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Room temperature synthesis of crystalline anatase TiO_2 on bamboo timber surface and their short-term antifungal capability under natural weather conditions

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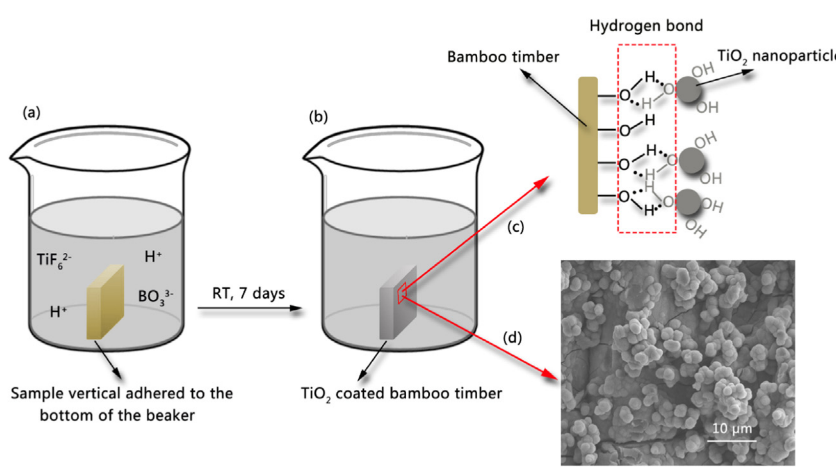
HIGHLIGHTS

- A room temperature route was developed for growing TiO_2 on bamboo timber surface.
- The as-prepared TiO_2 particles on the surface of bamboo timber were anatase.
- Anatase TiO_2-coated bamboo timber presented more superior antifungal capability.

GRAPHICAL ABSTRACT



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ABSTRACT

A facile room temperature route was developed for growing crystalline anatase TiO_2 on the bamboo timber surface by a unique hydrolysis of titanium complexes in the presence of H_3BO_3. The effect of aging time on TiO_2 crystallinity on the bamboo timber surface was studied. The crystal phase, microstructure, and chemical composition of the anatase TiO_2 formed on the bamboo timber surfaces were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and transmission electron microscopy (TEM). XRD characterization on the samples showed that, for crystallization occurred at room temperature, the longer the aging time, the greater the crystallinity. The TiO_2-coated bamboo samples look identical to the pristine samples as there is no essential effect on the optical properties of the bamboo timber surface. Moreover, the antifungal activity of TiO_2 photo-catalytic reaction against mould fungi was investigated for bamboo timber under natural weather conditions during periods of 16 weeks. Results show that compared with the pristine bamboo timber, the anatase

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TiO_2-coated bamboo timber presented more superior antifungal capability under natural weather conditions in Hangzhou, China.

1. Introduction

As known, bamboo is one of the fastest growing plants in the world [1]. It is plentiful, inexpensive, and a renewable natural resource. In many Asian countries, bamboo has traditionally been used in low-rise buildings, bridges, long-span roofs and construction platforms [2]. Bamboo products have also found more and more applications in daily necessities, furniture, flooring, crafts, indoor decoration constructions, and so on. Bamboo being considered as inexpensive and renewable material has potential to be used as a substitute for wood in bamboo producing countries [3]. However, in common with other cellulosed-based materials, the serious problem of bamboo and bamboo products is the susceptibility of the material to attack by decay fungi and moulds fungi [4,5]. Unlike wood in chemical characteristics, bamboo timber [6] has high content of sugar, starch and protein [7]. These nutrients, especially the sugar and starch, are the main factors leading to the decay and mould of bamboo timber [8,9]. The untreated bamboo products applied outdoors are usually severely infected by mould fungi in the rainy seasons. Considering the hazardous effect of moulds fungi to bamboo timber, it is necessary to develop an effective anti-moulds technique.

To avoid fungal deterioration of cellulose-based materials, effective biocides have been used successfully for decades. However, nowadays some biocides are banned due to health and environmental hazards. Therefore, the development of alternative environmentally friendly bamboo timber mildew preventive with low toxic impact has been given great attention. Currently, inorganic nanomaterials are characterized by a high surface-to-volume ratio, which gives them larger activities in surface related phenomena compared to bulky systems [10]. In particular, their application to environmental remediation are based on redox reactions from semiconductors, especially TiO_2, which has been the most popular and successful photo-catalyst for this purpose [11–13]. Recently, some research has demonstrated that TiO_2 particles inhibit *Aspergillus niger* colonization of Limestone and Carrara marble, when they are dispersed over protective organic coatings and applied to stone samples [14]. A lot of research has been recently devoted to the antifungal activity of TiO_2 particles against mould fungi on wood substrate. Filpo et al. [10] treated eight different types of wood, with a solution of TiO_2 nanoparticles and placed them in contact with two species of fungi, *Hypocrea lixii* (white-rot) and *Mucor circinelloides* (brown-rot). Results showed that the photo-catalytic activity of TiO_2 nanoparticles prevents the fungal colonization of wood samples over long time when compared to pristine wood samples. The antifungal activity of TiO_2 photocatalytic reaction against *Aspergillus niger* was investigated for moist wood boards during periods of several weeks [15]. The results indicated that TiO_2-coated film in the presence of UVA (365 nm) irradiation exhibited antifungal capability. Mahr et al. [16] have also drawn a conclusion that wood treated with titanium alkoxides diluted either with propanol or ethanol demonstrated effectiveness against brown-rot decay. However, the TiO_2 particles used to investigate the antifungal photo-activity on wood substrates were generally commercial available nanomaterials. In our previous study [17,18], the TiO_2 particles have been successfully prepared on the bamboo timber surface by the hydrothermal deposition at low temperature. So far, the most widely used method to prepare anatase TiO_2 at low temperature is hydrothermal treatment, in which the hydrothermal reactions can be carried on substrates with low melting points, such as bamboo timber, wood, cellulose, cotton textile, and so on [17–22]. Apart from hydrothermal treatment, aging is another technique to make transition of prepared titania from amorphous phase to crystalline phase [23,24]. To the best of our knowledge, few researches have reported to form the crystalline anatase on the cellulose-based materials at room temperature (RT).

Recently, a facile method for preparation of TiO_2 nanocrystals on the bamboo timber surface at RT is developed in our laboratory. In detail, the crystalline anatase TiO_2 could be prepared on the bamboo timber surface by a unique hydrolysis of titanium complexes in the presence of H_3BO_3 at RT. For crystallization occurred at RT, the longer the aging time, the greater the crystallinity. In addition, it has been found that the anatase TiO_2-coated bamboo timber presented more superior antifungal capability under natural weather conditions in Hangzhou, China.

2. Materials and methods

2.1. Materials

Moso bamboo (*Phyllostachys heterocycla*) blocks of 20 mm × 20 mm × 4 mm were ultrasonically cleaned with deionized water and ethanol before drying for use. Chemicals including ammonium fluorotitanate, boric acid, hydrochloric acid, and absolute ethanol were all of analytical reagent grade and purchased from Shanghai Boyle Chemical Co. Ltd. For all experiments, deionized water was used.

2.2. Deposition of anatase TiO_2 nanocrystallines on the bamboo timber surface

In a typical synthesis process, $(NH_4)_2TiF_6$ (2.0 g) and H_3BO_3 (1.85 g) were dissolved in 100 mL of deionized water under vigorous magnetic stirring. After vigorous stirring for 10 min at RT, the turbid mixture became clear. Then, 1.0% hydrochloric acid aqueous solution was added dropwise until the pH reached 3.2. Bamboo specimens were subsequently placed into the reaction solution. The final solution was kept without stirring at RT for several days. Finally, the samples were removed from the solution, washed with deionized water, and dried at 60 °C for more than 24 h in vacuum oven. The TiO_2-coated bamboo timber was labeled as TiO_2-BT (x °C, y days) or TiO_2-BT (x °C, y h), where x °C is the reaction temperature, and y days or y h is the reaction time.

2.3. Characterization

The surface morphologies of the samples were observed by scanning electron microscopy (SEM, Hitachi S3400, Japan) equipped with energy-dispersive X-ray spectroscopy (EDS). The crystalline structures of as-prepared samples were identified by X-ray diffraction (XRD, Rigaku, D/MAX 2200) operating with Cu Kα radiation (λ = 1.5418 Å) at a scan rate (2θ) of 8°/min with an accelerating voltage of 40 kV and an applied current of 30 mA ranging from 10° to 80°. The transmission electron microscopy (TEM) experiment was performed on a Tecnai G20 electron microscope