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Prolonging the combustion duration of wood by TiO_2 coating synthesized using cosolvent-controlled hydrothermal method

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Abstract Thin TiO_2 coating was grown on wood surface using a cosolvent-controlled hydrothermal method. The surface morphology, chemical composition, and functional groups were examined by the scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDXA), and Fourier transform infrared spectroscopy (FTIR), respectively. The crystalline phase of TiO_2 was investigated by the X-ray diffraction (XRD). The combustion test was carried out on the Dual Analysis Cone Calorimeter, according to the fire testing standard ISO 5660-1. Resulted from the combined analysis of SEM and EDXA, FTIR and XRD, it was demonstrated that the anatase TiO_2 layer accompanying some spheral morphology chemically bonded to wood surface with intact and smooth appearance. The significant differences in combustion parameters between the untreated and the TiO_2 coated wood were observed. In comparison to the untreated wood, the burning time of TiO_2 coated wood was doubled, and the smoke, CO, CO_2 emissions were markedly reduced. As a result, the TiO_2 coating can effectively act as a protective layer to prolong the combustion duration of wood and prevent the harmful gas from spreading.

Introduction

Essentially, wood is under the category of natural biopolymers due to its friendly properties of health, aesthetic, and environmental aspects. However, the flammability of wood, compared to other engineering materials, may prevent wood from replacing those that are based on un-renewable resources. When wood is exposed to fire or any other high-intensity heat source, it is easily subject to thermally degrading, igniting or combusting. To improve the fire performance of wood, using flame retardants is considered as the most common way [1–4]. Three major approaches can be used for fire-retardant treatments: impregnation, incorporation, and formation of surface coatings [1]. Compared to the other two, surface coatings have been prevalently used to increase the fire retardancy of wood due to the economical and practical aspects [5].

Interest has recently arisen in the development of inorganic coatings consisting of SiO_2 and TiO_2 on polymer surface, driven by their excellent characteristics of mechanical and thermal performances, optical behaviors, and bactericidal resistance [6–14]. Especially an increasing attention is being devoted to the application of nano-TiO_2 to polymer owing to its permanent stability at high temperatures [15–23]. Being different from conventional materials, these nano-materials exhibit excellent properties, e.g., the formation of TiO_2 layer on wood surface can significantly improve properties of fire-resisting [24], antifungal [25], and aging durability [23, 26]. Investigated by many researchers [24, 27–32], sol–gel methods were used to fabricate inorganic layer, and the hydrothermal method was utilized to formulate organic–inorganic composites efficiently [33–37].

This research was unique because the TiO_2 coating was grown on wood surface using an easy chemical technology, which was the cosolvent-controlled hydrolysis of tetrabutyl orthotitanate (TBOT) by means of the hydrothermal method at 130 °C, and the combustion property of the modified wood was also investigated using the Cone calorimeter technique.

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Methodology

Materials

Wood specimens from the air-dried birch lumber (*B. albo-sinensis Burk*) were cut into a size of 100 mm (longitudinal) × 100 mm (tangential) × 10 mm (radial). Without further purification, all chemicals including tetrabutyl orthotitanate (TBOT), sodium dodecyl sulfate (SDS), and anhydrous ethyl alcohol (EtOH) were supplied by the Shanghai Boyle Chemical Co. Ltd.

Synthesis

The synthetic conditions under which TiO_2 coating grew on wood surface are as follows. 10 g of TBOT was firstly dissolved into EtOH in a 500-mL glass beaker with an even agitation and transferred into a Teflon-lined stainless steel autoclave. No water was allowed to exist in all operating processes. Wood specimens were placed in the TBOT alcoholic solution. The reactor was sealed and heated at 130 °C for 8 h. After the heating process, the reactor, when cooled to room temperature, was opened and a solution of 9.1×10^{-4} mol/L SDS with a pH value of 10 was added. The reactor was then sealed again and re-heated at 70 °C for 4 h, after which, the treated wood specimens were collected and finally dried at 45 °C over 24 h. In order to quantify the TiO_2 grown on wood surface, some specimens were oven-dried and scaled before and after reaction using a regular procedure.

Characterization

The surface morphology of specimens was characterized using the FEI Quanta 200 scanning electron microscopy (SEM) operating at 12.5 kV. The surface chemical composition of specimens was determined by the energy dispersive X-ray analysis (EDXA) that connects SEM. The chemical functional groups were examined by the Fourier transform infrared spectroscopy (FTIR, Magna-IR 560, Nicolet). The crystalline phase of TiO_2 grown on the wood surface was revealed by the X-ray diffraction (XRD) using the Rigaku-XRD D/MAX 2200 operating with Cu Kα radiation ($\lambda = 1.5418$ Å) at a scan rate (2θ) of $4°\text{min}^{-1}$, the accelerating voltage of 40 kV and the applied current of 30 mA ranging from 5° to 70°.

Standard fire testing

According to the ISO 5660-1 standard, the combustion test was carried out on the Dual Analysis Cone Calorimeter (Fire Testing Technology Ltd, East Grinstead, West Sussex, UK) at an irradiance of 50 kW/m^2 (ca. 715 °C). Nominal duct flow rate is 24 s^{-1}, and sampling interval is 5 s. Prior to the testing, three samples from the treated group and the control group were placed in a chamber with a temperature of 23 °C and a relative humidity of 55% and conditioned to a constant weight. The samples were horizontally arranged and protected by a stainless steel grid to prevent the samples from bending and expansion during the heating. Specific software was used for the data processing. The definitions and the abbreviation of parameters adopted in the text are listed in Table 1.

Results and discussion

Visual and SEM observation

The camera images of the untreated and TiO_2 coated wood are shown in Fig. 1a, which demonstrate that there was no dramatic appearance changes occurred on wood appearance after the treatment. SEM image of the TiO_2 coated wood presented in Fig. 1b shows that the emergence of an apparently continuous coating covered the entire surface on the wood remaining intact and smooth. Some slippery TiO_2

Table 1 Parameters derived from cone calorimetry

Parameter	Abbreviation	Unit	Definition
Heat release rate	HRR	kW/m^2	Rate at which heat energy is released per unit area of burned material
Effective heat of combustion	EHC	MJ/kg	The heat released per unit mass of material being volatilized during flaming
Total heat release	THR	MJ/m^2	Cumulative heat energy released during flaming per unit area of burned material
Specific extinction area	SEA	m^2/kg	Smoke which is produced per unit mass of material being volatilized
Smoke production rate	SPR	m^2/s	Rate at which smoke is produced per unit time
Total smoke production	TSP	m^2/kg	Cumulative smoke produced per unit mass of burned material
Yield of CO and CO_2	COY, CO2Y	kg/kg	The mass of CO, CO_2 from the unit mass of burned material
Production of CO and CO_2	COP, CO2P	g/m^2	The mass of CO, CO_2 from the unit area of burned material
Mass loss rate	MLR	g/s	The mass loss per unit time on the basis of fuel
The percentage of mass loss	ML	%	The percentage of mass loss per unit time

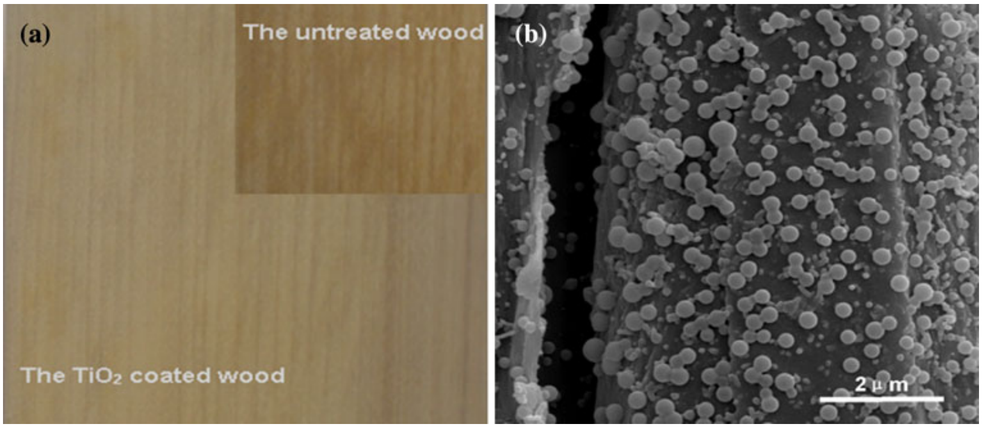
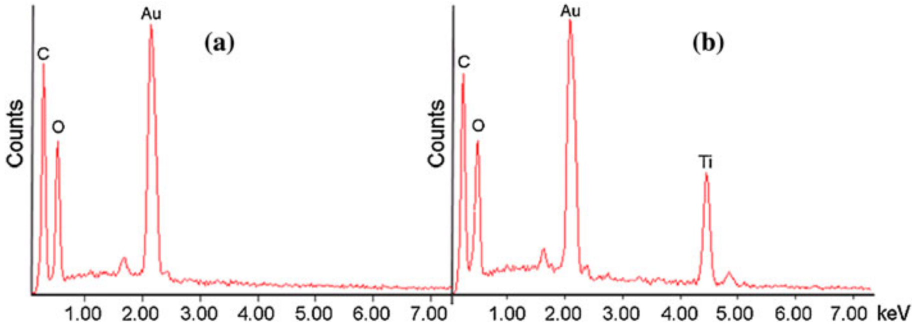


Fig. 1 **a** Camera image and **b** SEM image of TiO_2 coated wood

Fig. 2 EDXA spectra of (*a*) the untreated and (*b*) TiO_2 coated wood



spheres with about 300–600 nm in diameter evenly dispersed on the thin coating. Typically, the grown TiO_2 represented about 21.3% of the wood by weight. It was proved that the TiO_2 coating was strongly attached to the wood surface because no significant loss of titanium was found when the specimen was subjected to vigorous water washing. With the hydrophilic property, wood containing plentiful hydroxyl groups can promote the heterogeneous nucleation of TiO_2.

EDXA, FTIR, and XRD spectra analysis

With the EDXA spectra analysis presented in Fig. 2, compared to untreated specimens (Fig. 2a), the presence of titanium in the elemental composition of wood surface was confirmed by the strong peak labeled Ti in Fig. 2b for the treated one. It was reasoned on the major inorganic constituent element detected on the wood surface after the hydrothermal treatment.

The functional group composition on the wood surface before and after the hydrothermal treatment was examined with the infrared spectra and presented in Fig. 3. The hydrothermal treated wood illustrated a band at 3396 cm^{-1}, which was attributed to O–H stretch vibration of hydrogen bonded hydroxyl groups or absorbed water [38]. The peaks at 2928, 2858, and 1621 cm^{-1} were corresponding to CH_3 asymmetric, CH_2 symmetric stretch vibration, and O–H bending mode of absorbed or crystal water [39], respectively. The peaks at 1459, 1270, and 1128 cm^{-1} were attributed to C–H deformation and Ti–O–C stretch vibrations [40], respectively. The peak at 578 cm^{-1} was ascribable to the Ti–O–Ti stretch

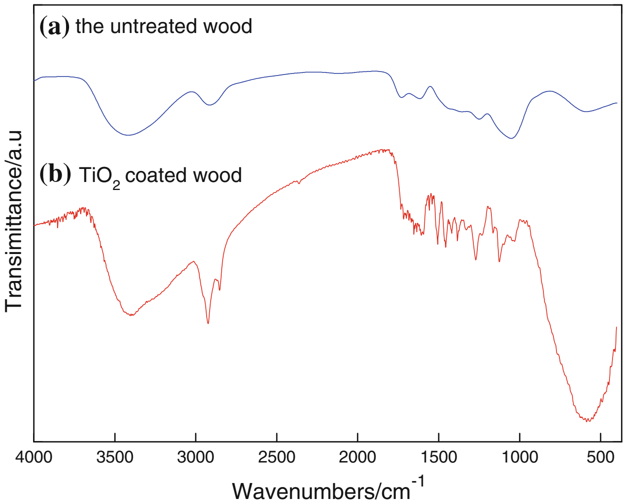


Fig. 3 FTIR spectra of (*a* top trace) the untreated wood and (*b* bottom trace) the TiO_2 coated wood

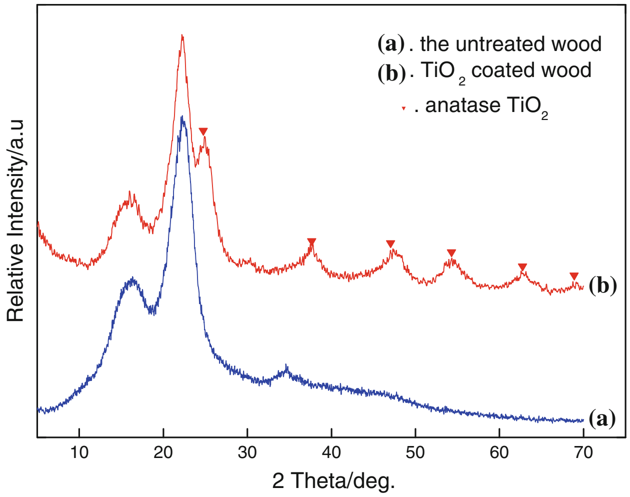


Fig. 4 XRD patterns of (*a*) the untreated wood and (*b*) TiO_2 coated wood

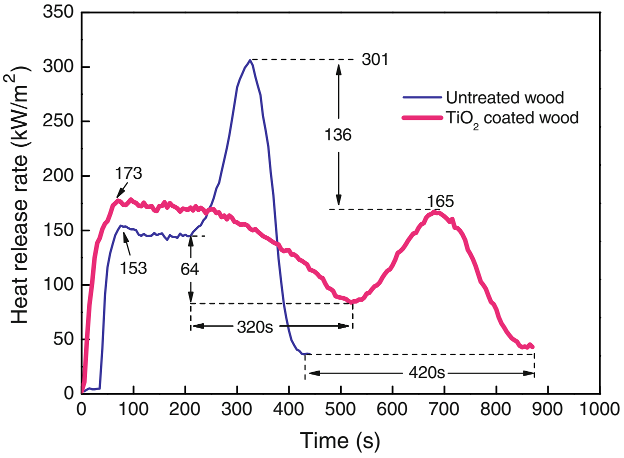


Fig. 5 HRR patterns of the untreated and TiO_2 coated wood

vibration. The wide band observed in the frequency range of 800–500 cm^{-1} was the characteristic bands of TiO_2 [41].

The crystalline phase of the coating grown on wood surface was investigated by the X-ray diffraction. Though both anatase and rutile TiO_2 phases can be achieved based on synthetic conditions, the typical diffraction peaks of anatase TiO_2 (Standard JCPDS Card No. 21-1272) emerged in treated wood (Fig. 4b).

The combinational analysis of SEM, EDXA, and FTIR spectra on the wood before and after treatment demonstrated that the intact anatase TiO_2 coating on the wood surface was bonded to hydrocarbon chains of the wood.

Cone calorimetry testing

Heat release rate

Heat release rate (HRR) data correspond directly to the intensity of fire. The earlier and middle stages of the HRR curve represent the gradual flame burning of the specimen through the thickness after the initial char layer was formed. The second peak corresponds to the increased rate of volatiles formation in the thin unburned part of specimen before the end of flame burning. The last stage of the curve after the volatiles were consumed corresponds to the non-flame burning, i.e., glowing. The flame burning is the most important step in the growth and fully developed phases of the fire and corresponds to the intensity of the fire, while the glowing corresponds mostly to the last phase of the fire and thus to the fire-resistance property.

It appears from the HRR curve (Fig. 5) that the TiO_2 promoted the very rapid ignition of the sample so the jump in HRR is almost immediate. After the ignition, the existence of TiO_2 coating had an even and low HRR value at a moderate level. The flaming and glowing of untreated sample is vigorous and fast, while that of TiO_2 coated sample is a bit moderate and relative slow. The second peak for the untreated sample with its more rapid combustion was likely more affected by the backside increasing degradation more and volatile combustion while backside impact on the second peak of the slower burning treated sample was less so it had a wider but lower peak more associated with glowing combustion. The overall burning time of TiO_2 coated wood was twice as long as that of untreated wood, even though the characteristics of the typical HRR curve for wood (double peak feature) was not greatly varied.

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 within the specified time. As seen in Fig. 6, EHC values of TiO_2 coated wood before the non-flame burning were about equal to that of untreated wood, which indicated that the combustion style and heat release mass between them were similar. For the entire test period, the EHC of the coated wood was 33% less that for the untreated wood (Table 2).

Total heat release

The total heat release (THR) of TiO_2 coated wood was twice as much as that of untreated wood (Fig. 7). The total mass loss of the coated wood was 26.6 g more than for the untreated wood. Further research is needed to fully understand the reasons for the higher total heat released results for the TiO_2 coated specimens. It is noted that the heat release measurements in the cone calorimeter is obtained by measuring the depletion of O_2.

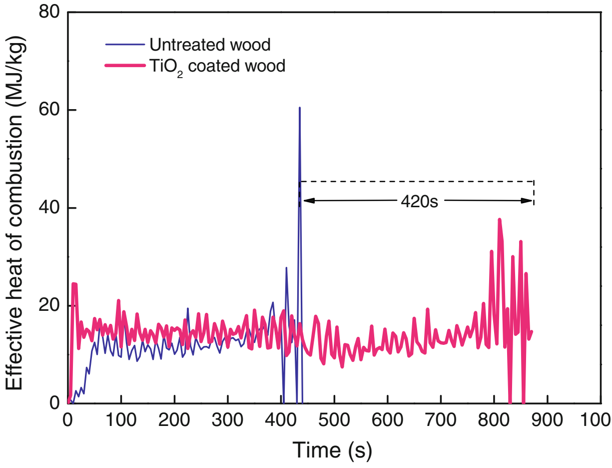


Fig. 6 EHC patterns of untreated and TiO_2 coated wood

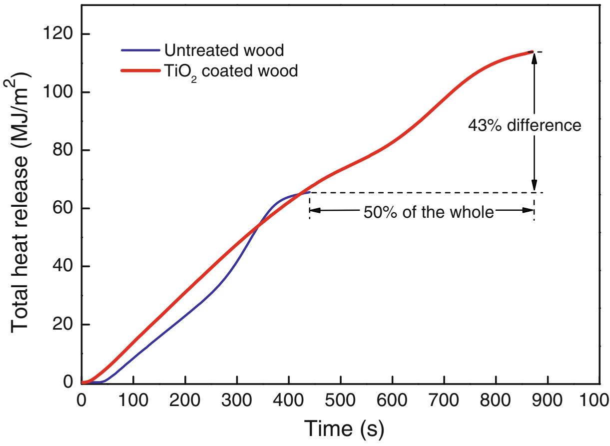


Fig. 7 THR patterns of the untreated and TiO_2 coated wood

Specific extinction area, smoke production ratio, and total smoke production

Smoke formed during a fire consists of small, mainly carbon containing particles that reduce the visibility. High smoke production in the early phases of a fire is very harmful considering the fire safety of buildings, because it endangers emergency egress through the reduction of visibility and the irritating and incapacitating effects of smoke gases. Smoke production is dependent on the burning material, but also external factors, such as fire type and oxygen supply, are important.

A common assumption is that fire retardants increase the smoke production in wood. This may be the case, since fire retardants may cause incomplete combustion, but a fire retardant can also reduce the smoke production. The effect of TiO_2 coating on smoke formation was also measured in this study. Specific extinction area (SEA), smoke production ratio (SPR), and total smoke production (TSP) as the function of time are shown in Figs. 8 and 9. In regard to untreated wood, smoke was observed mostly from the start of burning to the end of flame burning. In the case of wood covered with TiO_2 coating, the first peak of SPR and SEA was almost eliminated, the second peak of smoke formation was also diminished, and TSP and TSR only reached one-third of that for untreated wood. It is suggested that the TiO_2 coating remarkably inhibited the smoke emission from wood, and can be used as a substitute for smoke suppressants.

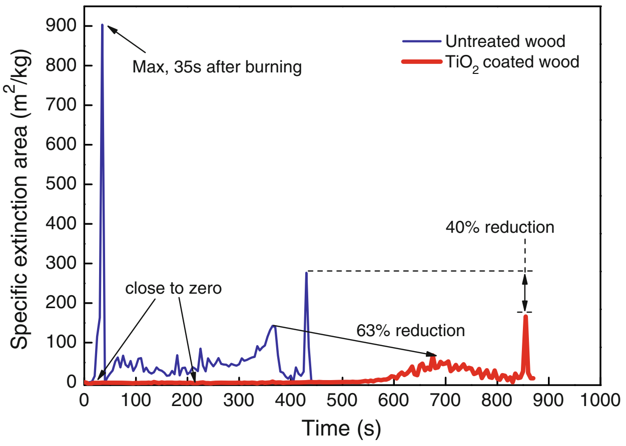


Fig. 8 SEA patterns of the untreated and TiO_2 coated wood

Production of CO, CO_2 (COY, CO2Y, COP, CO2P)

The main products of combustion are carbon dioxide and water, but also other chemical compounds can be released. The main cause of intoxication in fires is carbon monoxide (CO), which is the dominating toxic combustion product from burning wood. The yield of CO (defined as the mass of CO formed from the unit mass) and the production of CO (defined as the mass of CO formed from the unit area) for TiO_2 coated wood are shown in Fig. 10. Before the TiO_2 coating being disintegrated, the yield of CO and the production of CO were lower and slower than those of untreated wood. This trend also applied to those of CO_2 (Fig. 11).

Based on the figures illustrated above and the statistics data shown in Table 2, there are obvious differences between the untreated and the TiO_2 coated wood both in combustion time and on combustion parameters.

Mass loss and mass loss rate

As seen in Fig. 12, with the untreated sample, mass loss (ML) of sample occurred before there were right conditions for ignition of the gases and the combustion measured in the cone test, and a sharp mass loss rate (MLR) peak emerged at the start of burning. The TiO_2 also appeared to have slowed the rate of mass loss so prolonged the test and would likely increase the fire resistance in such test as noted. However, MLR for the TiO_2 coated wood decreased

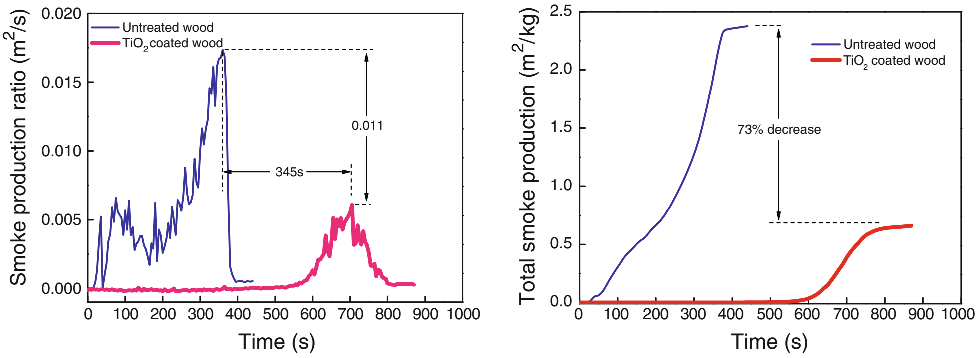


Fig. 9 SPR and TSP patterns of the untreated and TiO_2 coated wood

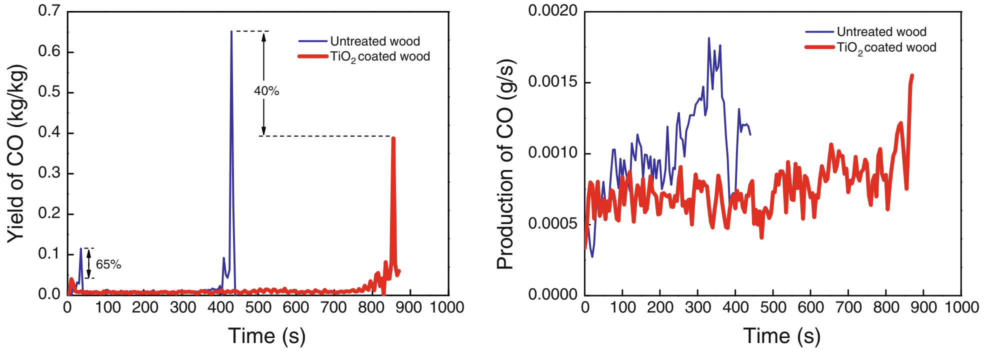


Fig. 10 COY and COP patterns of the untreated and TiO_2 coated wood

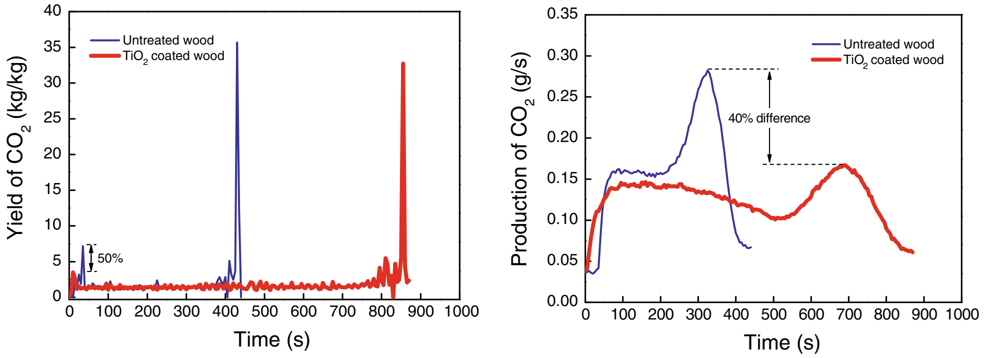


Fig. 11 CO2Y and CO2P patterns of the untreated and TiO_2 coated wood

Table 2 The averages of cone parameters during the entire test period

Parameter	Untreated wood	TiO_2 coated wood
HRR (kW/m^2)	20.3	76.8 ± 58.39
EHC (MJ/kg)	15.1	10.1 ± 4.03
MLR (g/s)	0.08	0.07 ± 0.040
SEA (m^2/kg)	49.9	8.2 ± 4.24
COY (kg/kg)	0.10	0.02 ± 0.014
CO2Y (kg/kg)	6.61	1.45 ± 0.396

as the burning time prolonging, and 40% smaller than that of untreated wood during the non-flame burning. The average specific MLR declined from 16.0 g/s of the untreated wood to 10.5 g/s of the TiO_2 coated wood, which meant the decomposition process taking place at different velocity. While the original weight of the treated wood specimens were 21% greater than the original weight of the untreated wood, the total percentage mass loss of the TiO_2 coated wood over the whole test was similar to that of untreated wood, nearly 83% of the original weight. The residuum of the treated and untreated was about the same. This observation can conclude that the retardant effect of TiO_2 coating was not strong enough to stop burning until the flammable content of wood was burned out.

Conclusions

Inorganic anatase TiO_2 coating has been synthesized chemically boned to wood surface using the cosolvent-controlled hydrothermal method. The thin coating can

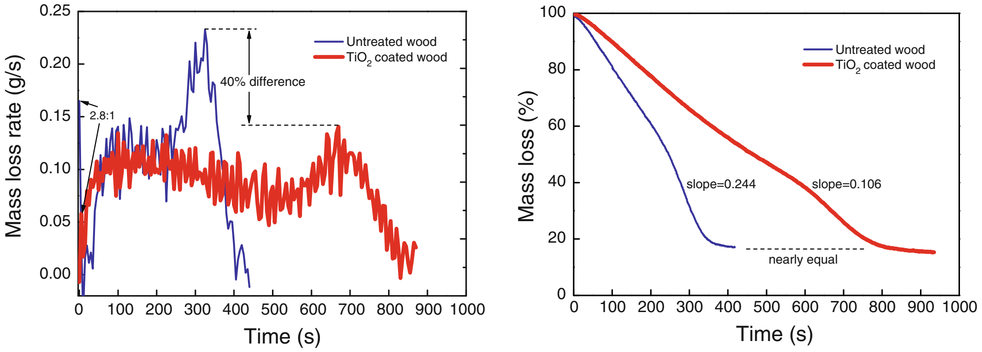


Fig. 12 MLR and ML patterns of the untreated and TiO_2 coated wood

functionally act as a protective layer to extend the combustion time, and an especially strong shield that inhibits smoke and carbon monoxide spreading.

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