely used in many applications such as photocatalysis, solar cells, paints, and coatings because of its chemical stability and low toxicity (Chen and Mao 2007). It has no absorption in visible light, nevertheless it can provide excellent protection against UV radiation. In this study, TiO$_2$ was selected to functionalize the wood surface to improve its weathering stability. A two-step treatment procedure was applied by first growing TiO$_2$ nanocoatings on wood substrates using a sol-gel process, followed by low-surface free-energy treatment with hydrolyzed hexadecyltrimethoxysilane (HDTMS). The introduction of nano-TiO$_2$ was attempted to generate secondary roughness on wood substrates, thereby favoring achievement of high hydrophobicity and imparting the
wood surface with excellent UV-shielding properties and enhanced photostability.

**MATERIALS AND METHODS**

**Materials**

Wood samples of 25 (radial) × 5 (tangential) × 45 (longitudinal) mm were obtained from the light-colored sapwood portion of Chinese fir (*Cunninghamia lanceolata*). Tetrabutyl titanate (98%), acetic acid, and anhydrous ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). HDTMS was obtained from Sigma-Aldrich (St. Louis, MO). All chemicals were used as received without further purification.

**Preparation of Titanium Dioxide Sol**

TiO$_2$ sol was prepared using the controlled hydrolysis of tetrabutyl titanate based on the reported method (Xue et al. 2008). A typical preparation procedure is described as follows: 10.5 mL of tetrabutyl titanate was added slowly into 20 mL of anhydrous ethanol to form a homogeneous solution A with continuous stirring. Solution B was prepared by mixing 2 mL of deionized water, 5 mL of acetic acid, and 20 mL of anhydrous ethanol. Solution A was then added slowly into solution B with stirring. The stirring was continued for 24 h at room temperature to form a transparent yellowish TiO$_2$ sol.

**Growth of Titanium Dioxide on Wood Surfaces**

As-prepared TiO$_2$ sol was diluted by adding anhydrous ethanol to prepare different concentrations of sol solutions ranging from 0.2 to 5%. All the concentrations used here were based on weight (w/w). Prior to treatment, the wood samples were ultrasonically washed with deionized water for 10 min and dried at 80°C for 5 h. The cleaned samples were immersed in the different concentrations of TiO$_2$ sol for 30 min to allow deposition of different amounts of TiO$_2$ nanoparticles on the wood surfaces. They were then dried at room temperature for 1 h and finally cured at 105°C for 6 h.

**Low-surface Energy Treatment**

To lower the surface energy of the TiO$_2$-coated wood, the treated wood samples were further immersed in the ethanol solution of hydrolyzed HDTMS with different concentrations ranging from 0.2 to 3 for 1 h. They were then dried at room temperature for 1 h and finally cured at 105°C for 3 h.

**Characterization**

The surface morphology and elemental composition of the samples were examined by a field-emission scanning electron microscope (FE-SEM, Zeiss SUPRA 55; Carl Zeiss, Jena, Germany) combined with energy dispersive X-ray (EDX) analysis. A thin platinum (Pt) layer was sputtered on the sample surfaces to improve conductivity prior to observation. Changes in surface chemistry of the samples were analyzed using a Fourier transform IR spectrometer (FTIR; Nicolet Magna-IR 750, Waltham, MA) equipped with an attenuated total reflection accessory.

Hydrophobicity of the samples was evaluated by water contact angle (WCA) measurements. A contact angle measurement instrument (Shanghai Digital Technology Model JC2000D, Shanghai, China) was used to determine WCA at ambient temperature. The WCA values were recorded 60 s after a water droplet of 5 μL was placed on the surface of the samples, and the average WCA value was obtained by measuring more than five positions for each sample.

To evaluate the transparency and UV-shielding properties of the TiO$_2$ nanocoatings, glass slides (quartz) were coated with the as-prepared TiO$_2$ sol solutions with different concentrations (0.2-5%) and 1% HDTMS solution using the same procedure for preparing wood samples. The absorbance spectra of the nanocoatings were examined by UV-Vis-NIR spectrophotometer (Varian Cary 5000, Palo Alto, CA) scanning in the wavelength range of 250-700 nm.
Accelerated UV radiation was performed using a weathering test chamber (Xenotest Alpha; Atlas, Rock Hill, SC) with a radiation intensity of 42 W/m$^2$ at 340 nm and a black panel temperature of 63°C at 50% RH for a total radiation duration of 120 h. The samples were exposed to continuous xenon light radiation without water spray. After a certain time interval of exposure, the samples were taken out for color measurement. Change in color of the samples caused by radiation was measured with a Minolta spectrophotometer (CM-A145; Osaka, Japan) using the CIE $L^*a^*b^*$ system according to the ISO 7724 standard test method. Three replicates were used for each treatment, and the average value was calculated. In the CIE $L^*a^*b^*$ system, $L^*$ represents lightness ranging from 0 (black) to 100 (white) and $a^*$ and $b^*$ are the chromaticity parameters ($+a^*$ for red, $-a^*$ for green, $+b^*$ for yellow, $-b^*$ for blue). The overall color change ($\Delta E^*$) was calculated according to the following equation:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$ (1)

where $\Delta L^*$, $\Delta a^*$, and $\Delta b^*$ represent the changes in $L^*$, $a^*$, and $b^*$ between the initial and final values, respectively. A lower $\Delta E^*$ value means lower color change and higher photostability.

**RESULTS AND DISCUSSION**

**Surface Morphology and Structure**

The morphology of the wood surfaces before and after treatment with TiO$_2$ sol and HDTMS is shown in Fig 1. At low magnification, the open cellular structure of wood could be seen, and there appeared to be no apparent difference between the native and the treated wood surfaces. The high-magnification image of the native wood revealed a ripple-like fibrillar appearance of the inner surface of the open-cell lumen. By contrast, after the two-step treatment, the fibrillar structure disappeared and instead a thin layer of nanoscale spherical protuberances was observed to be coated on the lumen surface. The formed nanoprotuberances were well distributed on the surface without obvious agglomeration with a diameter of $\approx$60-150 nm.

![Figure 1. Scanning electron microscope images of (a) untreated wood and (b) wood surface treated with titanium dioxide (TiO$_2$) sol and hydrolyzed hexadecyltrimethoxysilane. High-magnification images reveal changes in the lumen surface (c) before and (d) after treatment. Corresponding energy dispersive X-ray spectra are shown in (e) and (f).](image-url)
The elementary composition of the nanocoatings was further analyzed by EDX (Fig 1e-f). The signal of Pt originates from the conductive layer on the samples. Carbon and oxygen are the only elements in the native wood. After treatment, an additional strong signal of titanium appears in the spectrum, indicating that the nanoprotuberances formed on the wood surfaces are basically composed of TiO$_2$. As shown in the SEM images, wood itself possesses a heterogeneous and uneven surface consisting of alternating lumen and cell wall cross-sections, producing primary roughness of wood substrate. The introduction of TiO$_2$ nanoparticles generates secondary roughness on the surface and accordingly facilitates the formation of a dual-sized roughness on wood substrate, which is believed to be a crucial precondition for producing a superhydrophobic surface.

Changes in surface chemistry of the wood after treatment with TiO$_2$ sol and different concentrations of hydrolyzed HDTMS were studied by FTIR (Fig 2). The spectra of the treated wood revealed absorption peaks below 1000 cm$^{-1}$ attributed to Ti-O stretching vibration of TiO$_2$ (Sun et al 2012), which overlap with that of functional groups of wood constituents. The absorption peaks at 2850 and 2920 cm$^{-1}$, which are assigned to the C-H stretching vibrations of –CH$_2$ and –CH$_3$, respectively (Pandey 1999), became much stronger after treatment. The origin of –CH$_2$ and –CH$_3$ was the long-chain alkyl groups of HDTMS incorporated on the surface of TiO$_2$ nanoparticles. When the concentrations of hydrolyzed HDTMS were increased from 0.2 to 3%, the absorption peaks at 2850 and 2920 cm$^{-1}$ became increasingly stronger, indicating more long-chain alkyl groups were assembled on the surface. The self-assembly of HDTMS was achieved by the chemical reaction between the alkylsilanol from the hydrolyzed HDTMS and the surface hydroxyl groups of TiO$_2$ deposited on the wood surfaces, which is a strategy to lower the surface free energy and impart high hydrophobicity to the treated wood.

**Hydrophobicity**

The hydrophobicity of the treated wood was evaluated by WCA measurements. Images of water droplets on the wood surfaces are shown in Fig 3. As anticipated, the water droplet penetrated instantly into the surface of the native wood resulting in a WCA of $\approx$0° because of the hydrophilic nature of wood. The introduction of the TiO$_2$ nanocoatings only on the wood substrate improved water repellency with a WCA of $\approx$91°, transforming the wood surface from hydrophilic to hydrophobic. In contrast, treatment with nano-TiO$_2$ followed by HDTMS modification resulted in a further increase in WCA up to $\approx$138°, and sphere-shaped droplets were formed on the surface, displaying high hydrophobicity of the treated wood. An examination of the effect of the concentrations of TiO$_2$ sol on the surface wettability showed no apparent changes in WCA of the treated wood within the concentration range of 0.2-5%. The incorporation of more TiO$_2$ nanoparticles on the wood surface contributed little to the increase of WCA. Also, variation of the HDTMS concentrations from 0.2 to 3% resulted in no significant changes in WCA, indicating that a small amount of HDTMS is sufficient for imparting hydrophobicity to the wood surface (Fig 4).
The achieved high water repellency can be attributed to the combined effects of the hydrophobicity of HDTMS and the surface roughness of wood. It has been reported that the maximum WCA that can be achieved on a smooth surface is about 120° even when a material with the lowest surface free energy is used (Nishino et al. 1999). Therefore, increasing surface roughness of the substrate is necessary if high hydrophobicity is pursued according to the Wenzel model. Wood itself possesses a microscale surface roughness, and the incorporation of TiO$_2$ nanoparticles facilitates the formation of dual-sized roughness on wood substrate. Accordingly, compared with a smooth substrate, the roughened surface combined with low-surface free-energy treatment imparts high hydrophobicity to the treated wood with a WCA higher than 120°.

However, the achieved water repellency is not actual superhydrophobicity given that the WCA values were less than 150°. In fact, the introduction of TiO$_2$ nanoparticles caused no remarkable changes in the wood surface on the microscale, and the cellular and porous structure was basically retained. In this case, the water droplets could fill the lumen space of the longitudinally arranged cells, resulting in full contact between the water droplets and the protrusions formed by the ridges of the exposed cell walls without air being trapped inside, which is a typical wetting pattern.
behavior (complete wetting) that is described by the Wenzel model. Consequently, the achieved WCA on the treated wood is not high enough to be classified as superhydrophobic. This suggests that the mimicked dual-sized roughness on wood substrate still differs from the surface topology of the lotus leaf because of the particular structure of wood surfaces, and the surface roughness should be further increased up to a certain point at which water droplets can be suspended on top of the protrusions to achieve superhydrophobicity.

UV-Shielding Properties and Photostability

The UV-Vis spectroscopy measurements were carried out to evaluate the UV-shielding performance of the hydrophobic TiO2 coatings that were deposited on glass slides. The UV-Vis absorbance spectra of coatings derived from different concentrations of TiO2 sol are shown in Fig 5. All the coatings showed almost no absorption above 400 nm and were therefore basically transparent in the visible light region. The TiO2 coatings exhibited strong absorption in the UV region from 250 to 350 nm, which is the most harmful for photodegradation of wood surfaces. As the concentration of the TiO2 coatings was increased from 0.2 to 3%, much stronger UV absorption was achieved, indicating better UV-shielding properties. Such strong absorption of UV light was attributed to the high refractive index of TiO2 particles. Interestingly, the coating with a TiO2 concentration of 5% presents a different spectral behavior with a remarkable decrease in the UV absorption and an obvious shift of the absorption peak to a longer wavelength. The light-scattering efficiency of TiO2 has been reported to be highly dependent on its particle size, and large floccules of TiO2 particles scatter less light than well-dispersed particles (Nelson and Deng 2008). In this study, the use of 5% concentration may induce aggregation of TiO2 particles in the coatings, thereby producing lower light-scattering efficiency and resulting in decreased UV absorption. Nevertheless, the UV-shielding properties of the TiO2 coating have to be further verified with the accelerated weathering test on the treated wood.

The color changes of the TiO2-coated and native wood samples caused by UV radiation are shown in Fig 6. The native wood is susceptible to UV radiation, and the surface color changed rapidly. With increasing duration of radiation, the wood surfaces became darkened as indicated by a decrease in lightness ($L^*$) and also showed a tendency to turn reddish and yellowish as indicated by increases in the chromaticity parameters ($a^*$, $b^*$). After wood was coated with nano-TiO2, the changes in the relevant color parameters ($L^*$, $a^*$, $b^*$) of the wood surfaces were obviously inhibited and the overall color change ($ΔE^*$) was apparently decreased. This suggests that nano-TiO2 treatment significantly improved the photostability of wood. The photostabilizing effect of TiO2 can be attributed to its excellent UV-blocking efficacy, which minimizes the penetration of harmful radiation into the wood substrate underneath, as shown clearly by the UV-Vis spectrophotometry results. As anticipated, the concentration of TiO2 sol used in the coatings affected the efficiency of color protection. With increasing concentrations of TiO2 sol, more TiO2 particles were loaded on the wood surfaces and thus better UV-shielding properties and color protection were achieved.
Specifically, the overall color change ($\Delta E^*$) of the wood samples treated with the TiO$_2$ sol at a concentration of 5% was only 44% of the corresponding value of the control samples after 120 h accelerated UV radiation. Although the TiO$_2$ sol at the highest concentration provided the best color protection for the treated wood, its UV absorption was not the highest among the tested sol concentrations as indicated by the UV-Vis spectroscopy measurements. This discrepancy may be attributed to the different dispersion state of nanoparticles on the substrates of wood and glass. SEM images show that the particles were well dispersed on the wood surface without obvious agglomeration, which nevertheless may not be the case for glass slides, and thus different UV absorption efficiencies of TiO$_2$ coatings were achieved on wood and glass substrates.

CONCLUSIONS

The two-step treatment with TiO$_2$ sol and hydrolyzed HDTMS resulted in high hydrophobicity of wood surfaces with a WCA of $\approx138^\circ$ converting the wood from hydrophilic to hydrophobic. Incorporation of more TiO$_2$ nanoparticles on the wood surface contributed little to the increase of WCA, and a small amount of HDTMS was sufficient for generating high hydrophobicity. In addition, the TiO$_2$ coatings exhibited strong absorption of UV radiation and imparted the underlying wood substrate with enhanced photostability, which
was highly dependent on the TiO$_2$ loadings in
the coatings. The formed TiO$_2$ coatings were
basically transparent in the visible light region
and therefore retained the original wood color.
This two-step process to impart wood with high
hydrophobicity and enhanced photostability
simultaneously could be a promising alter-
native to the conventional chemical modifica-
tion strategy.

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REFERENCES
Ayadi N, Lejeune F, Charrier F, Charrier B, Merlin A
(2003) Color stability of heat-treated wood during arti-
Chang ST, Chang HT (2001) Comparisons of the photo-
stability of esterified wood. Polym Degrad Stabil 71(2):
261-266.
Chen X, Mao SS (2007) Titanium dioxide nanomaterials:
Synthesis, properties, modifications, and applications.
Evans PD, Pirie JDR, Cunningham RB, Donnelly CF,
Schmalzl KJ (1994) A quantitative weathering study of
wood surfaces modified by chromium VI and iron III
compounds. Part 2. Image analysis of cell wall pits
Photodegradation and photostabilisation of wood—The
Hsieh CT, Chang BS, Lin JY (2011) Improvement of
water and oil repellency on wood substrates by using
fluorinated silica nanocoating. Appl Surf Sci 257(18):
7997-8002.
Functionnalisation of wood by nanosol application. J Mater
Chem 18:3180-3192.
Müller U, Rätzsch M, Schwanninger M, Steiner M, Zöbl H
(2003) Yellowing and IR-changes of spruce wood as
result of UV-irradiation. J Photochem Photobiol B 69(2):
97-105.
Nelson K, Deng Y (2008) Effect of polycrystalline struc-
ture of TiO$_2$ particles on the light scattering efficiency.
J Colloid Interface Sci 319(1):130-139.
Nishino T, Meguro M, Nakamae K, Matsushita M, Ueda Y
(1999) The lowest surface free energy based on –CF3
Nuopponen M, Wikberg H, Vuorinen T, Maunu SL, Jämsä
Pandey KK (1999) A study of chemical structure of soft
and hardwood wood polymers by FTIR spectroscopy.
of modified rubberwood (Hevea brasiliensis). J Appl
Prakash GK, Pandey K, Ram RKD, Mahadevan KM (2006)
Dimensional stability and photostability of octanoylated
of superfroophobic wood surfaces treated with ZnO
Sudiyani Y, Tsujiyama S, Imamura Y, Takahashi M,
Minato K, Kajita H (1999) Chemical characteristics of
surfaces of hardwood and softwood deteriorated by
on wood surface using a hydrothermal method. J Mater Sci
46(24):7706-7712.
Sun Q, Lu Y, Zhang H, Zhao H, Yu H, Xu J, Fu Y, Yang D,
submicrospheres on wood surface: An efficient method
to prepare UV-protective wood. Mater Chem Phys 133(1):
253-258.
accelerated weathering on surface chemistry of modified
Wang C, Piao C, Lucas C (2011) Synthesis and characteri-
sation of superfroophobic wood surfaces. J Appl Polym
Wang X, Chai Y, Liu J (2013) Formation of highly hydro-
phobic wood surfaces using silica nanoparticles modified
with long-chain alkylysilane. Holzforschung. doi:10.1515/
hf-2012-0153.
Xue CH, Jia ST, Chen HZ, Wang M (2008) Super-
hydrophobic cotton fabrics prepared by sol-gel coating
of TiO$_2$ and surface hydrophobization. Sci Technol Adv
Mater 9(3):1-5.
photostability and antifungal performance of bamboo
with nanostructured zinc oxide. Wood Fiber Sci 43(3):
293-304.
ZnO nanofilms on wood with improved photostability.
Holzforschung 64(3):385-390.
842-846.