A Combination Coating of Rutile TiO_2 Nano Structures and Sol-Gel Films to Enhance Weathering Performance of Wood

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Abstract

A convenient room temperature approach was developed for growing rutile TiO_2 nanostructures on the wood surface by direct hydrolysis and crystallization of $TiCl_3$ in saturated NaCl aqueous solution. The weathering performance of wood coated with a combination of rutile TiO_2 nanostructures and a sol-gel deposit of alkoxysilanes was determined by exposing treated wood specimens to UV light and water spray. 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 had undergone degradation due to the photocatalytic activity of TiO_2. After 960-h UV light irradiation and water spray, SEM and EDX of WTHM showed that TiO_2 nanostructures had partially peeled off the wood surface. This suggested that the adjacent wood surface also suffered degradation due to the photocatalytic activity of TiO_2. Although TiO_2/HDTMOS/MTMOS coating apparently increased the weight stability of the wood, it made a relatively small contribution to the color stability of wood during 960-h accelerated weathering process. This study has shown that in order 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.

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

Introduction

When wood materials are used without protection outdoors, they undergo degradation due to 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, furfurlation, treatments with oils and waxes, silica, silicones and silanes, etc., 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*. 2011), hydro/solvothermal treatment (Li *et al*. 2010), and room temperature wet chemical route (Zheng *et al*. 2015).

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*. 2015). 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 coating enhanced wood samples' photostability (Sun *et al*. 2012, Wang *et al*. 2014), meanwhile low-surface free-energy materials increased the hydrophobicity of wood (Chu *et al*. 2014, Zheng *et al*. 2015). For instance, in order 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 TiO_2 coating using a sol-gel process followed by treatment with low-surface free-energy materials, hydrolyzed hexadecyltrimethoxysilane (HDTMS). After 120-h accelerated UV radiation without water spray, the overall color change (ΔE^*) of treated wood samples was apparently decreased. Notably, when the UV radiation time was prolonged from 20-h to 120-h, the value of ΔE^* (5% TiO_2 sol concentration) continuously increased from about 3 to about 9 although it was only 44% (after 120-h UV exposure) of that of control samples. Furthermore, Sun *et al*. (2011) showed that wood samples coated with TiO_2 submicrospheres exhibited excellent UV resistance when exposed for 1200 h to UV light and water spray. However, they did not investigate the effect of inherent

photocatalytic activity of TiO_2 on the wettability of the wood surface, or its effect on adhesion of TiO_2 to the wood surface, both of which are key in determining durability of the wood surface. It is well known that in addition to good UV blocking properties, TiO_2 or ZnO also shows photocatalytic activity (Fujishima, *et al.* 1972; Zheng *et al*. 2009a, 2009b), which is believed to promote photodegradation of adjacent bio-based materials (Goncalves *et al*. 2009), components of cosmetics (Furusawa *et al*. 2008) and low surface free-energy materials (Shi *et al*. 2011). For example, Goncalves *et al*. (2009) demonstrated that TiO_2/cellulose nanocomposites acquired a yellowish color after permanent light exposure due to the photocatalytic activity of TiO_2. Shi *et al*. (2011) also showed that super-hydrophobic octyltrimethoxysilane/TiO_2/filter paper was converted to super-hydrophilicity after 20-h exposure to UV light irradiation. Although some literature has focused on the coating of TiO_2 or ZnO nanostructures on wood surface to enhance weathering performance (mainly evaluated by color change), there has not been any literature that has focused on the investigation of the effect of photocatalytic activity of TiO_2 or ZnO on the weathering performance of wood, especially the weight change, the final fate of initial hydrophobicity and TiO_2 nanostructures, which are all key elements for durable weathering resistance of wood.

The objective of the current study was to establish a room temperature wet chemical route to coat rutile TiO_2 nanostructures on wood surface, to evaluate accelerating weathering performance of treated wood specimens, and to test the hypothesis that both the low-surface free-energy materials and adjacent wood component can be degraded due to the inherent photocatalytic activity of TiO_2. The results of this study suggest that enhancement of weathering resistance of TiO_2 coated wood may be accomplished by inhibiting the photocatalytic activity of TiO_2.

Results and discussion

Deposition of rutile TiO_2 nanostructures on the wood surface

A room temperature wet chemical route was developed to oxidize $TiCl_3$ by atmospheric O_2 in saturated NaCl aqueous solution to grow hierarchical nanostructures of rutile TiO_2 on the wood surface. Fig 1 illustrates the coating process. Rutile TiO_2 microspheres, about 1-μm in size were constructed on the wood surface after treatment with the $TiCl_3$ in saturated NaCl aqueous solution at room temperature. Since the reaction is so slow (it will take 10 days to react), the coverage of

TiO_2 coating was uniform and complete (Fig 2A and 2D). Rutile TiO_2 microspheres not only deposited on the cross-sectional walls, but also deposited on the lumina surface (Fig.2a) to endow the wood with lotus leaf-like surface. The enlarged image (Fig. 2b) further revealed that some nanospheres of less than 100 nm in size decorated both the microsphere surfaces and the spaces between the microspheres to form nanoscale-microscale hierarchical structures. The crystal structure of TiO_2 coated on the wood surface was characterized by XRD (Fig. 2C), which indicated that the crystalline structure of T1 surface was dominated by the peaks of rutile TiO_2 and wood.

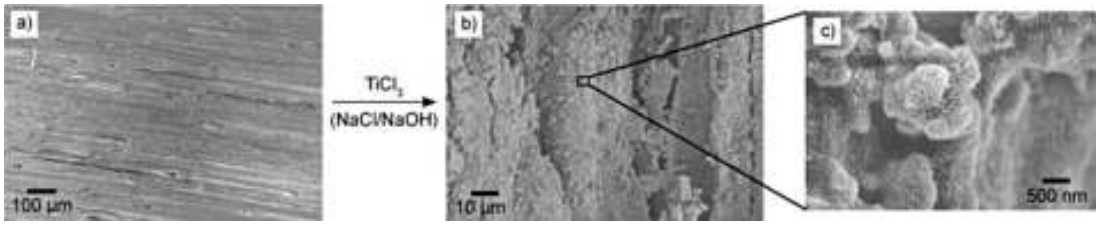

Fig. 1. Illustration of the construction of rutile TiO2hierarchical structures on the wood surface. (a) untreated wood surface; (b) treated wood surface; (c) close-up. (Zheng et al. 2015)

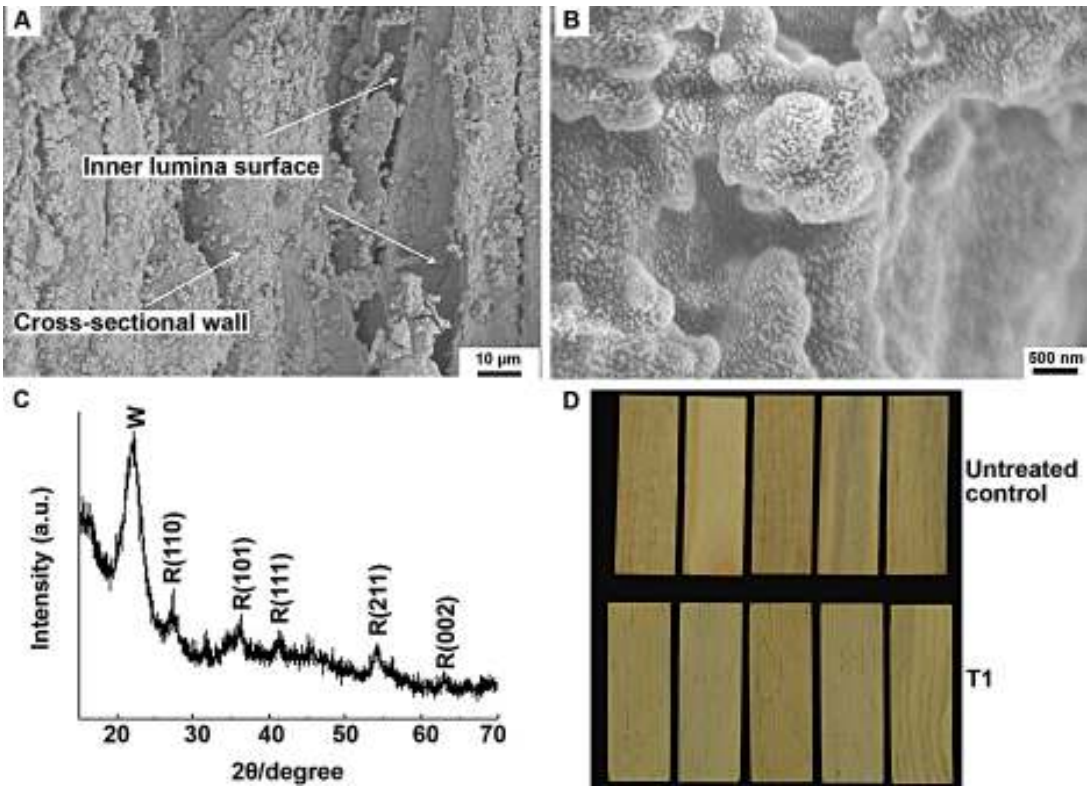

Fig. 2 (a and b) SEM; (c) XRD; (d) photo of untreated control and TiO_2-treated wood samples (T1). The peak labeled W (Fig. 2c) can be indexed to the diffraction pattern of wood. (Zheng et al. 2015)

Accelerated weathering performance of rutile TiO_2 coated wood specimens

With the synergistic action of UV light and water spray, the weight of the wood specimens decreased due to the washing away of both photodegraded wood components and some of the TiO_2 coating. In a previous study Tshabalala et al. (2003) found that a sol-gel deposit of a mixture of MTMOS and HDTMOS decreased weight loss of wood exposed to weathering. Results of the present study suggest that specimens coated with a combination of TiO_2 nanostructures and a mixture of MTMOS and HDTMOS (HMTW) perform even better in terms of preventing weight loss by weathering-induced surface erosion. The rate of weight loss (Fig.3) decreased in the order: BW > WHM > WTHM. Thus the presence of rutile TiO_2 nanostructures covered with a thin film of a mixture of MTMOS and HDTMOS resulted in significant improvement in resistance of the wood surface to weathering.

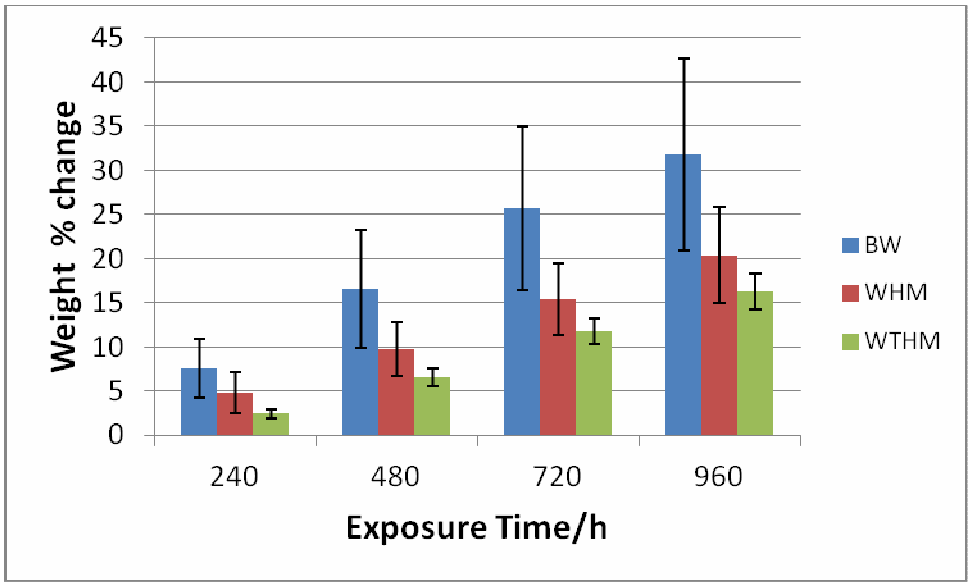

Fig. 3. Weight changes of wood specimens with different treatment before and after exposure to UV and water spray for different time.

Color change

After the initial 240-h exposure, the rate of color change, ΔE* of the specimens coated with rutile nanostructures (HMTW) was slightly faster than the uncoated controls (BW) or specimens coated only with MTMOS/HDTMOS only (HMW). Thereafter the color change of HMTW progressed at a much slower rate than BW or HMW (Fig. 4). These differences in color changes between uncoated (BW) and coated specimens (HMW or HMTW) are the result of different changes in color

parameters, ΔL*, Δa* and Δb* induced by accelerated weathering.

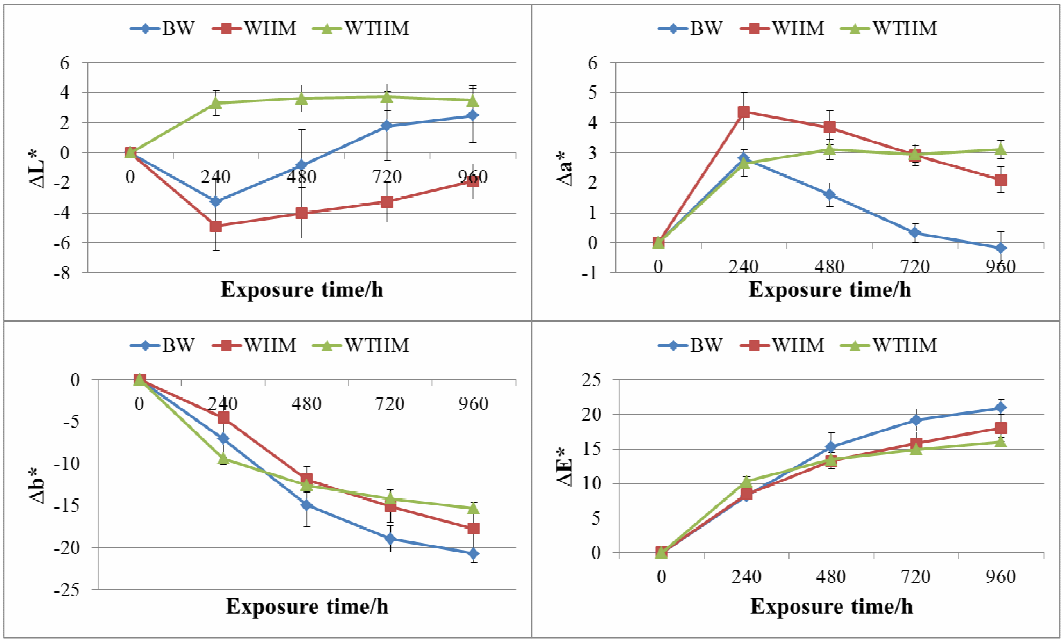

Fig. 4 Surface color changes of wood specimens with different treatment before and after exposure to UV light and spray water for 960 h.

For uncoated control (BW) (Fig. 4) the color change, Δ E* was strongly influenced by a large decrease in Δb*, (shift to blue) and less so by the slight increase in, Δa*, (shift to redness) and also less so by the slight decrease in ΔL*, (lightness). During the course of weathering, ΔL* first decreased to a minimum of -3.82 ± 1.42, and then increased to a level of approximately 2.48 ± 1.80, after 960-h accelerated weathering. On the other hand, Δa* first increased to a maximum of 2.89 ± 0.28, and then decreased to the level of approximately zero after 960-h accelerated weathering.

For specimens coated with MTMOS/ HDTMOS only (HMW), (Fig. 4) color change, ΔE* was influenced in a similar fashion to BW, except that during the course of weathering, ΔL* decreased to a minimum of -4.90 ± 1.60 before increasing to zero, and Δa* first increased to a maximum of 4.37 ± 0.62 before decreasing to a level of 2.10 ± 0.43 after 960-h accelerated weathering.

For specimens coated with rutile nanostructures (HMTW), (Fig. 6) color change, ΔE*, during 960-h accelerated weathering, was strongly influenced by a decrease in Δb* but only slight increases in both ΔL* and Δa*.

Photocatalytic degradation of rutile TiO_2 coated wood specimens

After modification with low-surface free-energy materials, such as HDTMOS/MTMOS, TiO_2 coated wood specimens not only became hydrophobic, but also showed enhanced color stability due to the UV light blocking property of rutile TiO_2 and its rough surface. Since TiO_2 also possesses photocatalytic activity it is important to know its effect on the stability of the organic low-surface-energy alkoxysilanes and the underlying wood components to weatheering.

The wettability of the treated wood specimens was evaluated by water contact angle (WCA) measurements (Table 1). Before UV-exposure, WCA value of blank wood (BW) specimens was 28.2±3.7°. The WCA values increased to 116.7±14.6° when the blank wood specimens were treated with the mixture of HDTMOS and MTMOS (referred to as WHM), showing transformation of the wood surface from hydrophilic to hydrophobic. In comparison with the hydrophilic surface of BW, WTHM exhibited significantly higher hydrophobicity, with a WCA of 140.0±2.0°. After 155-h UV exposure, although the WCA of BW (24.5±2.0°) and WHM (102.8±7.0°) were slightly decreased, the WTHM transformed from high hydrophobicity to hydrophilicity with WCA of about 15.9±8.5°. This transformation is similar to that of the rutile TiO_2 nanorod film coated on the glass substrate [Feng et al. 2005]. When the photosensitive rutile TiO_2 film is irradiated with UV light, the photo generated hole will react with HDTMOS/MTMOS molecules to destroy the HDTMOS/MTMOS monolayer instead of with lattice oxygen to form surface oxygen vacancies, which lead to the high hydrophilic surface. As shown in Table 1, if the wood was only modified with HDTMOS/MTMOS (WHM), the value of WCA remained stable, which further indicated that the photoactivity of TiO_2 was the main contributor to the transformation from hydrophobicity to hydrophilicity during the UV irradiation.

Table 1 Water contact angles (WCA) uncoated and coated wood

Specimen ID	Description	Before exposure	After 155-h exposure to program 0	After 960-h exposure program 1
BW	Blank wood	28.2±3.7	24.5±2.0	≈0
WHM	HDTMOS/MTMOS-coated	116.7±14.6	102.8±7.0	43.3±8.6
WTHM	TiO_2/HDTMOS/MTMOS-coated	140.0±2.0	15.9±8.5	≈0

Similar to low-surface free-energy materials, if the adjacent wood component was also photo catalytically degraded, this might lead to the peeling off of the TiO_2 nanostructures coating from the wood surface under the synergistic action of UV light and water spray. In order to investigate the final fate of TiO_2 nanostructures coating, WTHM samples were exposed to UV light and water spray for 960h. The change of surface morphology and Ti/C ratio demonstrated that some of the TiO_2 coating was washed away from wood surface after UV light and water spray irradiation. Fig 5 shows the morphology of the WTHM before and after UV light and water spray in the WeatherOmeter^{TM}. These changes were manifested as loss of the nanostructural protrusions that decorated the surfaces of the microstructures prior to exposure. These changes were accompanied by appearance of micro-cracks on the surface (Fig.5). These two changes were probably caused by the photocatalytic degradation of adjacent wood components, which led to the decrease in the bonding strength between wood and TiO_2 coating. The EDX results of WTHM (Fig 5) also showed a significant decrease in relative intensity of the titanium peak (Fig. 5) after 960-h exposure in the WeatherOmeter^{TM}, which further demonstrated the peeling off of TiO_2 nanostructures coating from wood surface.

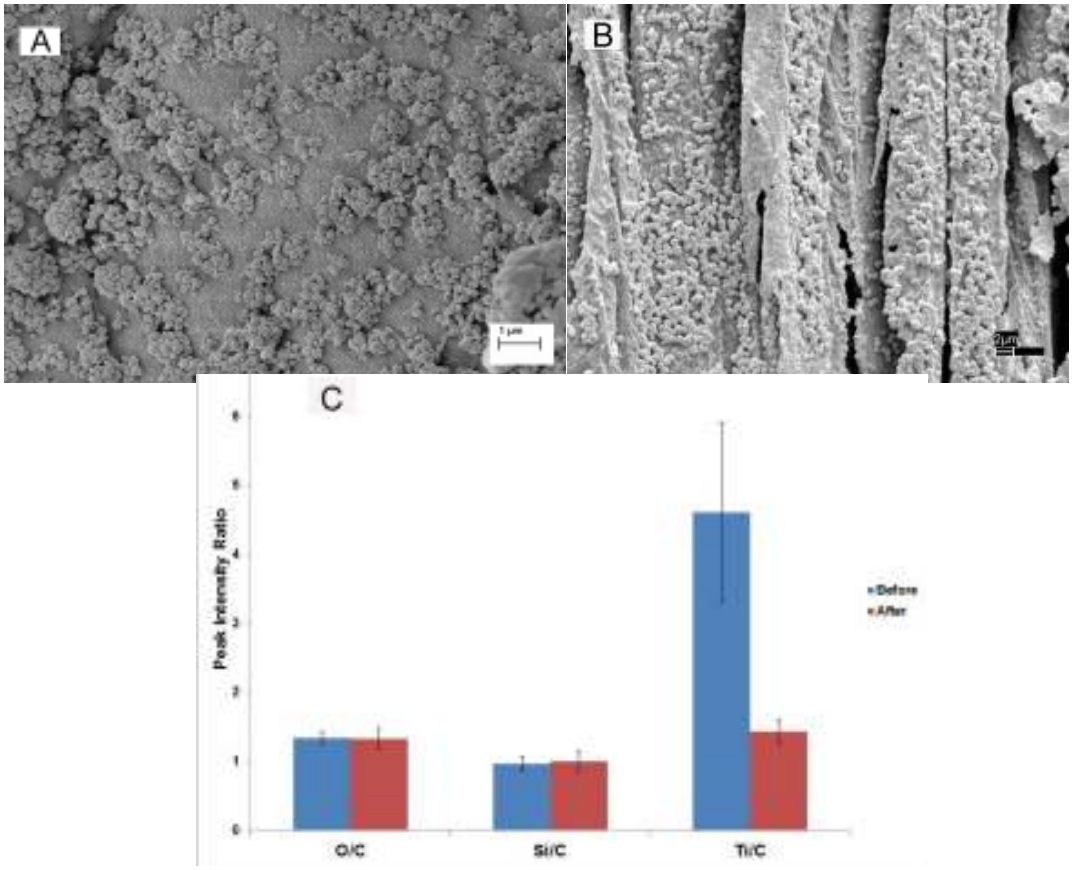

Fig. 5. SEM images of WTHM (A) before, (B) after 960-h exposure to program 1. (C) EDX peak ratios before and after 960-h exposure to UV light and water spray.

Conclusions

In summary, we developed a room temperature wet chemical route to in-situ deposition of rutile TiO_2 nanostructures on wood surface by direct hydrolysis and crystallization of $TiCl_3$ in saturated NaCl aqueous solution. Then, the weathering performance of TiO_2 treated wood was evaluated by exposure of the treated wood to UV light and water spray. Although TiO_2/HDTMOS/MTMOS coating apparently increased the weight stability of the wood, it made a relatively small contribution to the color stability of wood during 960-h accelerated weathering process. The possible reason is that TiO_2 coating also possesses native photocatalytic property, which not only changed the wettability of WTHM from initial hydrophobicity to hydrophilicity after 155-h UV irradiation due to the photocatalytic property of TiO_2, but also washing away of some of the TiO_2 coating from the wood surface after WTHM was exposed to 960-h UV irradiation and water spray. This study has shown that in order 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.

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