Photocatalytic Degradation of Wood Coated with a Combination of Rutile TiO_2 Nanostructures and Low-Surface Free-Energy Materials

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To test the hypothesis that wood coated with rutile TiO_2 nanostructures can undergo degradation because of the photocatalytic activity of TiO_2, three sets of wood specimens were aged at an accelerated rate. These three sets consisted of blank wood (BW), HDTMOS/MTMOS-coated wood (WHM), and TiO_2/HDTMOS/MTMOS-coated wood (WTHM). After exposure to 155-h UV irradiation, the wettability of WTHM changed from hydrophobic to hydrophilic. This indicated that the initial low-surface free-energy materials underwent degradation because of the photocatalytic activity of TiO_2. After exposure to 960 h of UV light irradiation and water spray, scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDXA) of WTHM showed that rutile TiO_2 nanostructures had partially peeled off the wood surface. This suggested that the adjacent wood surface also suffered degradation because of the photocatalytic activity of TiO_2. Although the rutile TiO_2 coating noticeably enhanced the color stability during UV light aging, it made a relatively small contribution to the color stability of the wood during UV light and water spray weathering process. This study suggests that to derive the greatest benefit from modification of wood surfaces with rutile TiO_2 nanostructures for weathering resistance, it is necessary to take measures to inhibit the photocatalytic activity of TiO_2 or to fix the TiO_2 coating on the wood surface.

Keywords: Coating; Hydrophobic; Nanostructure; Photocatalytic; Rutile; Titanium dioxide; Weathering; Wood

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INTRODUCTION

When wood materials are used without protection outdoors, they undergo degradation because of the effect of sunlight and water. Deterioration of the wood surface caused by exposure to sunlight and rain is referred to as weathering. Approaches, such as heat treatment, acetylation, furfurylation, treatments with oils and waxes, silica, silicones and silanes, to improve the weathering performance of wood and preserve its aesthetic qualities are being continually refined, and other new approaches are being developed. These include nanosol treatment (Mahltig *et al*. 2008; Xu *et al*. 2010; Tshabalala *et al*. 2003, 2011), hydro/solvothermal treatment (Li *et al*. 2010), and the room temperature wet chemical route (Zheng *et al*. 2015a).

It is well known that some inorganic oxides such as TiO_2, ZnO, or FeO are good UV light absorbers. Thus, weathering performance (*i.e.*, color stability or hydrophobicity) of wood can be improved by either adding TiO_2 into clear stain coatings (Cristea *et al*. 2011; Saha *et al*. 2011; Fufa *et al*. 2012) or *in-situ* coating with barrier films comprised of nanostructures of TiO_2 and low-surface free-energy materials (Sun *et al*. 2011; Wang *et al*. 2011; Chu *et al*. 2014; Wang *et al*. 2014; Zheng *et al*. 2015a, 2015b). TiO_2 nanostructures are expected to provide both UV light resistance and liquid water repellence, and the low-surface free-energy materials are expected to enhance the moisture resistance of the wood substrate. As anticipated, TiO_2 coatings have been found to enhance the wood samples' photostability (Sun *et al*. 2012; Wang *et al*. 2014); meanwhile low-surface free-energy materials were found to increase the hydrophobicity of wood (Chu *et al*. 2014; Zheng *et al*. 2015a). For instance, to enhance the resistance of wood against the action of UV light and water, Wang *et al*. (2014) modified Chinese fir wood *via* a two-step process by first growing a TiO_2 coating using a sol-gel process, followed by treatment with low-surface free-energy materials, hydrolyzed hexadecyltrimethoxysilane. After 120 h of accelerated UV radiation without water spray, the overall color change of treated wood samples was apparently decreased. Notably, when the UV radiation time was prolonged from 20 h to 120 h, the overall color change value of ΔE^* (5% TiO_2 sol concentration) continuously increased from approximately 3 to approximately 9, although this value was only 44% (after 120 h of UV exposure) of that of the control samples. Furthermore, Sun *et al*. (2011) showed that wood samples coated with TiO_2 nanospheres exhibited excellent UV resistance when exposed for 1200 h to UV light and water spray. However, they did not investigate the effect of titanium's inherent photocatalytic activity on the weathering durability.

It is known that, in addition to good UV blocking properties, TiO_2 (anatase, noncrystal, or rutile) also show photocatalytic activity (Fujishima and Honda 1972; Wang *et al.* 2007; Furusawa *et al.* 2008; Goncalves *et al*. 2009; Zheng *et al*. 2009a, b; Shi *et al*. 2011), something that is believed to promote the photodegradation of adjacent bio-based materials, the components of cosmetics and low-surface free-energy materials. For example, Goncalves *et al.* (2009) demonstrated that anatase TiO_2/cellulose nanocomposites acquired a yellowish color after permanent light exposure because of the photocatalytic activity of anatase TiO_2. Shi *et al*. (2011) also showed that super-hydrophobic octyltrimethoxysilane/noncrystal TiO_2/filter paper was converted to super-hydrophilicity after 20 h of exposure to UV light irradiation. Furusawa *et al.* (2008) indicated that even rutile TiO_2 nanoparticles possess photocatalytic activity, which causes the degradation of organic components contained in sunscreen agent. In recent articles (Zheng *et al.* 2015a,b), the authors have demonstrated that TiO_2 nanostructures (mainly rutile phase) could be coated on the wood surface. Unexpectedly, this only slightly enhanced wood's weathering performance. Therefore, it is necessary to clarify whether such rutile TiO_2 can contribute to photodegradation of the wood due to the final fate of initial hydrophobicity and TiO_2 nanostructures, which account for the durable weathering resistance of wood (Zheng *et al.* 2015b).

The objective of the current study was to test the hypothesis that both the low-surface free-energy materials and adjacent wood component can be degraded by the inherent photocatalytic activity of TiO_2, especially rutile phase (Zheng *et al.* 2015a, b). The water contact angle of the treated wood samples was measured to evaluate whether adjacent low-surface free-energy materials were photocatalytically degraded. By analogy, the photocatalytic degradation of adjacent wood was evaluated by measurements of changes in color, morphology, as well as the loss of TiO_2. Finally, the accelerated weathering performance of TiO_2 coated wood specimens were evaluated by their color change. The results of this study suggest that enhancement of the weathering resistance of TiO_2 coated wood may be accomplished by inhibiting the photocatalytic activity of TiO_2 or fixing the TiO_2 coating more tightly to the wood.

EXPERIMENTAL

Materials

Wood specimens were obtained from Mountain pine beetle-killed Lodgepole pine logs. The specimens were each cut into wafers 1.0 mm x 15.8 mm x 51.3 mm in the tangential, radial, and longitudinal directions, respectively. A 12% $TiCl_3$ solution and hexadecyltrimethoxysilane (HDTMOS) and methyltrimethoxysilane (MTMOS) were obtained from Sigma-Aldrich.(Milwaukee, WI) All other laboratory chemicals used were American Chemical Society (ACS) reagent-grade.

Methods

Synthesis of rutile TiO_2-wood specimens and modification with low-surface free-energy material

Typically, 8 mL of $TiCl_3$ solution, which contains 12 wt.% of $TiCl_3$ in hydrochloric acid, was dissolved in 240 mL of NaCl saturated aqueous solution. The solution pH was controlled by adding a solution of NaOH to the saturated NaCl solution (Zheng *et al*. 2015). After mixing for 12 h with a magnetic stirrer, 12 replicates of the wood wafers were placed in the coating solution and allowed to react for 10 days without stirring. After reaction, the specimens were rinsed with deionized water and allowed to dry under ambient conditions.

Ethanol was mixed with a solution of MTMOS and a solution of HDTMOS in volume ratios of 100:1:1 (95% ethanol:MTMOS:HDTMOS). Wood specimens (TiO_2 coated and blank wood) were placed in the coating solution to react overnight at room temperature. After reaction, the specimens were rinsed with ethanol and dried for 6 h in an oven at 65 °C, before conditioning at 105 °C for 24 h.

Accelerated weathering

For accelerated weathering studies, six replicates each of control uncoated (BW), HDTMOS/MTMOS-coated (WHM), and HDTMOS/MTMOS/TiO_2-coated (WTHM) wood specimens were exposed in a Ci-65 WeatherOmeter^{TM} for a total of 960 h using Program 1, which consisted of a 2-h cycle (102 min of UV radiation followed by 18 min of radiation and water spray at 0.2 L min^{-1}). The light source was a Xenon arc lamp with borosilicate inner and outer filters, and its irradiance at 340 nm was set at 0.35 W m^{-2}. The light-only black panel temperature (BPT) was 65 ± 28 °C; and relative humidity (RH) was 48 ± 5%. The light and spray BPT was 50 ± 5 °C and the RH was 80 ± 5%. To another group, BW, WHM and WTHM with another six replicates, were exposed to Program 0, which consisted of permanent UV radiation only. The light source was a Xenon arc lamp with borosilicate inner and outer filters, and its irradiance was controlled at 0.35 W m^{-2} at 340 nm. For Program 0, the BPT was 65 ± 2 °C, and RH was 30 ± 5%.

Surface characterization

The surface water repellence properties of the wood specimens before and after accelerated weathering were characterized by dynamic contact angle measurement of a 4-µL deionized water droplet using a PGX+ Contact Angle Tester (Thwing-Albert Instrument Company, West Berlin, NJ). The water contact angle (WCA) for each specimen was determined by taking the average of three measurements made at three different locations on each specimen. There were six replicates per treatment.

The surface morphology of the specimens was obtained by scanning electron microscopy (SEM) on a LEO 1530 field emission scanning electron microscope (Carl Zeiss AG). The surface chemistry was characterized by energy dispersive X-ray analysis (EDXA). EDXA was performed on a LEO EVO40 scanning electron microscope with an attached Vantage EDX Analyzer (Carl Zeiss AG).

Surface color measurements were made in the CIEL*a*b* color space with a Minolta CR-400 Chroma Meter (Osaka, Japan). The L^*, a^*, and b^* values for each specimen were measured at three contiguous locations on the surface of each specimen before and after exposure in a Ci65 WeatherOmeter^{TM} (Atlas Material Testing Solutions, Chicago, IL). Changes in L^*, a^*, b^* were calculated according to Eqs. 1 through 3:

$$\Delta L^* = L^*(\mathrm{w}) - L^*(\mathrm{u}) \tag{1}$$

$$\Delta a^* = a^*(\mathrm{w}) - a^*(\mathrm{u}) \tag{2}$$

$$\Delta b^* = b^*(\mathrm{w}) - b^*(\mathrm{u}) \tag{3}$$

where ΔL^*, Δa^*, and Δb^* are the differences between the weathered (w) and unweathered (u) surfaces. A positive value signifies an increase, while a negative value signifies a decrease. The corresponding total color difference was calculated according to Eq. 4:

$$\Delta E^* = \{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}\}^{1/2} \tag{4}$$

Higher values of ΔE^* signify greater discoloration.

RESULTS AND DISCUSSION

After modification with low-surface free-energy materials, such as HDTMOS/MTMOS, TiO_2-coated wood specimens not only become hydrophobic, but also show enhanced color stability because of the UV light blocking property of TiO_2 and its rough surface (Zheng *et al.* 2015b). It is vital to test the hypothesis that both the adjacent low-surface free-energy materials and wood components might be photocatalytically degraded during UV irradiation and water spray because the rutile TiO_2 may also possess significant photocatalytic activity.

The effect of photoactivity of rutile TiO_2 on low-surface free-energy materials

As shown in a previous paper (Zheng *et al.* 2015a, 2015b), wood surfaces coated with rutile TiO_2 nanostructures exhibit high hydrophobicity after modification with HDTMOS/MTMOS. To investigate the effect of the photoactivity of TiO_2 on hydrophobicity, wood/TiO_2/HDTMOS/MIMOS (WTHM) samples were exposed for 155 h to UV irradiation only. The wettability of the treated wood specimens was evaluated by WCA measurements (Fig. 1). Before UV exposure, the WCA value of blank wood (BW) specimens was 28.2 ± 3.7°. The WCA value increased to 116.7 ± 14.6° when the blank wood specimens were treated with a mixture of HDTMOS and MTMOS (WHM), showing transformation of the wood surface from hydrophilic to hydrophobic. In comparison with the hydrophilic surface of BW, WTHM exhibited noticeably higher hydrophobicity, with a WCA of 140.0 ± 2.0°. After 155 h of UV exposure, although the WCA of BW (24.5 ± 2.0°) and WHM (102.8 ± 7.0°) slightly decreased, WTHM transformed from high hydrophobic to hydrophilic, with a WCA of approximately 15.9 ± 8.5°. This transformation is similar to that which occurs when a rutile TiO_2 nanorod film is coated on a glass substrate (Feng *et al.* 2005). When the photosensitive rutile TiO_2 film is irradiated with UV light, the photogenerated holes will react with HDTMOS/MTMOS molecules to destroy the HDTMOS/MTMOS monolayer, as opposed to reacting with lattice oxygen to form surface oxygen vacancies, which leads to the highly hydrophilic surface. As shown in Fig. 1, when the wood was only modified with HDTMOS/MTMOS (WHM), the value of WCA remained stable. This further indicates that the photoactivity of TiO_2 is the main contributor to the transformation from hydrophobicity to hydrophilicity during UV irradiation.

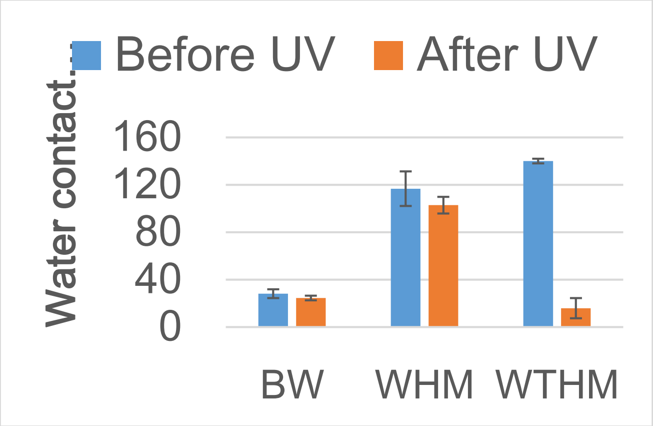

Fig. 1. WCA of wood specimens before and after 155-h UV irradiation

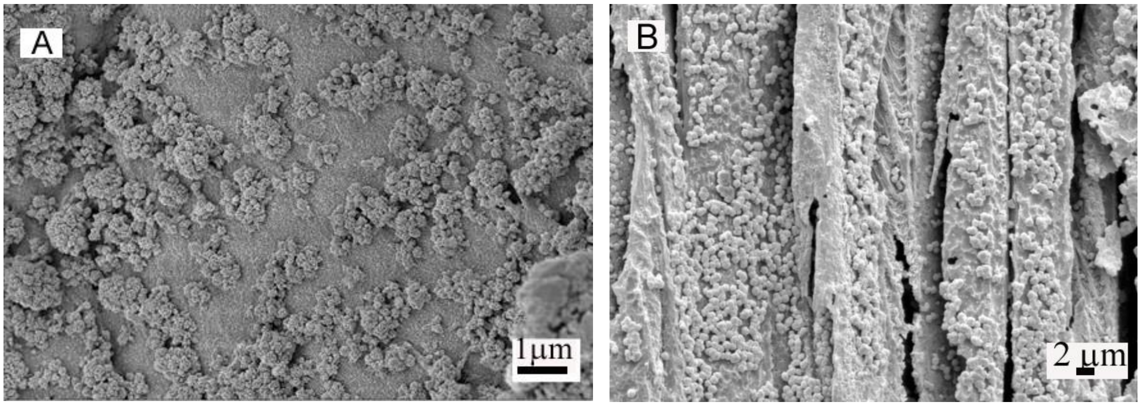

Fig. 2. SEM images of WTHM (A) before and (B) after 960-h exposure to program 1 before and after 960-h exposure to program 1

The effect of photoactivity of TiO_2 on the TiO_2 coating itself

Similar to low-surface free-energy materials, if the adjacent wood components were also photocatalytically degraded, it might lead to the peeling of the TiO_2 nanostructure coating from the wood surface under the synergistic action of UV light and water spray. To investigate the final fate of the TiO_2 nanostructure coating, WTHM samples were exposed to UV light and water spray for 960 h. The changes in surface morphology and Ti/C ratio demonstrate the partial TiO_2 peeling of the TiO_2 coating from the wood surface after UV light and water spray irradiation. Figure 2 shows the morphology of the WTHM before and after UV light and water spray in the WeatherOmeter^{TM}. Figure 3 shows the corresponding atomic compositions.

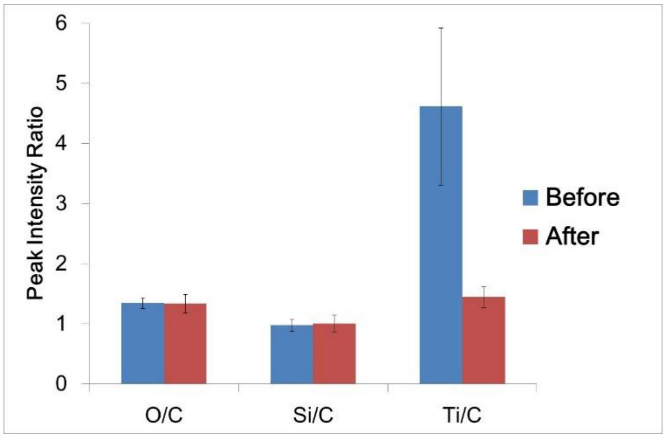

Fig. 3. EDX peak ratios of WTHM before and after 960-h exposure to program 1

These changes were manifested as a loss of the nanostructural protrusions that decorated the surfaces of the microstructures prior to exposure. These changes were probably caused by the photocatalytic degradation of adjacent wood components, which led to a decrease in the bonding strength between the wood and TiO_2 coating. The EDX results for WTHM (Fig. 3) also showed a noticeable decrease in the relative intensity of the titanium peak after 960 h of exposure in the WeatherOmeter^{TM}, which further demonstrated the peeling of the TiO_2 nanostructure coating from the wood surface.

Accelerated weathering performance

Because TiO_2 coatings possess inherent photocatalytic activity, the weathering performance (*e.g.*, color stability) of the rutile TiO_2-coated wood specimens might not be as good as expected after exposure to UV light only or UV light and water spray in the WeatherOmeter^{TM}.

Figure 4 shows the changes in color parameters (L^*, a^*, b^*, and E^*) of the BW, WHM, and WTHM specimens after exposure to Program 0. After exposure to UV for 155 h, the BW surfaces had become darkened, as indicated by a decrease in lightness ($\Delta L^* = -15.47$). There was also a reddish and yellowish change, as indicated by increases in the chromaticity parameters ($\Delta a^* = 10.93$, $\Delta b^* = 19.06$). After the wood was coated with rutile TiO_2 and subsequently modified with HDTMOS/MTMOS, the changes in the color parameters of the WTHM were obviously inhibited (($\Delta L^* = 0.08$, $\Delta a^* = 3.52$, $\Delta b^* = -7.01$). It is known that higher values of ΔE^* represent greater overall discoloration. After 155 h of UV light irradiation, WTHM specimens showed the least discoloration ($\Delta E^* = 7.90$)

compared with BW (ΔE^* = 26.89) and WHM (ΔE^* = 21.92). This indicates that the rutile TiO_2 nanostructure coating confers considerable enhancement of UV resistance properties on the wood surface (29.4% of that of BW) during the UV aging process. This weathering performance is even better than previous results (Wang *et al.* 2014). However, during the initial 240-h exposure to UV irradiation and water spray, ΔE^* of WTHM samples was slightly higher than that of the BW or that of the WHM (Zheng *et al.* 2015b). Moreover, ΔE^* values for BW and WHM, after exposure to UV light only for 155 h, were clearly larger than those observed after exposure for 240 h to UV light and water spray, something inversely true for WTHM samples.

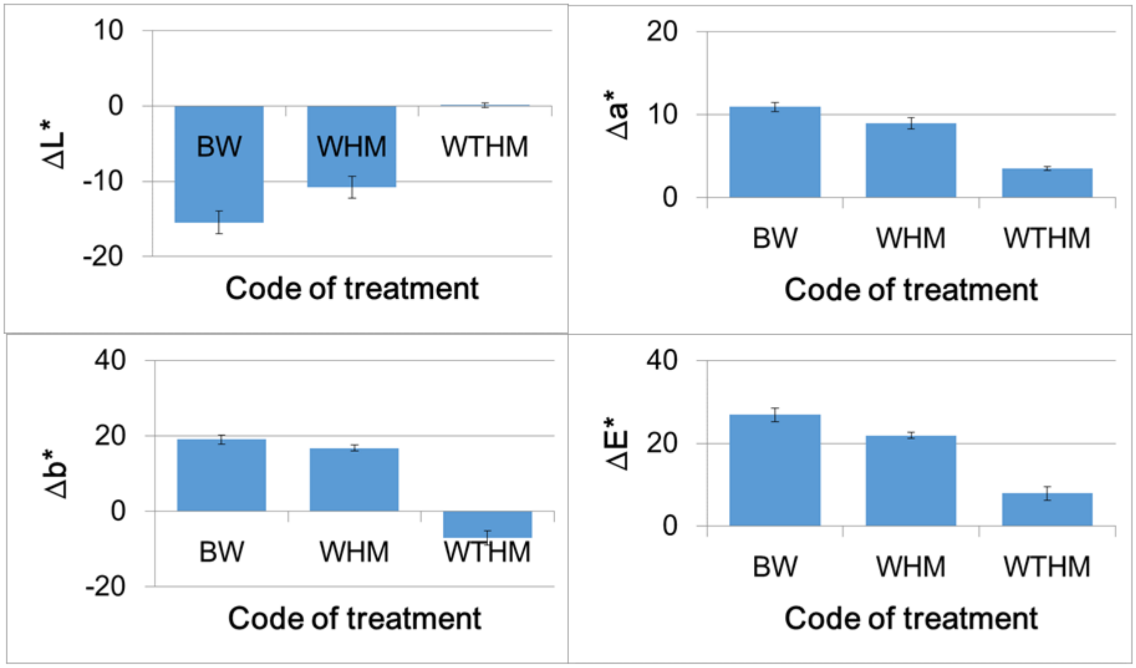

Fig. 4. Surface color changes of wood specimens before and after exposure to UV light for 155 h

The aging phenomena documented above may be attributed to the following three factors: the rinsing action of spray water, the inherent photoactivity of TiO_2, and the UV light blocking ability of TiO_2. First, the HDTMOS/MTMOS monolayer was photodegraded by TiO_2 and the surface transformed from hydrophobicity to hydrophilicity (Fig. 1), which facilitated the washing away of the products of photodegradation induced by UV irradiation. Second, adjacent wood components were photocatalytically degraded, thus resulting in a decrease in the bonding strength between the wood and TiO_2 coating. Finally, if WTHM was only exposed to UV light, because the TiO_2 coating would not peel from the wood surface without the rinsing action of the spray water, the TiO_2 coating could still shield the UV light from the wood surface (Fig. 4). If WTHM was exposed to UV light and spray water, a partial TiO_2 coating would peel from the wood surface with the rinsing action of the spray water (Figs. 2 and 3). As for the phenomena that ΔE^* of WTHM was the fastest compared with that of BW and WTH after the initial 240 h of irradiation to UV light and water spray (Zheng *et al.* 2015b), this may result from the differentiation of color between the wood surface and TiO_2, something further demonstrated by the stability of both ΔL^* and Δa^* of WTHM during the subsequent 720-h exposure (Zheng *et al.* 2015b).

According to the aforementioned hypothesis, Δ*L** and Δ*a** of WTHM must be continually maintained so that the TiO_2 coating would not peel from the wood surface. Thus, the color change of HMTW progressed at a much slower rate than BW or HMW because of the relative stability of the remaining TiO_2 coating during the following 720-h exposure. In turn, WTHM exhibited the best performance (smallest Δ*E** value) after 960 h of UV irradiation and water spray (Zheng *et al.* 2015b). The results of the color change suggest that the enhancement of weathering resistance of wood coated with a combination of rutile nanostructures and low-surface free-energy materials may be accomplished by taking appropriate measures to inhibit the photocatalytic activity of TiO_2 or to fix TiO_2 coating more tightly to the wood.

CONCLUSIONS

1. The photocatalytic property of TiO_2 had an effect on both the initial hydrophobicity and the TiO_2 coating stability when WTHM was exposed to UV irradiation and water spray.
2. The wettability of WTHM changed from initial hydrophobicity to hydrophilicity after 155 h of UV irradiation because of the photocatalytic property of TiO_2.
3. The TiO_2 coating peeled off the wood surface after WTHM was exposed to 960 h of UV irradiation and water spray.
4. The TiO_2 coating could apparently enhance the color stability of wood during UV light irradiation without water spray.
5. Additional studies are required to inhibit photocatalytic properties of TiO_2 or to fix TiO_2 coating more tightly to the wood to enhance the weathering performance of wood.

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