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Author

Sun, QF, Lu, Y, Xia, YZ, Yang, DJ, Li, J, Liu, YX

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Flame retardancy of wood treated by TiO₂/ZnO coating

Q. F. Sun^{*1}, Y. Lu¹, Y. Z. Xia², D. J. Yang³, J. Li¹ and Y. X. Liu¹

In this work, one-pot hydrothermal method was used for modifying a wood surface by the deposition of TiO₂/ZnO coating at a relatively low temperature. The prepared wood samples were characterised using SEM, energy dispersive X-ray analysis and powder X-ray diffraction. Results showed that wood surface was coated by anatase TiO₂ and würtzite structured ZnO at 110°C. To explore the flameproof properties of the modified wood, cone calorimetry technique was employed to measure the significant difference in combustion parameters between the untreated and the treated wood. As compared with the untreated wood sample, the time to ignition was 37 s, increasing about four times; the burning duration was around doubled, and smoke production rate and total smoke production were almost zero. As a result, the treated wood had an improved fire resistance, and one-pot hydrothermal method was a feasible method to fabricate non-flammable wood materials.

Keywords: Flame retardancy, Anatase TiO₂, ZnO, Cone calorimetry, Wood, Hydrothermal method

Introduction

Wood, a natural composite of cellulose fibres embedded in a matrix of lignin, has been used for hundreds of thousands of years for both fuel and construction material. As an abundant, carbon neutral renewable resource, wood materials have been of intense interest due to their versatile characteristics such as aesthetic superiority and uniform finish, because they are easily biodegradable and their reduced maintenance service provides unlimited scope for property manipulation and product development.^{1–4} However, wood materials are vulnerable to thermal decomposition and combustion when coming in contact with fire or high intensity heat source, which hinders the application of wood materials under high temperature conditions. To enlarge wood practical applications, improvement of wood flame retardancy is becoming much more necessary and significant. Presently, much research work has been carried out for improving wood flame retardancy. However, three major approaches including impregnation, incorporation and formation of surface coatings were considered as efficient and feasible in practice.^{5–7} Especially, surface coating with inorganic materials covered onto the wood surface was considered as a potential and promising way to increase the fire retardancy due to its economical and practical aspects.^{8–13}

It could be expected that the synergistic effects resulting from the physical or chemical interactions between the inorganic coating and the wood substrate are able to produce such properties as improved thermal, mechanical and dimensional stability.^{13–17} For instance, according to Saka's and Sun's researches,^{7,18} TiO₂/wood composite showed a great improvement for fire resistance. Meanwhile, ZnO and its derivatives were used extensively in fire retardants, and those zinc compounds have since been the subject of extensive research and development for preparation of fire retardant compositions for a variety of substances.^{19,20}

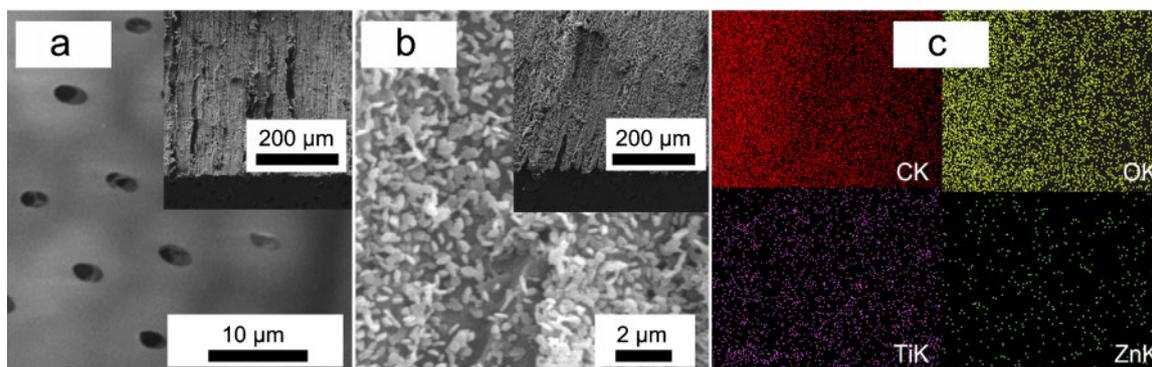
However, at present, the inorganic coating for the flame retardancy of wood materials is only composed of monomeric inorganic materials such as TiO₂, SiO₂ and ZnO.^{7,21–29} The inorganic coating with dual or multi-inorganic materials for wood flame retardancy is scarcely studied because of the complexity and difficulty in controlling the crystal growth of two or more different materials. Based on previous researches, TiO₂ and ZnO species have the merits of non-toxic, low cost, environmentally friendly and highly thermal stability.^{1,7,18–20,22,25,30,31} Hence, in this study, a novel and facile one-pot hydrothermal method was introduced to modify wood by TiO₂/ZnO coating for greatly improved flame retardancy. The as prepared samples were characterised by SEM, energy dispersive X-ray analysis (EDXA) and X-ray diffraction (XRD). The flame retardant properties of the wood by TiO₂/ZnO coating were also investigated using the cone calorimeter technique. This work potentially provided a feasible pathway to fabricate inorganic/wood, fibre, bamboo and paper hybrid materials with controllable and designed functions.

¹Key Laboratory of Bio-based Material Science and Technology, Ministry of Education, Northeast Forestry University, Harbin 150040, China

²State Key Lab Cultivating Base of Advanced Fibers and Modern Textiles, Qingdao University, Qingdao 266071, China

³Centre for Clean Environment and Energy, and Griffith School of Environment, Griffith University, Gold Coast Campus, Qld 4222, Australia

*Corresponding author, email qfsun@nefu.edu.cn



1 Plane view and cross-sectional SEM images of wood substrates *a* before and *b* after deposition and *c* chemical mapping images of wood substrate after deposition

Experimental

Materials

All the reagents used in the experiments were of analytical grade (purchased from Shanghai Boyle Chemical Co. Ltd) and used without further purification. Wood specimens from the air dried poplar lumber were cut into a size of 100 (longitudinal) × 100 (tangential) × 10 mm (radial).

Wood modified by TiO₂/ZnO coating using one-pot hydrothermal method

In a typical process, 7 g tetrabutyl orthotita [Ti(OCH₂CH₂CH₂CH₃)₄], 3.6 g zinc nitrate hexahydrate [Zn(NO₃)₂·6H₂O] and 1.68 g hexamethylenetetramine (C₆H₁₂N₄) were added into 800 mL absolute ethanol (C₂H₅OH) in a capped bottle. The solution was stirred for 3–5 h to generate a homogeneous solution. Then, the solution was transferred into a 100 mL autoclave. Wood specimens were subsequently placed into the above reaction solution. The autoclave was sealed and maintained at 110°C for 18 h and then cooled to room temperature naturally. Finally, the prepared samples were removed from the solution, ultrasonically rinsed with deionised water for 30 min and dried at 45°C for >24 h in vacuum.

Characterisations

The morphologies and sizes of samples were performed on SEM (FEI, Quanta 200) and TEM (CM12, Philips). Chemical compositions were measured by EDXA (attached to the SEM). Crystalline structures were identified by XRD (Rigaku, D/Max 2200) operating with Cu K_α radiation ($\lambda=1.5418$ Å) at a scan rate (2θ) of 4° min⁻¹ with the accelerating voltage of 40 kV and the applied current of 30 mA ranging from 5 to 70°.

Standard fire testing¹⁸

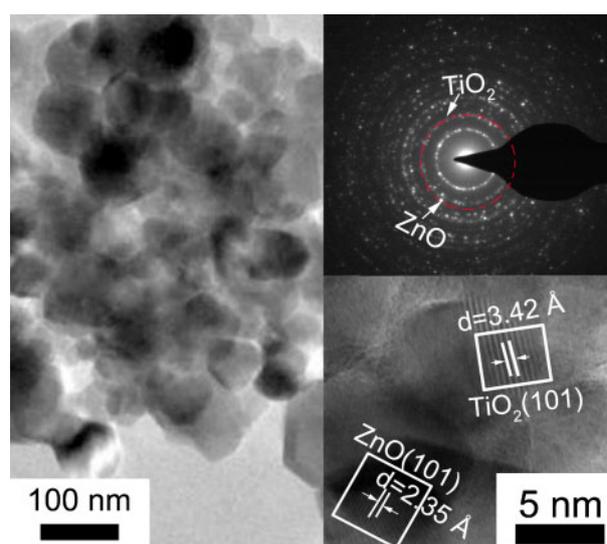
According to the ISO 5660-1 standard, the combustion test was carried out on a dual analysis cone calorimeter (Fire Testing Technology Ltd, East Grinstead, West Sussex, UK) at an irradiance of 50 kW m⁻² (~715°C). Before the test, three samples from the untreated and treated groups were placed in a chamber with a temperature of 23°C and a relative humidity of 55% for balancing to a constant weight. These samples were horizontally arranged and protected by a stainless steel grid to prevent the samples from bending and expansion during heating. Commercial software was used for the data processing.

Results and discussion

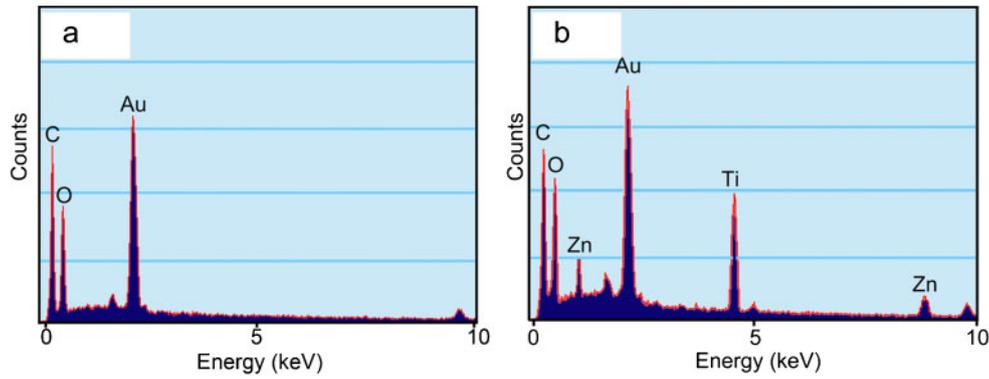
SEM, EDXA and XRD analysis

Typical plane view and cross-sectional SEM images of the wood substrates before and after deposition are presented in Fig. 1*a* and *b*. It can be clearly seen from the cross-sectional SEM image after the deposition (inset image of Fig. 1*b*) that the wood surface, including wood vessels, was covered by dense TiO₂/ZnO nanoparticles in comparison with that of the inset image of Fig. 1*a*. The plane view SEM images show detailed morphologies of the wood substrates before and after deposition (Fig. 1*a* and *b*). It is obvious that the wood pits and surface were totally coated by TiO₂/ZnO compound particles. The chemical mapping images from the cross-section of the coated specimens are shown in Fig. 1*c*. The red and yellow dots show the wood elements of carbon and oxygen. The pink and green dots illustrate the titanium and zinc elements onto the wood surface after the hydrothermal process. It is evident that the wood surface was covered by inorganic constituent element.

To determine the size of the TiO₂/ZnO nanoparticles, TEM image is shown in Fig. 2. From the TEM image, the size of TiO₂/ZnO nanoparticles is around 80–200 nm. The corresponding selected area electron diffraction



2 Images (TEM) of TiO₂/ZnO nanoparticles (top right corner image, corresponding electron diffraction pattern of TiO₂/ZnO nanoparticles; bottom right corner image, corresponding HRTEM image)

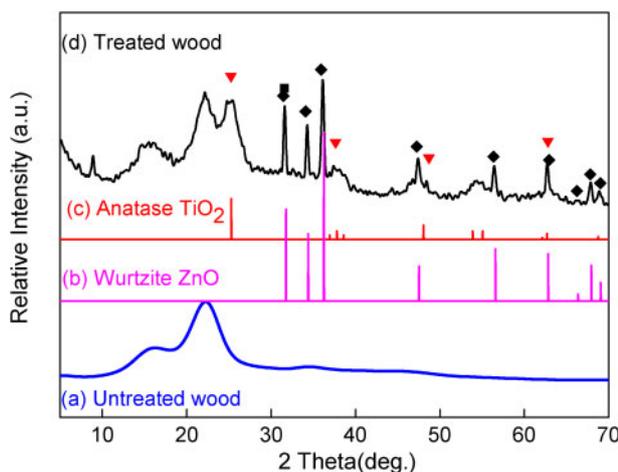


3 Energy dispersive X-ray analysis spectra of samples *a* before and *b* after hydrothermal treatment

pattern in the top right corner inset in Fig. 2 indicates that the TiO₂/ZnO nanoparticle was a polycrystalline structure. Along with the rings of anatase TiO₂, bright spots corresponding to wurtzite ZnO are observed with good crystallinity. The high resolution TEM (HRTEM) image of TiO₂/ZnO nanoparticles in the bottom right corner inset in Fig. 2 exhibits the lattice spacing of ~ 3.42 Å corresponding to the (101) plane of anatase TiO₂ structure and the lattice spacing of ~ 2.35 Å corresponding to (101) plane of wurtzite ZnO structure.

The elemental composition of wood samples before and after hydrothermal treatment was analysed with the EDXA spectra and presented in Fig. 3. The strong peaks at ~ 1.0 , 8.7 and 4.6 keV shown in Fig. 3*b* confirmed the presence of zinc and titanium compared with that in Fig. 3*a*, which was caused by the major inorganic constituent element discovered on the wood surface after the hydrothermal treatment. The element of gold is from the coating layer used for SEM observation, and oxygen and carbon elements are from the wood substrate.

X-ray diffraction analysis was employed to investigate the crystal phase of the untreated and treated wood samples. As shown in Fig. 4, new strong diffraction peaks were observed from the XRD pattern of the treated wood sample (curve *d*) in comparison with that of the untreated wood (curve *a*). All these diffraction



4 X-ray diffraction patterns of *a* untreated wood, *b* standard ZnO (JCPDS card no. 36-1451), *c* standard anatase TiO₂ (JCPDS card no. 21-1272) and *d* treated wood respectively (◆: wurtzite phase of ZnO; ▼: anatase phase of TiO₂)

peaks could be well indexed as wurtzite type ZnO and anatase TiO₂ according to the standard diffraction peaks of wurtzite ZnO (curve *b*) and anatase TiO₂ (curve *c*). It means that the TiO₂/ZnO coating has been successfully deposited on the surface of the wood substrate using the one-pot hydrothermal method.

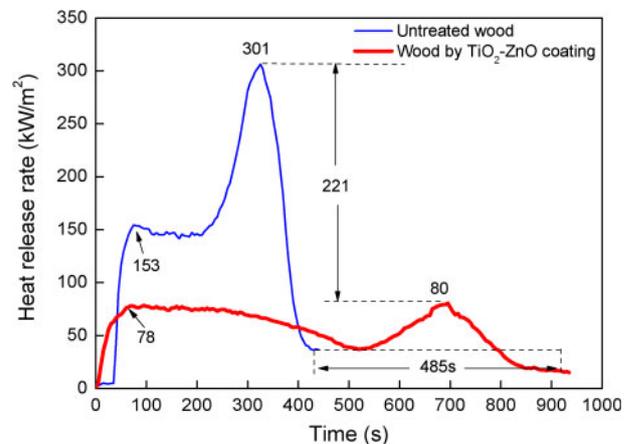
Cone calorimetry testing

Time to ignition

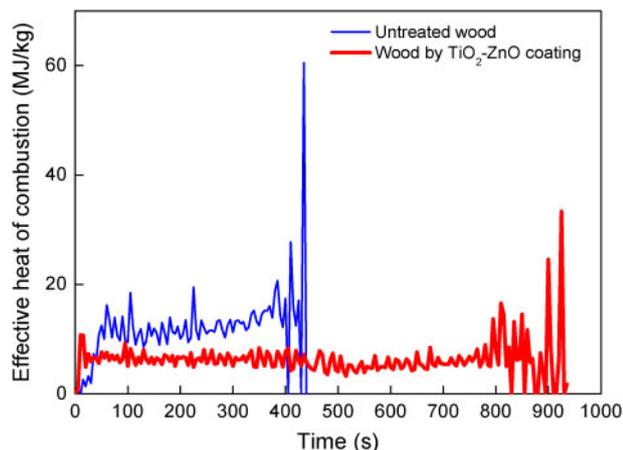
The time to ignition (TTI) test is one of the most important parameters to evaluate the fire resistance ability of woody material. Longer TTI means better flame retardancy. Herein, the TTIs of the untreated and TiO₂/ZnO coated wood were 10 and 37 s respectively. The TTI of TiO₂/ZnO coated wood was about four times compared with the untreated wood. Apparently, the flame retardancy of the wood substrate was efficiently enhanced by depositing the wood by TiO₂/ZnO coating on the wood surface.

Heat release rate

The heat release rate (HRR)–time curves of the untreated wood and TiO₂/ZnO coated wood are shown in Fig. 5. The temperature of absorbed water loss is from ~ 30 to 130°C . The temperature of volatile combustible compounds ranges from ~ 120 to 420°C . The temperature of char formation and gases release takes place from ~ 400 to 550°C . For the untreated wood, the HRR curve was vigorous and fast, which means that untreated was quickly burning and released heat. However, the HRR curve of TiO₂/ZnO coated wood was much more



5 Heat release rate patterns of untreated wood and wood by TiO₂/ZnO coating



6 Effective heat of combustion patterns of untreated wood and wood by TiO₂/ZnO coating

moderate and relatively lower, indicating that the burning intensity and heat release were slowed and decreased. Additionally, the two heat release peaks of TiO₂/ZnO coated wood decreased significantly in comparison with the untreated wood sample, which suggested that the treated wood had a better flame retardancy. The overall burning time of wood by TiO₂/ZnO coating was twice longer than that of untreated wood, even though the characteristics of the typical HRR curve for wood (double peak feature) were not greatly varied. Apparently, the TiO₂/ZnO coating delayed the heat transfer to the wood substrate and thus decreased the rates of the flammable volatiles from wood thermal decomposition.^{32,33}

Effective heat of combustion

The effective heat of combustion (EHC) is calculated from the ratio of values of total heat evolved and the mass loss (ML) within the specified time. As shown in Fig. 6, EHC values of the TiO₂/ZnO coated wood were always lower than those of the untreated wood, which demonstrated that the wood by TiO₂/ZnO coating effectively reduced the heat release mass and increased the fire resistance when wood was burned.

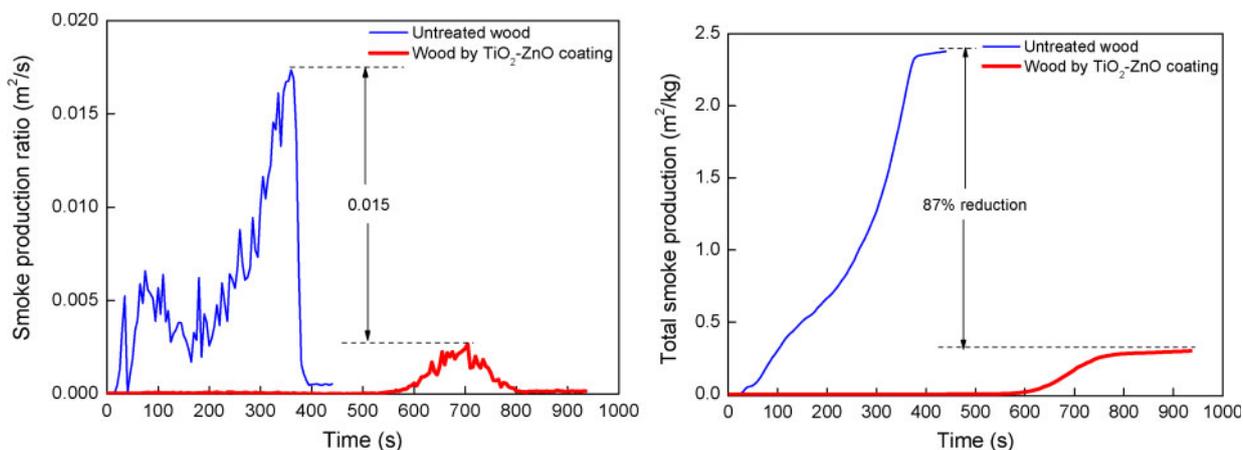
Smoke production rate and total smoke production

Smoke is mainly comprised of carbon particles, which can diminish the visibility when wood was ignited. High

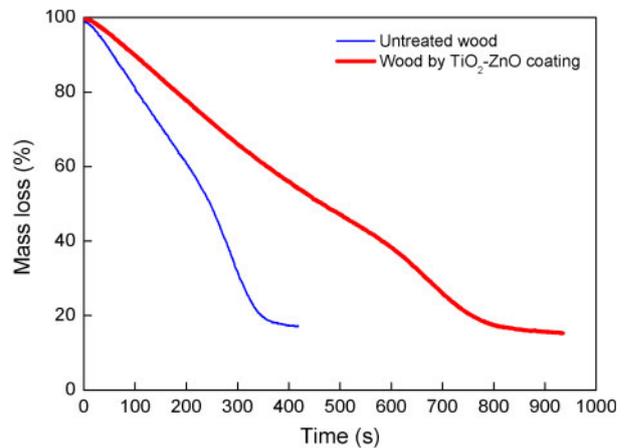
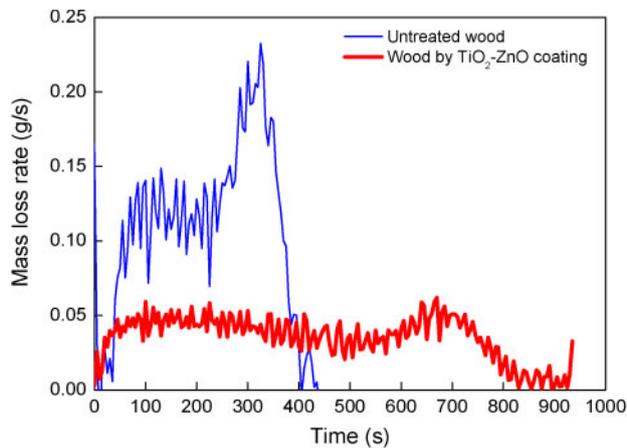
smoke production in the early stage of a fire is very harmful because it can reduce the visibility and release the irritating and incapacitating smoke gases. The smoke production rate (SPR) refers to the amount of dense smoke released per unit time that can be calculated from the division of a specific extinction area by the mass loss rate (MLR). The total smoke production (TSP) is defined as the total amount of smoke released by material in the process of burning and pyrolysis. It can be calculated by a process of integration of SPR over time; it is also called the cumulative smoke release product. Compared with the untreated wood, the SPR and TSP of the TiO₂/ZnO coated wood shown in Fig. 7 were all reduced. The total TSP was decreased by 87%. So it could be concluded that the TiO₂/ZnO coated wood was able to effectively inhibit the smoke emission and production. This suggested that the TiO₂/ZnO inorganic composite could be applied as a substitute for smoke suppressants.

Mass loss and mass loss rate

Figure 8 shows the variation tendencies of the MLRs of the untreated and TiO₂/ZnO coated wood. It was clearly seen that the MLR values of the wood by TiO₂/ZnO coating were always lower than those of the untreated wood, which suggested that the less weight decreased along with the burning time. Less weight decreased means lower heat produced. As a result, the wood by TiO₂/ZnO coating was in favour of fire resistance. The total ML value of TiO₂/ZnO coated wood during the whole test was similar to that of the untreated wood, ~80% of the original weight. The residuum of the treated and untreated was about the same, which suggested that the retardant effect of TiO₂/ZnO coated wood was not strong enough to stop burning until the flammable content of wood was burned out. Combined with the HRR curves, it was obvious that the MLR curves of untreated and TiO₂/ZnO coated wood were consistent with their HRR curves, which demonstrated that the heat release and ML were synchronised when wood was fired. Higher HRR value means bigger ML. Therefore, the HRR of the wood coated with TiO₂/ZnO obviously decreased due to the existence of TiO₂/ZnO compound, which suggested that the TiO₂/ZnO compound was more effectively performed for prohibiting heat release than that of ML.



7 Patterns (SPR and TSP) of untreated wood and wood by TiO₂/ZnO coating



8 Patterns (MLR and ML) of untreated wood and wood by TiO₂/ZnO coating

Conclusion

Wood surface treated by TiO₂/ZnO coating was synthesised using a facile one-pot hydrothermal method. The prepared wood sample had a significant performance for flame retardancy. The TiO₂/ZnO compound could functionally act as a protective material to change inflammable wood into non-flammable wood, protect wood to extend the combustion time, and an especially strong shield that inhibits smoke spreading. This work potentially provided a feasible pathway to fabricate inorganic/wood, fibre, bamboo and paper hybrid materials with controllable and designed functions.

Anatase TiO₂ and würtzite structured ZnO nanoparticles with sizes of around 80–200 nm have been successfully deposited onto the wood surface using a facile one-pot hydrothermal method. With the measurement of cone calorimetry technique, the prepared wood sample showed a significant performance for flame retardancy. In comparison with the untreated wood materials, the TTI was increased to 37 s, the burning duration was around doubled and SPR and TSP were almost zero. Therefore, the deposition of TiO₂/ZnO nanoparticles onto the wood surface is a feasible method to fabricate non-flammable wood materials.

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