Controlled Growth and Properties of TiO$_2$ Coating onto Wood Surface Using a Low-Temperature-Cosolvent Hydrothermal Method

Qingfeng Sun$^1$* - Yun Lu$^1$ - Jian Li$^1$ - Haipeng Yu$^1$ - Yixing Liu$^1$*

$^1$ Key laboratory of Bio-based Material Science and Technology, Ministry of Education, Northeast Forestry University

*Corresponding author

yxliu@nefu.edu.cn and qfsun@nefu.edu.cn

Abstract

Growth of TiO$_2$ inorganic coating onto the wood surface has great research values and practical significance to the persistent, functional and high value-added utilization of wood materials. In the present paper, TiO$_2$ coating with controlled morphologies, sizes, and crystalline type was successfully grown onto the wood surface using a low-temperature-cosolvent hydrothermal method. SEM, EDS, FTIR, and XRD techniques were employed to characterize the as-prepared wood sample. Dimensional stability, UV-resistance, wettability, antibacterial property, and photocatalytic activities of the prepared wood sample were also measured. The morphologies, sizes, and crystalline type of TiO$_2$ grown onto the wood surface could be controlled through the regulations of the reaction parameters. Compared with the control wood, water absorption of TiO$_2$-coated wood decreased by 11 times after 90-days cold water immersion and the dimensions had no obvious change under different relative humidity (20%~90%). Rutile TiO$_2$-coated wood exhibited significant UV-resistance after 1200-hour UV irradiation due to high UV light absorption capability, superior light scattering property and high recombination of the photogenerated electron and hole of the deposited rutile TiO$_2$ on the wood surface. With further modification of the hydrothermal grown TiO$_2$, the hydrophilic wood surface presented the superhydrophobicity with WCA of 154°. Meanwhile, anatase TiO$_2$-coated wood revealed favorable antibacterial property and photocatalytic degradation of gas formaldehyde, the bactericidal rates of $E$.coli and $S$. aureus aureus were 94.7% and 92.6%, respectively; and the degradation rate of gas formaldehyde was about 98.7%. This paper potentially provided a feasible pathway for fabrication of inorganic/wood, fiber, or bamboo composites.

Keywords: Low-temperature-cosolvent hydrothermal method, TiO$_2$, superhydrophobicity, photocatalysis, UV-resistance, wood.
Introduction

Wood continues to be used for wide applications (Fig. 1) because of its many excellent material properties (such as a good strength to weight ratio, aesthetic appearance etc.). However, it also suffers from a number of disadvantages which are presented in Fig. 2. Dimensional changes in response to altering atmospheric conditions, susceptibility to biological attack and changes in appearance when wood exposed to weathering place restrictions on the potential end-uses of wood.

![Fig. 1 Wide applications of wood](image1.png)

![Fig. 2 Disadvantages of wood](image2.png)

Wood surface modification can overcome these wood disadvantages and grant some other unique characteristics such as superhydrophobicity, antibacterial property and so on. But conventional surface modification like mechanical brush or direct immersion can result in uneven dispersion and negative bonding which are illustrated in Fig. 3. The currently most method for surface modification methods are summarized as painting, sol-gel method, plasma or corona discharge etc. However, most of the above processes require expensive equipment or reagents, which suggest that they are unlikely to be used on a large scale in the foreseeable future. Therefore, how to develop a facile method for surface modification is a hot tissue in wood science and technology.

![Fig. 3 Disadvantages of conventional wood surface modification](image3.png)
As one of the most promising functional materials, titanium dioxide (TiO$_2$) has been extensively used in photocatalysis, solar cells and paints because of its superior chemical stability and nontoxicity. TiO$_2$ exists mainly in four polymorphs in nature, namely, anatase (tetragonal, space group $I4_1/amd$), rutile (tetragonal, space group $P4_2/mnm$), brookite (orthorhombic, space group $Pbc$), and TiO$_2$ (B) (monoclinic, space group $C2/m$) (Fig. 4). Because of instability and scarcity of the latter two, the former two are often employed and studied in many fields.

![Fig. 4 Anatase, rutile and brookite TiO$_2$ single crystals in nature (a, d, g) and their crystal structure (b, e, h); unit cells (c, f, i) of anatase, rutile and brookite TiO$_2$.](image)

In the present paper, TiO$_2$ nanomaterials were grown onto the wood surface through LTCHM. The inherent properties of wood have been greatly improved and some new special characteristics were also granted by the thin grown inorganic TiO$_2$ layer.

**Materials and Methods**

Low-temperature-cosolvent hydrothermal method (LTCHM) is a new method proposed by our research group. Wood materials are set in the solution or colloid containing inorganic free ions or colloidal particles, which will grow into nanometer materials with the hydrothermal energy effect. The groups generated on the surface react with hydroxide radical on the wood surface and forms hydrogen bond, in this way to be connected on the wood surface and further generate the inorganic nanometer crystal layer on the wood surface. Finally, the wood properties are improved and new special properties are derived.

The possible mechanism of LTCHM is presented in Fig. 5.
Results and Discussion

Water resistance and dimensional stability: Moisture absorption and dimensional distortion are the major drawbacks of wood utilization as building material. In this study, poplar wood coated with a thin layer of titanium dioxide (TiO₂) was prepared by LTCHM. Afterwards, its moisture absorption and dimensional stability were examined. SEM images revealed that the wood substrate was closely and entirely covered with the TiO₂ coat and micro-scale features were visible despite masking of the ultrastructural features of the cell wall (Fig. 6). To explore the effects of TiO₂ coating on the water-repellency and dimensional stability of wood, a 90-day water immersion test was carried out. Results show that water absorption and thickness swelling of TiO₂-coated wood increase very slowly and minimally. Weight change after 90 days of water immersion was reduced to 20.5%, nearly one-tenth of untreated control wood, and that maximum cross-sectional relative swelling was only 1.2% (Fig. 7). Specimens were conditioned for 3 months at different relative humidity (RH, 20%~90%) to determine the effects of RH on moisture absorption and dimensional swelling of TiO₂-coated wood. There was no change in weight after 3 months of being exposed to humidity conditions below 60% while there was linear weight increase above 60% RH, but the maximum change was less than 6%. Cross-sectional relative swelling was less than 0.3% below 60% RH but increased as RH exceeded 60%. The maximum change was approximately 3%. Anisotropic thickness swelling of wood was almost eliminated after coating. The corresponding graph data were shown in Fig. 8 and 9. It is obvious that TiO₂ coating can act as a moisture barrier for wood and is an exceptionally strong water vapor-inhibiting shield under very humid conditions.
Fig. 6 SEM images of the TiO$_2$-coated wood at low (100x, scale bar 400 μm) and high (2 000x, scale bar 20 μm; 5 000x, scale bar 5 μm; 10 000x, scale bar 2 μm) magnification. Low-magnification image (a) shows the TiO$_2$ coat on the cut cellular nature of wood with its micro-scale features. High-magnification image (b) shows the changes in the lumen surface and ray cells with the film masking the exposed surfaces. (c) shows the vessel-ray cross-field pits in radial section and (d) shows the intervessel pits in tangential section.

Fig. 7 the weight percentage change of untreated control wood (square symbols) and TiO$_2$-coated wood (triangle symbols) during ninety days of water immersion test.

Fig. 8 the weight percentage change of untreated control wood (solid circle symbols) and TiO$_2$-coated wood (open circle symbols) due to water vapor absorption as different RH conditions for a period of three months.

Fig. 9 Difference in cross-sectional relative swelling between the untreated control wood (solid square symbols) and TiO$_2$-coated wood (open circle symbols) due to water vapor absorption in different relative humidity conditions.
UV-resistance} Wood with UV-resistant ability was successfully prepared by depositing submicrometer-sized rutile TiO$_2$ spheres on wood surface using LTCHM. Meanwhile, anatase TiO$_2$ coated-wood was also fabricated using the LTCHM. SEM images showed the diameters of anatase and rutile TiO$_2$ were about 150 nm and 200 nm, respectively (Fig. 10). XRD and ATR-FTIR spectra demonstrated that firmly chemical bonds were formed at the interfaces between rutile TiO$_2$ and wood owing to the presence of hydroxyl groups, the schematic illustration was also proposed (Fig. 11 and 12). Accelerated aging test was used to measure the UV resistance of the original wood (OW), anatase TiO$_2$/wood (ATW) and rutile TiO$_2$/wood (RTW). Comparison with OW and ATW samples, RTW exhibited more superior UV-resistant ability due to high UV light absorption capability, superior light scattering property and high recombination of the photogenerated electron and hole of the submicrometer-sized rutile TiO$_2$ spheres on the wood surface (Fig. 13 and 14).

Fig. 10 SEM images of the (a) OW, (b) ATW and (c) RTW, respectively

Fig. 11 XRD patterns (a) and ATR-FTIR spectra (b) of the OW, ATW and RTW, respectively

Fig. 12 Schematic illustration of the hydrothermal deposition of submicrometer-sized TiO$_2$ spheres on wood surface. Bu: C$_4$H$_9$
Wettability Inspired by surface topography-induced superhydrophobicity of lotus leaves and water strider’s legs, a barrier TiO$_2$ coating could also be grown on wood surface to exhibit hydrophobic properties for meeting higher water repellent requirements. Hydrophobic TiO$_2$ was grown onto the wood surface using LTCHM. XRD and FTIR proved that anatase TiO$_2$ chemically bonded to the wood surface through the combination of hydrogen groups during the hydrothermal process (Fig. 15 and 16). The values of WCAs manifested that the hydrophobicity of the treated wood was mainly dependent on specific reaction conditions, especially on reaction pH value and hydrothermal temperature. The highest WCA reached 154° when the hydrothermal temperature was 130 °C, the schematic illustrations for fabricating the hydrophobic wood were also described in the text. (Fig. 17 and 18).
Antibacterial property and degradation of formaldehyde

Antibacterial property and the degradation ratio of anatase TiO$_2$ coated wood were measured, respectively. From SEM images observation and XRD analysis, the wood surface was totally covered by smooth anatase TiO$_2$ with the diameter of about 80~200 nm and AFM image revealed the thickness is about 1.2 µm (Fig. 19). The anatase TiO$_2$/wood has good antibacterial property and photocatalytic degradation of gas formaldehyde; the sterilization rates of *escherichia coli* and *staphylococcus aureus* are 94.7% and 92.6%, respectively under ultraviolet light (Fig. 20). The degradation rate of gas formaldehyde can amount to 98.7% in 168 hours at room temperature (Fig. 21). The mechanism of anatase TiO$_2$/wood can be ascribed to anatase TiO$_2$ grown onto the wood surface. Under the UV light, the electrons ($e^-$) in the conduction band and positive holes (h$^+$) in the valence band of TiO$_2$ were formed. Excited state electrons and holes can recombine and then dissipate the input energy as heat, get trapped in metastable surface states, and react with electron donors/acceptors. If a suitable reductant (electron donor) or oxidant (electron acceptor) is available to trap the hole or electron, recombination is prevented and subsequent photocatalytic reactions may occur efficiently on the semiconductor surface. Actually, photocatalytic reactions may occur by either directly via the valence-band hole or indirect oxidation via the surface-bound hydroxyl radicals (i.e., a trapped hole at the particle surface reacts with HO or H$_2$O to be transformed into •OH). The •OH radicals produced by TiO$_2$ are one of the most powerful oxidizing species with an oxidation potential. Unlike other radicals, hydroxyl radicals are non-selective and thus readily attack a large group of organic chemicals to be hydroxylated or form partially oxidized intermediates. At sufficient contact time and proper operation conditions, it is practically possible to mineralize the target pollutants to CO$_2$ and H$_2$O (Fig. 22).
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Fig. 19 (a) XRD patterns, (b) SEM images, and (c) AFM imaged of treated wood, (d) SEM images of E. coli and S. aureus

Fig. 20 Percent reduction of E. coli and S. aureus by the control wood and TiO$_2$-coated wood

Fig. 21 Formaldehyde adsorption and degradation curve of control wood and TiO$_2$-coated wood

Fig. 22 Mechanism illustration of TiO$_2$-coated wood for antibacterial and photodegradative activities

Flame retardancy Using the cone calorimetry technique, the significant difference in combustion parameters between the untreated and the TiO$_2$ coated wood was observed. In comparison to the untreated wood, the burning time of TiO$_2$ coated wood was doubled (Fig. 23) and the initial yield of CO2 and CO was almost zero (Fig. 24). As a result, the TiO$_2$ coating can effectively act as a protective layer for wood and convert wood from a flammable material into a fireproof material.

Fig. 23. HRR patterns of the untreated and TiO$_2$ coated wood

Fig. 24 CO2Y and COY patterns of untreated and TiO$_2$ coated wood

Conclusions
(1) Low-temperature-cosolvent hydrothermal method is a feasible method for growing inorganic TiO$_2$ onto the wood surface.

(2) With the combination of wood and the grown TiO$_2$, the intrinsic properties of wood can be improved and some special properties were also granted.

(3) This paper potentially also provides a feasible pathway for synthesis of inorganic nanomaterials/wood, fiber, or bamboo hybrid composites.

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