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Construction of hydrophobic wood surfaces by room temperature deposition of rutile (TiO_2) nanostructures

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ABSTRACT

A convenient room temperature approach was developed for growing rutile TiO_2 hierarchical structures on the wood surface by direct hydrolysis and crystallization of $TiCl_3$ in saturated NaCl aqueous solution. The morphology and the crystal structure of TiO_2 coated on the wood surface were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. The TiO_2 morphology on the wood surface could be tuned by simply changing either the reaction time or pH value of the reaction mixture. After modification with perfluorodecyltriethoxysilane (PFDTS), the water contact angle (WCA) of the TiO_2-treated wood (T1) surface increased to $140.0 \pm 4.2^\circ$, which indicated a highly hydrophobic wood surface. In addition, compared with untreated control wood, PFDTS-TiO_2 treatment (PFDTS-T1-treated) not only reduced liquid water uptake, but also delayed the onset of water saturation point of the wood substrate. The weight change of PFDTS-T1-treated wood after 24 h of water immersion was 19.3%, compared to 81.3% for the untreated control wood. After 867 h of water immersion, the weight change for the treated and untreated wood specimens was 117.1%, and 155.1%, respectively. The untreated control wood reached the steady state after 187 h, while the PFDTS-T1-treated wood did not reach the steady state until after 600 h of immersion.

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1. Introduction

When wood materials are used outdoors, they swell and shrink from absorption and desorption of moisture. These swelling and shrinking cycles induce stresses in the wood cell wall that often lead to warping and cracking of the wood. The wood surface can also be disfigured by mold growth or discolored by the action of sunlight in combination with rain. Deterioration of the wood surface caused by exposure to sunlight and rain is referred to as weathering. Novel methods for improving the weathering performance of wood have been reported in the literature. These include nanosol treatment [1,2], plasma enhanced chemical vapor deposition of thin barrier films on the wood surface [3], and hydro/solvo thermal treatment [4]. Recently, Tshabalala et al. [5] demonstrated the feasibility of using a combination of organic light stabilizers and sol–gel deposits of hybrid inorganic thin films to improve weathering resistance of softwood substrates. They concluded that sol–gel treatment improved resistance to moisture uptake, and the presence of some organic light stabilizers improved the photostability of the wood substrate.

The objective of the current study was to test the hypothesis that hydrophobicity of a wood substrate can also be attained by creating nanostructural protrusions on the wood substrate surface that will render the surface super hydrophobic similar to the superhydrophobicity of the lotus leaf. A superhydrophobic surface can be obtained by a combination of a rough surface comprised of inorganic hierarchical nanostructures and low surface energy materials. It is well known that some inorganic oxides such as TiO_2, ZnO, or FeO are good UV light absorbers. Thus, weathering resistance of wood can be improved by coating with barrier films comprised of hierarchical nanostructures of TiO_2 and low surface energy materials. The hierarchical TiO_2 nanostructures are expected to provide both UV light resistance and liquid water repellence, and the low energy materials are expected to enhance the moisture resistance of the wood substrate.

TiO_2, as one of the most widely used multifunctional nanomaterials, has attracted a great deal of attention because of its

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applications in photocatalysts, pigments, and cosmetics [6–9]. Yang et al. [10] demonstrated that anatase TiO_2 is more suitable as a photocatalyst, and rutile TiO_2 is preferable for blocking UV radiation. Motivated by this observation, Sun et al. [11] designed a high-temperature hydrothermal route to deposit sub-micrometer-sized rutile TiO_2 spheres on wood surfaces, which exhibited higher UV resistance compared with anatase-coated wood surfaces. As wet wood fiber is susceptible to the possibility of autohydrolysis at elevated temperatures [12], it is important to develop methods for coating wood surfaces with rutile nanostructures under more moderate reaction conditions.

This study reports development of a room temperature route 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. The morphology of rutile TiO_2 hierarchical structure can be controlled by either changing the reaction time or the pH of the reaction mixture. After modification with low surface energy material, hydrophobicity and liquid water uptake of TiO_2-wood specimens were characterized by contact angle analysis and water immersion test.

2. Experimental

2.1. Materials

Wood specimens were obtained from mountain pine beetle-killed lodgepole pine logs. The specimens were each cut into wafers, 1.0 mm × 15.8 mm × 51.3 mm in the tangential, radial, and longitudinal directions, respectively. 12% $TiCl_3$ solution and 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane (PFDTS) were obtained from Sigma-Aldrich. All other laboratory chemicals used were American Chemical Society (ACS) reagent-grade.

2.2. Synthesis of rutile TiO_2 and rutile TiO_2 wood specimens

In a typical synthesis, 3 mL titanium (III) chloride–hydrochloride acid solution, which contains 12 wt% of $TiCl_3$, was dissolved in 90 mL NaCl saturated aqueous solution. The pH of the reaction mixture was adjusted from −0.23 to −0.02 by addition of NaOH–NaCl aqueous solution. The NaOH–NaCl solution was prepared by adding 1.00 g NaOH to 25.00 mL NaCl saturated solution. The reaction mixture was allowed to stand for 3 days under constant stirring before the resulting white precipitate was collected, dried, and analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). To grow rutile TiO_2 nanostructures on the wood surface, the reaction mixture was only stirred for 1 day before careful immersion of the wood specimen in it. The stirring was stopped and the reaction was allowed to proceed for 10 days at room temperature before the wood specimens were removed for washing, drying, and analysis. The samples were washed with deionized water to remove residual reagents. The samples were dried under the hood at ambient temperature and are designated as T1. In order to optimize the deposition conditions, we obtained treated wood samples T2, T3, T4, and T5 by selecting different reaction time, as well as the different volume of NaOH solutions (Table 1). All the samples were analyzed by SEM, and T1 was selected for further modification with PFDTS and analysis by water contact angle and liquid water uptake measurements.

Table 1
Reaction conditions and corresponding tests.

	T1	T2	T3	T4	T5
pH value	−0.02				1.27
Reaction time/days	10	1	3	15	3
Characterization and test[a]	SEM, XRD Water contact angle Liquid water uptake	SEM	SEM	SEM	SEM

[a] T1 specimens were tested by water contact angle and liquid water uptake measurements, prior to modification with PFDTS.

2.3. Modification with low surface energy material

Treatment of the untreated control wood and TiO_2-treated wood specimens (T1) with PFTDS, a low surface energy material, was accomplished by immersing them in a 1.0 wt% PFDTS solution of n-hexane for 4 h at room temperature. After rinsing with acetone and drying under the hood at room temperature, PFTDS-treated and PFTDS-T1-treated wood specimens were obtained.

2.4. Characterization

The wettability of untreated control, PFTDS-treated and PFTDS-T1-treated wood specimens were evaluated by measuring the dynamic contact angle of a 4-μL deionized water droplet using a PGX+ Contact Angle Tester (Thwing-Albert Instrument Company, West Berlin, NJ, USA). The water contact angle (WCA) for each specimen was determined by taking the average of three measurements made at three different spots on each specimen. There were six replicates per treatment (SEM) images were obtained by using a LEO 1530 field emission scanning electron microscope. The crystalline phase of TiO_2 was determined by XRD (DX-2700, Rigaku) with Cu Kα radiation (λ = 1.5418 Å).

2.5. Liquid water uptake

Liquid water uptake was determined by keeping the specimens (untreated control and PFTDS-T1-treated) submerged under deionized water in the 65% relative humidity (RH) room at 27.6 °C for a

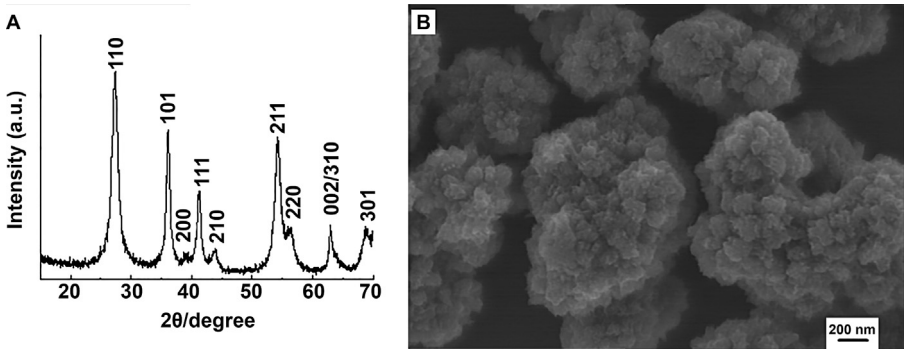

Fig. 1. (a) XRD and (b) SEM of TiO_2 obtained via hydrolysis and crystallization of the $TiCl_3$ in saturated NaCl aqueous solution for 3 days at room temperature.

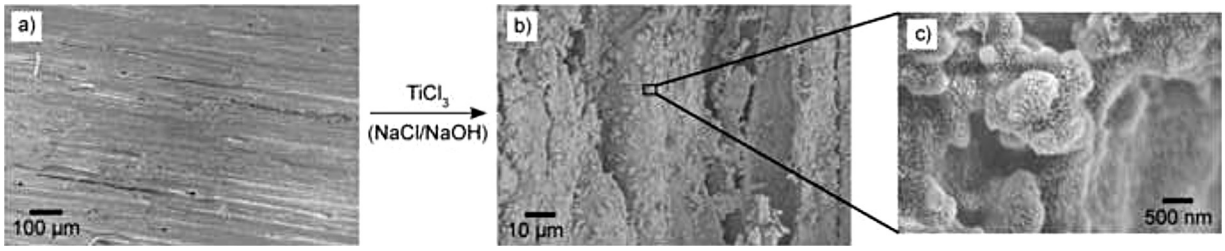

Fig. 2. Illustration of the construction of rutile TiO_2 hierarchical structures on the wood surface. (a) untreated wood surface; (b) treated wood surface; (c) close-up.

total of 867 h. There were six replicates per treatment. The specimens were withdrawn periodically from the water, blotted lightly with absorbent paper and weighed. The percentage of weight change Eq. (1) was used to determine the liquid water uptake of wood.

$$\Delta W\,(\%) = \frac{W_1 - W_0}{W_0} \times 100\% \quad (1)$$

where W_0 and W_1 is the weight of the wood specimen before and after water immersion, respectively. W_0 and W_1 were determined by measuring the equilibrium weight of each specimen at 65% RH.

3. Results and discussion

3.1. Structure and morphology

Prior to deposition of rutile TiO_2 hierarchical structures on the wood surface at room temperature, preparation of rutile TiO_2 hierarchical structures in solution at room temperature was first investigated. After hydrolysis and crystallization of the 3-mL $TiCl_3$ in saturated NaCl aqueous solution for 3 days, a white precipitate was formed. The precipitate was collected, washed with water and ethanol and allowed to dry at room temperature for analysis by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The XRD pattern (Fig. 1a) showed reflection peaks that can be indexed to pure rutile TiO_2 (JCPDS file No. 21-1276) [6]. The SEM image of the rutile TiO_2 powder (Fig. 1b) showed cauliflower-like spheres with an average diameter of about 0.3–1 μm. A closer examination showed that the surface of the cauliflower-like spheres consisted of many loosely packed nanoparticles. It has been suggested that rutile TiO_2 hierarchical structure such as those in Fig. 1 can be generated by direct oxidation of the $TiCl_3$ with atmospheric O_2 in saturated NaCl aqueous solution at room temperature [9]. Thus, similarly to the rutile TiO_2 films prepared by $TiCl_3$ under hydrothermal conditions (200 °C) [13], formation of rutile TiO_2 nanostructures at room temperature is proposed to follow the same reaction pathway as summarized in Eq. (2).

$$Ti^{3+} + H_2O + O_2 \rightarrow \text{Ti(IV)oxospecies} + H^+ + O_2^- \rightarrow TiO_2(\text{rutile}) \quad (2)$$

Based on results of the above-mentioned preliminary experiments we developed a method for constructing rutile TiO_2 hierarchical structures on the wood surface. Fig. 2 is the schematic of 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. After a 10-day reaction time, the wood surface was covered with a uniform TiO_2 coating (Fig. 3a and b). Rutile TiO_2 microspheres not only deposited on the cross-sectional walls, but also deposited on the lumina surface (Fig. 3a) 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

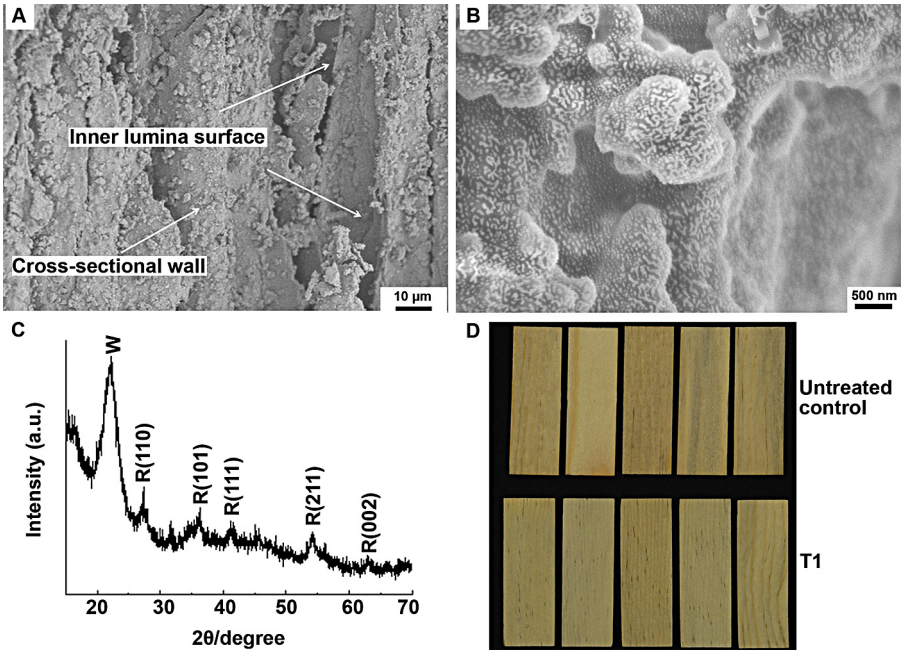

Fig. 3. (a and b) SEM; (c) XRD; (d) photo of untreated control and TiO_2-treated wood samples (T1). The peak labeled W (Fig. 3c) can be indexed to the diffraction pattern of wood.

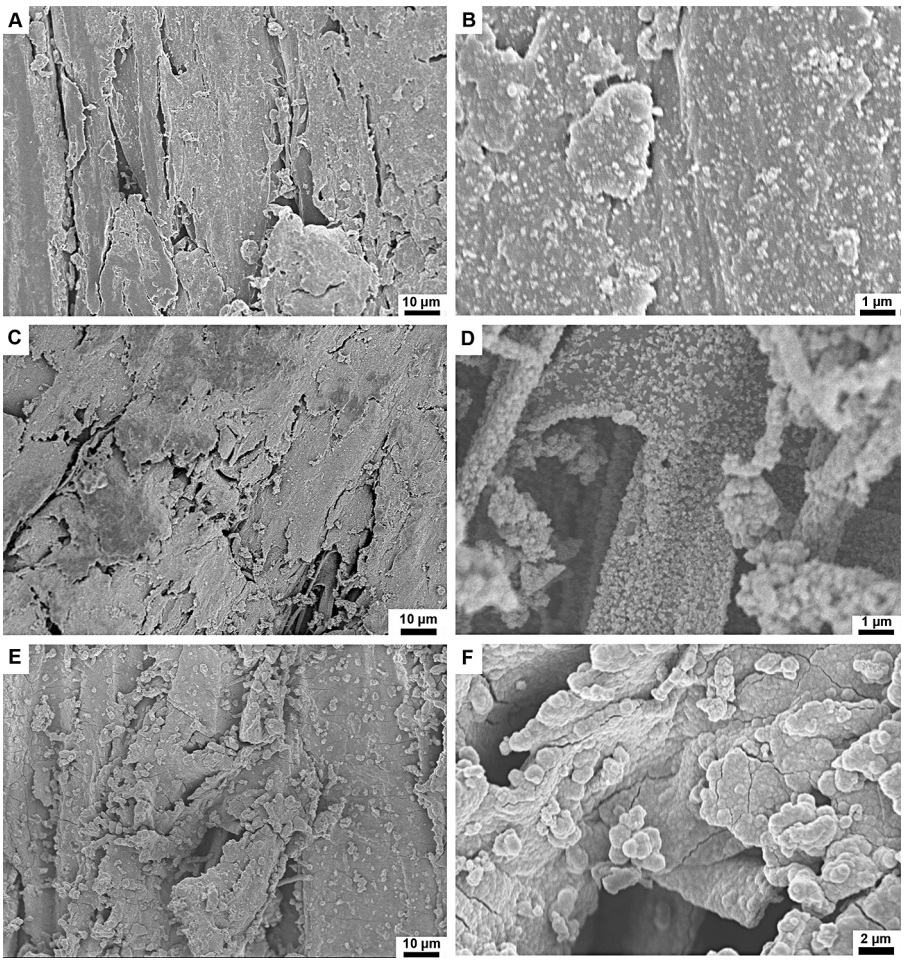

Fig. 4. SEM of the surface of TiO_2-treated wood samples obtained by hydrolysis and crystallization of the $TiCl_3$ for different times at room temperature: (a and b) T2, 1 day; (c and d) T3, 3 days; (e and f) T4, 15 days.

to form nanoscale–microscale hierarchical structures. The crystal structure of TiO_2 coated on the wood surface was characterized by XRD (Fig. 3c), which indicated that the crystalline structure of T1 surface was dominated by the peaks of rutile TiO_2 and wood. In addition, the weak intensity peaks with 2θ value of 31.6, 45.5, 56.6, and 66.4 could be indexed to the diffraction peak of NaCl.

3.2. Effects of experimental parameters on the TiO_2 hierarchical structure

3.2.1. Effect of reaction time

The evolution of the rutile TiO_2 hierarchical structure with reaction time is illustrated in Fig. 4. After reaction time of 1 day (i.e., when the solution became turbid), TiO_2 particles with the size in the range of 50–300 nm were deposited on the wood surface (Fig. 4a and b). After reaction time of 3 days, the size of TiO_2 particles increased to approximately 100–500 nm. It is worth noting that these nanoparticles were also deposited on the inner luminal surfaces (Fig. 4c and d). After reaction time of 10 days, lotus leaf-like structures formed on the wood surface (Fig. 3a and b). After reaction time of 15 days, the surface of the microspheres became smooth (Fig. 4e and f), which may be ascribed to the further growth of the nanoscale protrusions. Uniformity of the nanostructures on the wood surface was varied.

3.2.2. Effect of pH

The pH of the solution was adjusted by adding a saturated solution of NaCl, containing different amounts of NaOH, into the original

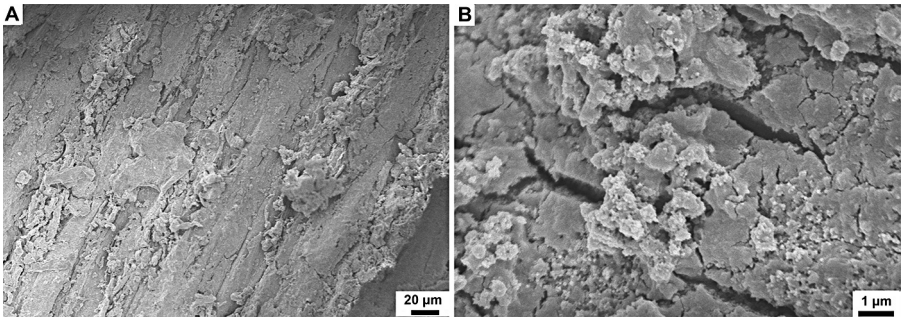

Fig. 5. SEM of the surface of TiO_2-treated wood samples (T5) obtained by hydrolysis and crystallization of the $TiCl_3$ in saturated NaCl aqueous solution with pH value 1.27 for 3 days at room temperature.

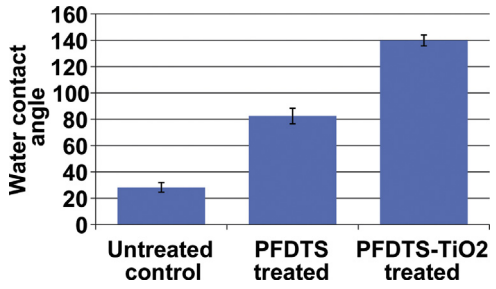

Fig. 6. Average water contact angle of untreated control and PFDTS-T1-treated wood specimens (error bars represent standard deviation of six replicates).

solution. It is known that the higher the pH, the higher the rate of hydrolysis of $TiCl_3$. Different rates of hydrolysis will lead to different TiO_2 morphology. When the reaction was carried out in the absence of NaOH (at pH ≈ −0.23), the hydrolysis rate was so slow that no TiO_2 was generated even after 10 days. On the other hand, when the pH was increased to 1.27, the reaction time decreased to about 3 days, but the hydrolysis rate was so high that no hierarchical structure was generated. Instead, the wood surface was coated with a cracked TiO_2 film, decorated with a few TiO_2 particles (Fig. 5).

3.3. Hydrophobicity of treated wood

In order to obtain a superhydrophobic surface (WCAs higher than 150°), two important conditions should exist: hierarchically rough surface and low surface energy [14,15]. Because wood surfaces are rough at the macro scale, and not optically smooth, growth of rutile TiO_2 on the wood surface should provide three levels of surface roughness at the nano, micro, and macro scales, similar to the lotus leaf surface. Such surfaces should be highly hydrophobic with high WCA values. The WCAs of the untreated control, and treated specimens are summarized in Fig. 6. The untreated control wood specimens had an average WCA of *t* 28.2° ± 3.7. The average WCA for PFDTS-treated wood was 82.5° ± 5.9. By comparison, PFDTS-T1-treated wood surface exhibited high hydrophobicity, with an average WCA of 140.0 ± 4.2°, which was slightly lower than the literature value of 150° [16].

3.4. Liquid water uptake

PFDTS-T1-treated specimens showed a significant decrease in liquid water uptake compared with untreated control specimens (Fig. 7). During the initial 3-h immersion period, the percentage of weight change of untreated control specimens decreased from 63.2% to 47.5%, while that of PFDTS-T1-treated wood specimens increased continuously from 13.5% to 15.7%. However after immersion for 24 h, the weight change of treated wood specimens was only 19.3%, while that of the untreated control specimens had reached 81.4%. After 187 h the weight change of the untreated control specimens had increased to 148.6%, and remained practically unchanged until termination of the experiment after 867 h of immersion. Thus, it is reasonable to conclude that untreated control specimens had reached the steady state after 187 h of immersion. By comparison, the weight change of PFDTS-T1-treated wood specimens did not reach equilibrium until 600 h immersion when weight change reached 116.0%. At this point, the weight change remained practically constant until termination of the experiment after 867 h of water immersion. The liquid water uptake by PFDTS-T1-treated wood specimens was approximately 75% of that of the untreated control specimens.

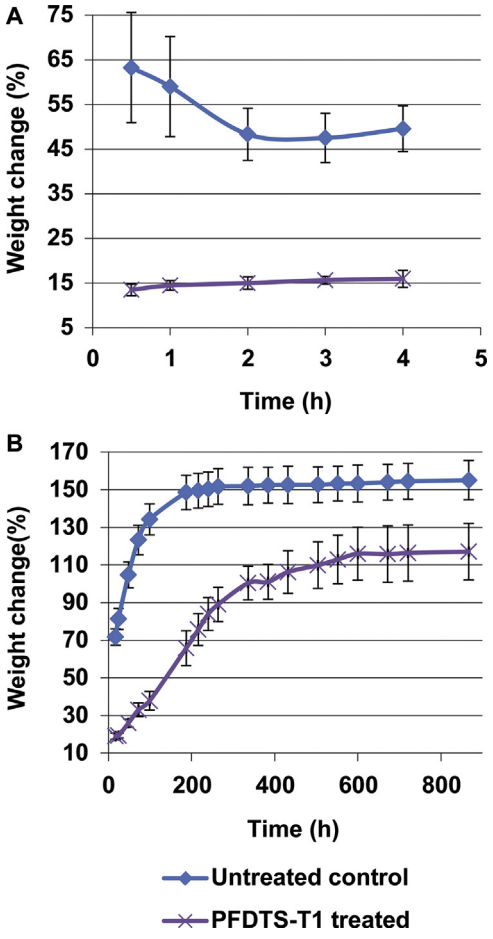

Fig. 7. Percentage of weight change of untreated control and PFDTS-T1-treated wood specimens immersed in water over different time periods: (a) 0.5–4 h; (b) 17–867 h. Error bars represent standard deviation of six replicates.

4. Conclusion

In summary, rutile TiO_2 hierarchical structures were constructed on the wood surface by direct hydrolysis and crystallization from the $TiCl_3$ in saturated NaCl aqueous solution at room temperature. The type of TiO_2 structure on the wood surface can be tuned by simple manipulation of the pH or reaction time. The water contact angle of PFDTS-T1-treated wood specimens in this study was approximately 140.0 ± 4.2°. PFDTS-T1-treated wood specimens not only reduced liquid water sorption but also delayed the onset of sorption equilibrium. After 867 h of water immersion, the weight change of PFDTS-T1-treated wood specimens was about 25% lower than untreated control specimens. It took only 187 h for the untreated control specimens to reach sorption equilibrium compared with approximately 600 h for the PFDTS-T1-treated specimens. Since the present method can be performed in aqueous solutions at room temperature, it may be applicable to the other biopolymer materials, such as cellulose nanocrystals, textiles, or paper.

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