Improvement of Color Stability of Acacia Hybrid Wood by TiO_2 Nano Sol Impregnation

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In this study, the TiO_2-impregnation of wood from acacia hybrid (*Acacia mangium x auriculiformis*) was achieved by combined pressure-impregnation and hydrothermal post-treatment. The ultraviolet (UV) resistance of the obtained TiO_2-impregnated wood was examined by measuring the changes in color after 960 h of UV irradiation. Results showed that the color stability against UV irradiation of the TiO_2-impregnated wood was significantly improved compared to that of the untreated acacia hybrid wood. Furthermore, the prepared wood samples were characterized using a field-emission scanning electron microscope (FE-SEM), energy-dispersive X-ray (EDX) spectroscopy, and X-ray diffraction (XRD) techniques. FE-SEM and EDX analyses showed that the TiO_2 micro- and nanoparticles, with rod-like shapes, were located on the inner surfaces of the wood vessels. Additionally, the crystal structure of the TiO_2, with an anatase phase, was demonstrated by XRD analysis. This study suggests that the presence of an anatase TiO_2 can improve the UV resistance of fabricated wood samples.

Keywords: Acacia hybrid wood; Color; Impregnated-wood; FE-SEM, TiO_2; UV irradiation; XRD

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INTRODUCTION

Wood is an environmentally friendly material that is used extensively in indoor and outdoor applications. However, there are many unfavorable end-product properties of products that are composed of wood, such as biodeterioration, combustibility, and photodegradability. In particular, one of the drawbacks of wood for outdoor applications is a tendency for significant changes in its appearance over time (discoloration, roughening, checking), principally because of the ultraviolet (UV) light component of the sun's rays (Rowell 2005). Thus, enhancing the UV resistance of wood is important in that it could extend the areas of use of wood.

Acacia hybrid (*Acacia mangium x auriculiformis*) is a low-quality wood species abundantly available in Vietnam. At present, a large proportion of the available wood of this type is used for outdoor furniture production. To help this wood meet the requirements of outdoor applications, it needs a special treatment. A previous report showed the potential of improving the dimension stability of this wood (Tuong and Li 2010). In another report of Chu *et al*. (2014), the wettability of this wood was improved with TiO_2 gel treatment. However, there has been a lack of research on improvement of UV resistance of acacia hybrid wood.

Regarding UV resistance of wood, many reports describe ways to improve the weathering performance of wood and wood-based products *via* pretreatments such as

heat treatment, impregnation with preservatives (Deka *et al*. 2008), chemical modification (Pandey *et al*. 2010), and the application of a coating layer (Fjellstrom *et al*. 2009). In recent years, several methods of depositing thin barrier layers on wood surfaces to improve their moisture resistance (Rassam *et al*. 2011), dimensional stability (Sun *et al*. 2010), reduced wettability (Sun *et al.* 2011; Chu *et al.* 2014), and UV radiation resistance (Sun *et al.* 2012; Devi *et al.* 2013) properties were investigated. In these studies, film deposition was carried out primarily using the hydrothermal or sol-gel methods. Beside these mentioned methods, the sol-gel process also was applied to fabricate wood-inorganic composite (Saka *et al.* 1992; Saka and Ueno 1997; Miyafuji *et al.* 2004). These studies mostly used tetraethoxysilane (TEOS) as a precursor to prepare the wood composites.

Titanium dioxide (TiO_2) nanoparticles are the most useful because of their excellent chemical stability and nontoxicity (Fujishima and Honda 1972; Kim *et al*. 2005). Nano-TiO_2 has become an interesting functional material involved in photocatalysis (Fujishima and Honda 1972; Linsebigler *et al.* 1995), anti-UV, antibacterial, and self-cleaning surface and material applications (Wang *et al.* 1999; Yamagishi *et al.* 2003; Jiang and Zeng 2010).

In this study, the color stability during UV irradiation of acacia hybrid wood samples following a combined impregnation and hydrothermal treatment process, was examined. Additionally, the microstructure of the TiO_2-impregnated wood and the crystal structure of the TiO_2 in the wood samples were evaluated by a field-emission scanning electron microscope (FE-SEM) and X-ray diffraction (XRD), respectively.

EXPERIMENTAL

Materials

Wood specimens free of defects were cut from an eight-year-old acacia hybrid (*Acacia mangium x auriculiformis*) tree collected from the Hoa Binh province, Vietnam. Approximately the same amount of heartwood at breast height diameter position in the trunk was cut to prepare each wood sample, *i.e.*, 10 mm (T) x 20 mm (R) x 30 mm (L) in size (R: radial direction; T: tangential direction; and L: longitudinal direction), for the fabrication of the TiO_2-impregnated wood. All samples were conditioned for three weeks at 20 °C and 65% relative humidity (RH) prior to fabrication of the wood samples.

Tetrabutyl orthotitanate (TBOT, AR grade) was used as the precursor for the TiO_2 nanoparticles. Sodium dodecyl sulfate (SDS) was used as a surfactant. Ethanol (EtOH) was used as the solvent. All chemicals were supplied by Tianjin Baishi Chemical Industry Co., Ltd. and used without further purification. Distilled water was used for the preparation of all sol and solutions.

Synthesis of TiO_2 Nano Sol

The typical procedure used to prepare the aqueous nano sol was as follows. Approximately 5 mL of TBOT was dissolved into a mixture of 2 mL of acetic acid and 18 mL of anhydrous ethyl alcohol (EtOH) with magnetic stirring for 30 min until a homogenized solution was obtained. Then, 80 mL of distilled water (the pH of which was

adjusted to 4 by the addition of acetic acid) was added to this solution, dropwise, under vigorous stirring for several hours at room temperature.

Preparation of TiO_2-impregnated wood

Wood samples were first impregnated with the as-prepared sol solution. The impregnation process was carried out in a vessel under 7 bar pressure for 4 h at room temperature.

In the second step, impregnated wood samples and the remaining solution were transferred into a Teflon-lined stainless-steel autoclave and heated at 110 °C for 4 h in an oven.

After the heating process, the autoclave was allowed to cool to room temperature, was opened, and a solution of 3.4×10^{-4} M SDS at pH 6.5 was added. The autoclave was sealed again and reheated at 70 °C for 4 h in an oven. Finally, the wood samples were removed from the autoclave, ultrasonically rinsed with distilled water for 30 min, and oven-dried at 103 ± 2 °C overnight.

UV Irradiation Test

The photostability of the TiO_2-impregnated wood was determined using a 40-W UV light source for 960 h. The color of the tangential surfaces of TiO_2-impregnated wood was measured using an NF-333 spectrophotometer (Nippon Denshoku, Japan) with measurement diameter of 8 mm before and after UV irradiation.

The CIELAB system used in this study is characterized by three parameters: L^*, a^*, and b^*. The L^* axis represents the lightness, and $+a^*$ is red, $-a^*$ is green, $+b^*$ is yellow, and $-b^*$ is blue. L^* varies from 100 (white) to 0 (black). The L^*, a^*, and b^* color coordinates of each sample before and after UV irradiation were used to calculate the total color change, ΔE, according to the following equations,

$$\Delta L^* = L^*_{UV} - L^*_o \quad (1)$$

$$\Delta a^* = a^*_{UV} - a^*_o \quad (2)$$

$$\Delta b^* = b^*_{UV} - b^*_o \quad (3)$$

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

where ΔL^*, Δa^*, and Δb^* are the changes between before- and after-UV irradiation color values. Each parameter L^*, a^*, and b^* contributes to the total color change, ΔE. A low ΔE value corresponds to a small color change.

Characterization Methods

The microstructure morphologies of the TiO_2 formed in the TiO_2-impregnated wood were characterized by a field-emission scanning electron microscope (FE-SEM, 7600F, JEOL, Japan) combined with energy-dispersive X-ray (EDX, Oxford Instruments) spectroscopy at the voltage of 10kV. The crystal structures of the TiO_2-impregnated wood were analyzed by X-ray diffraction with a Siemens (Germany) D5000 X-ray diffractometer, operating with Cu K_α radiation with a weighted average wavelength of 0.154184 nm, and the scan angle (2θ) ranging from 5^o to 70^o.

RESULTS AND DISCUSSION

Morphological Studies

Scanning electron microscopy study

FE-SEM images of the TiO_2-impregnated wood are presented in Fig. 1. The apparently continuous layer of TiO_2 gels was located on the inner surface of the wood vessels (Fig. 1a), and some intervessel pits were blocked by TiO_2 gels (Fig. 1b and 1d). In addition, a number of evenly distributed, rod-like TiO_2 particles were observed on the thin coating (Fig. 1c). The morphology of the TiO_2 in this impregnated wood was similar to that observed by Sun *et al*. (2011), who hydrothermally treated the sol at pH 6.72.

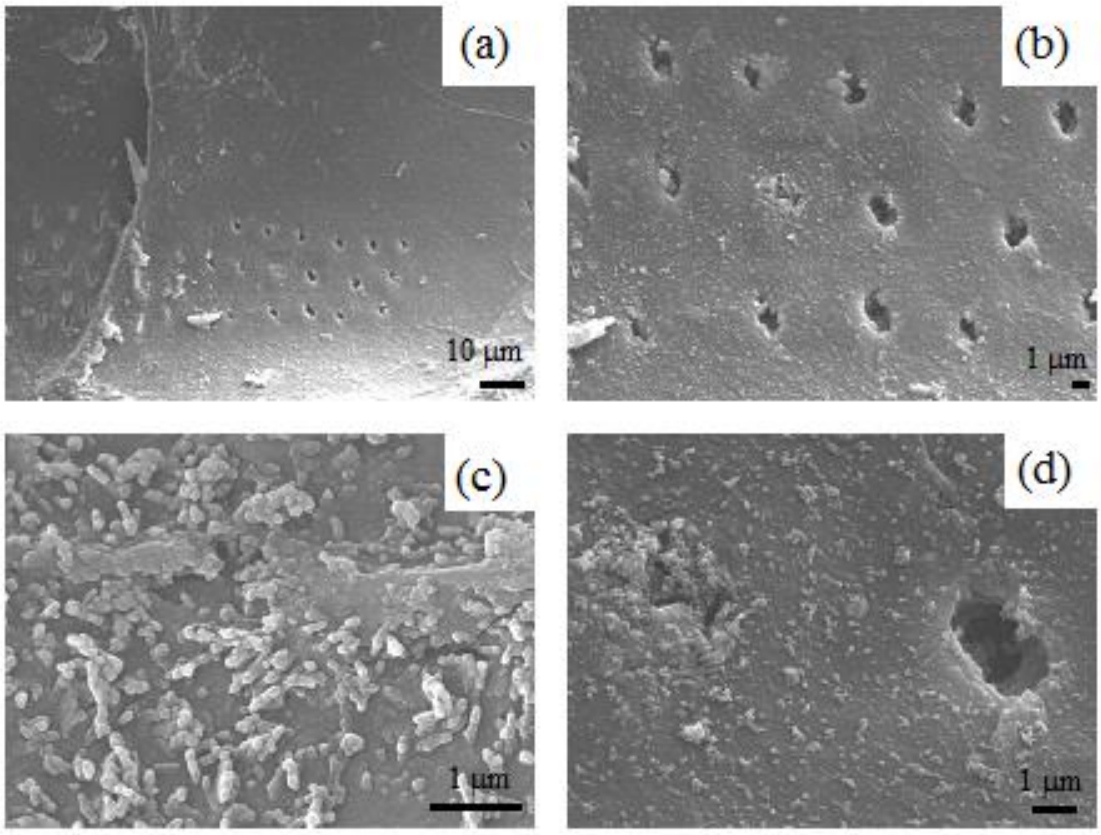

Fig. 1. FE-SEM images of TiO_2-impregnated wood samples at various magnifications: (a) the inner surface of the wood vessels (magnification: 1000X, scale bar: 10 μm); (b, c, and d) the intervessel pits in the tangential section: (b) magnification: 3000X, scale bar: 1 μm; (c) magnification: 10,000X, scale bar: 1 μm; (d) magnification: 20,000X, scale bar: 1 μm

Energy-dispersive X-ray analysis (EDX)

The presence of TiO_2 inside the wood, as observed by FE-SEM, was also investigated with energy-dispersive X-ray analysis (EDX). Figure 2 shows the EDX spectroscopy spectra of untreated wood and TiO_2-impregnated wood samples. There was a significant titanium (Ti) peak in the spectra of the TiO_2-impregnated wood samples (Fig. 2b) compared to those of untreated wood samples (Fig. 2a). This suggests that TiO_2 was a constituent element present in the samples after impregnation and hydrothermal treatment.

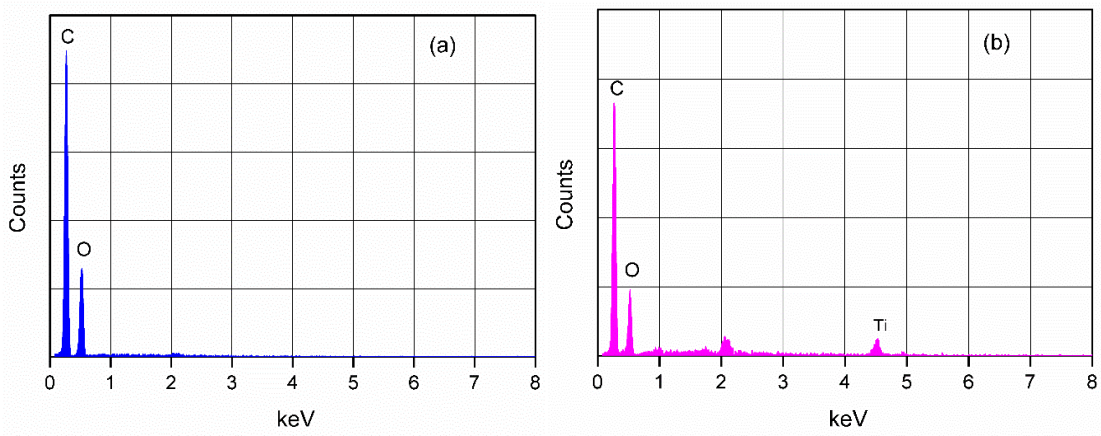

Fig. 2. EDX spectra of (a) untreated wood and (b) TiO_2-impregnated wood samples

X-Ray Diffraction Analysis

The XRD patterns of the untreated and TiO_2-impregnated wood samples were collected across a 2θ range of 10° to 70° to characterize their crystal structures. As shown in the diffraction patterns of the samples (Fig. 3), untreated and impregnated wood samples exhibited distinctly different characteristic peaks. In the pattern of the untreated wood sample (Fig. 3a), the only diffraction peaks, located at 2θ of 16° and 22.6°, were assigned to peaks of the cellulose crystal planes 101 and 002, respectively (Li 2003). However, in the pattern of the impregnated wood (Fig. 3b), other strong diffraction peaks were observed. The diffraction peaks at 2θ of 25°, 38°, 48°, and 55° were assigned to peaks related to anatase TiO_2. This result indicates that anatase TiO_2 was present in the impregnated wood (Chen and Mao 2007; Yang *et al.* 2009; Sun *et al.* 2012).

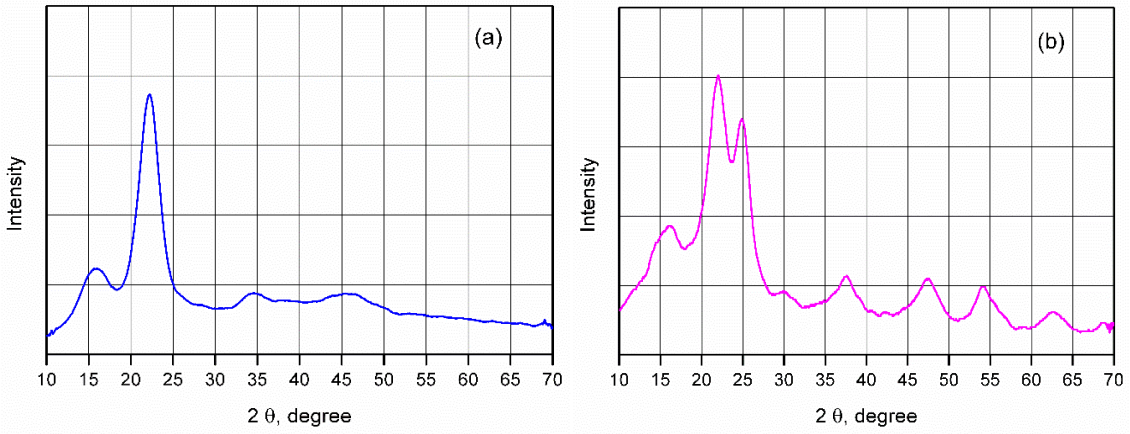

Fig. 3. XRD patterns of (a) untreated wood and (b) TiO_2-impregnated wood samples

Color Changes by UV Irradiation

Sun *et al.* (2011) reported that during hydrothermal treatment, anatase TiO_2 was chemically bonded to the wood surface *via* hydrogen groups. This finding was confirmed by many characterization methods, including SEM, EDX, XRD, and FTIR. It was inferred that the adherence of TiO_2 to the wood was strong when no significant loss of

titanium occurred, even after vigorous washing of the specimens (Sun *et al*. 2010). The remaining hydrophobicity of the TiO_2-impregnated wood, even after immersion in boiling water for 20 h (Chu *et al*. 2014), is further evidence supporting this point.

To determine the effect of TiO_2 on the UV resistance of the fabricated wood samples, the color changes of the TiO_2-impregnated wood surfaces after UV irradiation for 960 h were examined. The experimental results are presented in Fig. 4. As shown in Fig. 4a, the ΔL^* value of the untreated wood decreased from 0 to -8.68 with increasing irradiation time, indicating darkening. However, the ΔL^* value of the TiO_2-impregnated wood increased, from 0 to 0.98, indicating slight brightening. The ΔL^* value of the TiO_2-impregnated wood had only a slight change compared to that of the untreated wood. As shown in Fig. 4b, the Δa^* value of both untreated wood and TiO_2-impregnated wood indicated reddening that increased with UV irradiation time. However, the Δa^* value of the TiO_2-impregnated wood was smaller than that of the untreated wood. As shown in Fig. 4c, the Δb^* value of both untreated wood and the wood-TiO_2 composites exhibited a tendency opposite to that of their respective ΔL^* values. The total color change (ΔE^*) is shown in Fig. 4d. The ΔE^* value of both untreated wood and TiO_2-impregnated wood increased with increasing irradiation duration. Moreover, the ΔE^* value of the TiO_2-impregnated wood was smaller than that of the untreated wood, suggesting that the TiO_2-impregnated wood had greater UV resistance than untreated acacia hybrid wood, thereby preventing damage to the samples.

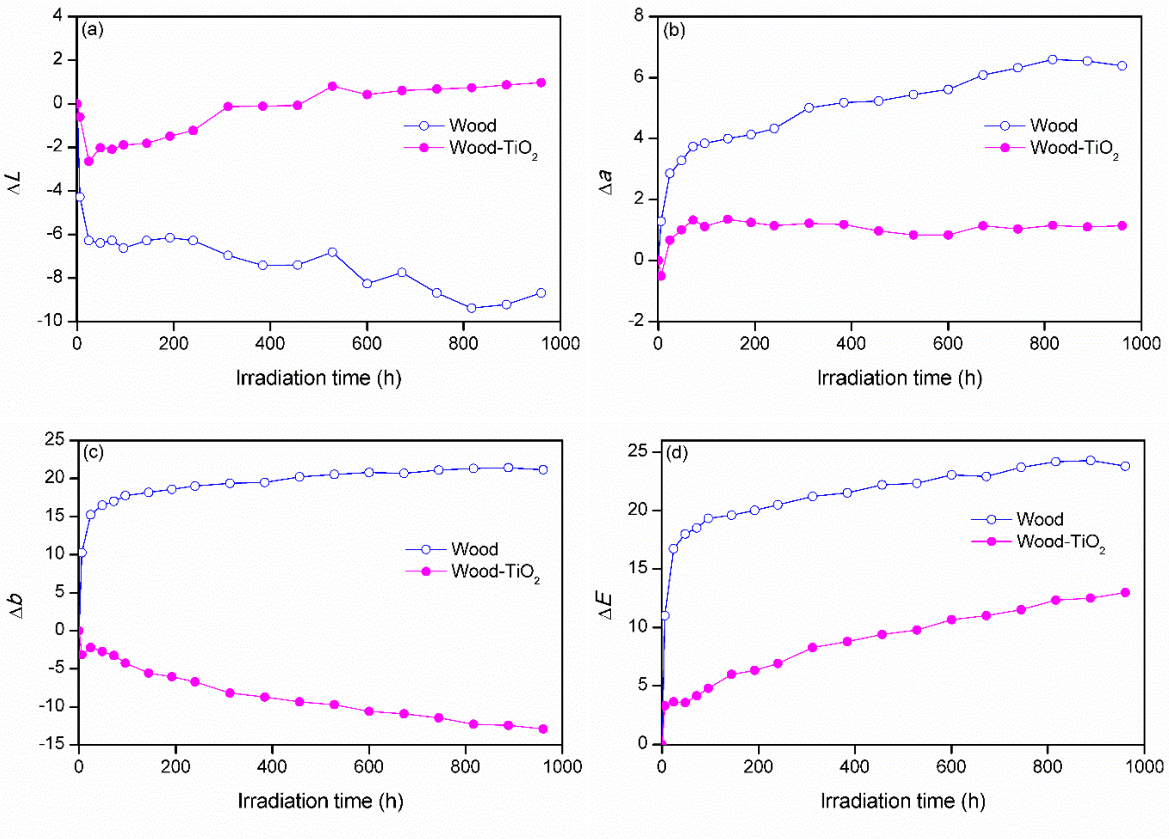

Fig. 4. Color changes of untreated wood and TiO_2-impregnated wood *versus* irradiation time

It is well known that under UV irradiation, lignin, one of the components of wood, is subjected to photo-oxidation by the formation of carbonyl-based chromophoric compounds. This induces the color change of irradiated wood surfaces (George *et al*. 2005). TiO_2 particles absorbed UV radiation and thus decreased the UV intensity when contact to wood components, slowing the oxidation of the TiO_2-impregnated wood. The increase in the samples' ability to resist UV irradiation with the incorporation of TiO_2 was reported by Sun *et al*. (2012) and (Devi *et al.* 2013). Hence, the UV resistance of the TiO_2-impregnated wood was improved compared to that of untreated wood, perhaps because of the high UV radiation absorption capability of anatase TiO_2.

CONCLUSIONS

1. TiO_2-impregnated wood made from acacia hybrid wood and TiO_2 were successfully fabricated by a combined impregnation and hydrothermal post-treatment process. The existence of anatase micro- and nano-sized TiO_2 particles with rod-like shapes on the wood surfaces was verified by FE-SEM, EDX, and XRD analyses.
2. The UV resistance of the TiO_2-impregnated wood, expressed as their color change during UV irradiation, was significantly higher than that of untreated wood, indicating that the impregnation and hydrothermal post-treatment process improves the ability of acacia hybrid wood to resist UV irradiation.

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REFERENCES CITED

Chen, X., and Mao, S. S. (2007). "Titanium Dioxide Nanomaterials: Synthesis, properties, modifications, and applications," *Chem. Rev.* 107(7), 2891-2959. DOI: 10.1021/cr0500535

Chu, T. V., Chuong, P. V., and Tuong, V. M. (2014). "Wettability of wood pressure-treated with TiO_2 gel under hydrothermal conditions," *BioResources* 9(2), 2396-2404. DOI: 10.15376/biores.9.2.2396-2404

Deka, M., Humar, M., Rep, G., Kricej, B., Sentjurc, M. S., and Petric, M. (2008). "Effects of UV light irradiation on colour stability of thermally modified, copper ethanolamine treated and non-modified wood: EPR and DRIFT spectroscopic studies," *Wood Sci. Technol.* 42(1), 5-20. DOI: 10.1007/s00226-007-0147-4

Devi, R., Gogoi, K., Konwar, B., and Maji, T. (2013). "Synergistic effect of nano TiO_2 and nanoclay on mechanical, flame retardancy, UV stability, and antibacterial properties of wood polymer composites," *Polym. Bull.* 70(4), 1397-1413. DOI: 10.1007/s00289-013-0928-x

Fjellstrom, H., Hoglund, H., Forsberg, S., and Paulsson, M. (2009). "The UV-screening

properties of coating layers: The influence of pigments, binders and additives," *Nordic Pulp & Paper Research Journal* 24(2), 206-212. DOI: 10.3183/NPPRJ-2009-24-02-p206-212

Fujishima, A., and Honda, K. (1972). "Electrochemical photolysis of water at a semiconductor electrode," *Nature* 238(5358), 37-38. DOI:10.1038/238037a0

George, B., Suttie, E., Merlin, A., and Deglise, X. (2005). "Photodegradation and photostabilisation of wood – The state of the art," *Polym. Degrad. Stab.* 88(2), 268-274. DOI:10.1016/j.polymdegradstab.2004.10.018

Jiang, G., and Zeng, J. (2010). "Preparation of nano-TiO_2/polystyrene hybride microspheres and their antibacterial properties," *J. Appl. Polym. Sci.* 116(2), 779-784. DOI: 10.1002/app.31484

Kim, T. K., Lee, M. N., Lee, S. H., Park, Y. C., Jung, C. K., and Boo, J. H. (2005). "Development of surface coating technology of TiO_2 powder and improvement of photocatalytic activity by surface modification," *Thin Solid Films* 475(1-2), 171-177. DOI:10.1016/j.tsf.2004.07.021

Li, J. (2003). *Wood Spectroscopy (in Chinese)*, Science press, Beijing.

Linsebigler, A. L., Lu, G., and Yates, J. T. (1995). "Photocatalysis on TiO_2 surfaces: Principles, mechanisms, and selected results," *Chem. Rev.* 95(3), 735-758. DOI: 10.1021/cr00035a013

Miyafuji, H., Kokaji, H., and Saka, S. (2004). "Photostable wood-inorganic composites prepared by the sol-gel process with UV absorbent," *J. Wood Sci.* 50(2), 130-135. DOI: 10.1007/s10086-003-0550-x

Pandey, K. K., Hughes, M., and Vuorinen, T. (2010). "Dimensional stability, UV resistance, and static mechanical properties of scots pine chemically modified with alkylene epoxides," *BioResources* 5(2), 598-615. DOI: 10.15376/biores.5.2.598-615

Rassam, G., Abdi, Y., and Abdi, A. (2011). "Deposition of TiO_2 nano-particles on wood surfaces for UV and moisture protection," *J. Exp. Nanosci.* 7(4), 468-476. DOI: 10.1080/17458080.2010.538086

Rowell, R. M. (2005). *Handbook of Wood Chemistry and Wood Composites*, CRC Press, Boca Raton, Florida.

Saka, S., Sasaki, M., and Tanahashi, M. (1992). "Wood-inorganic composites prepared by sol-gel processing .1. Wood-inorganic composites with porous structure," *Mokuzai Gakkaishi* 38(11), 1043-1049.

Saka, S., and Ueno, T. (1997). "Several SiO_2 wood-inorganic composites and their fire-resisting properties," *Wood Science and Technology* 31(6), 457-466. DOI: 10.1007/BF00702568

Sun, Q., Lu, Y., and Liu, Y. (2011). "Growth of hydrophobic TiO_2 on wood surface using a hydrothermal method," *J. Mater. Sci.* 46(24), 7706-7712. DOI: 10.1007/s10853-011-5750-y

Sun, Q., Lu, Y., Zhang, H., Zhao, H., Yu, H., Xu, J., Fu, Y., Yang, D., and Liu, Y. (2012). "Hydrothermal fabrication of rutile TiO_2 submicrospheres on wood surface: An efficient method to prepare UV-protective wood," *Mater. Chem. Phys.* 133(1), 253-258. DOI:10.1016/j.matchemphys.2012.01.018

Sun, Q., Yu, H., Liu, Y., Li, J., Lu, Y., and Hunt, J. F. (2010). "Improvement of water resistance and dimensional stability of wood through titanium dioxide coating," *Holzforschung* 64(6), 757-761. DOI: 10.1515/hf.2010.114

Tuong, V. M., and Li, J. (2010). "Effect of heat treatment on the change in color and dimensional stability of acacia hybrid wood," *BioResources* 5(2), 1257-1267.

Wang, R., Sakai, N., Fujishima, A., Watanabe, T., and Hashimoto, K. (1999). "Studies of surface wettability conversion on TiO_2 single-crystal surfaces," *J. Phys. Chem. B* 103(12), 2188-2194. DOI: 10.1021/jp983386x

Yamagishi, M., Kuriki, S., Song, P. K., and Shigesato, Y. (2003). "Thin film TiO_2 photocatalyst deposited by reactive magnetron sputtering," *Thin Solid Films* 442(1–2), 227-231. DOI:10.1016/S0040-6090(03)00987-8

Yang, D., Liu, H., Zheng, Z., Yuan, Y., Zhao, J.-c., Waclawik, E. R., Ke, X., and Zhu, H. (2009). "An efficient photocatalyst structure: TiO_2(B) nanofibers with a shell of anatase nanocrystals," *J. Am. Chem. Soc.* 131(49), 17885-17893. DOI: 10.1021/ja906774k

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