Efficient and Durable Flame-Retardant Coatings on Wood Fabricated by Chitosan, Graphene Oxide, and Ammonium Polyphosphate Ternary Complexes via a Layer-by-Layer Self-Assembly Approach

Yutao Yan,* Sijie Dong, Haochong Jiang, Bohan Hou, Zhe Wang, and Chunde Jin*

ABSTRACT: An efficient and durable flame-retardant coating was constructed on wood via a layer-by-layer (LBL) self-assembly approach by using a chitosan (CS), graphene oxide (GO), and ammonium polyphosphate (APP) ternary flame-retardant system. Both scanning electron microscopy (SEM) characterization and Fourier transform infrared spectroscopy (FT-IR) analysis indicated that CS-GO and APP polyelectrolytes were successfully deposited on wood, and the deposition amount was increased with the numbers of the LBLs. Thermogravimetric analysis revealed that the CS-GO-APP coating could decrease the initial and maximum thermal decomposition temperature of the coated wood while increase the char residue significantly, which may be attributed to the earlier degradation of CS and APP and effective heat barrier of the incorporated GO, thus increasing the thermal stability of the modified wood. The limited oxygen index (LOI) and cone calorimeter analysis results of the pristine and coated wood indicated that the fire resistance was significantly improved after CS-GO-APP modification; when 15 BLs were deposited on the wood, the LOI was increased from pristine 22 to 42, while the heat release rate and total heat release decreased from pristine 105.50 kW/m² and 62.43 MJ/m² to 57.51 kW/m² and 34.31 MJ/m², respectively. What is more, the 24 h immersion experiments and abrasion tests proved the excellent durability of the deposited coating. Furthermore, the SEM images of the char residues after flaming test proved that the CS-GO-APP assembly coating could promote the char layer formation on the wood surface and block the heat and flame spread, thus protecting the wood from fire attacking.

1. INTRODUCTION

As a kind of natural renewable biomass polymer material, wood has many advantages such as light weight, high strength, beautiful texture, easy processing, and good environmental characteristics.1,2 It is widely used in furniture making, interior decoration, and architecture. However, due to its innate lignocellulosic chemical composition, wood possesses poor fire resistance and is susceptible to combustion, which limits its wide utilization. Therefore, using flame-retardant technology to convert wood into non-flammable or incombustible material effectively reduces the possibility of fire occurrence, extending its application range, which is of great significance.

To reduce the combustibility of wood, impregnating fire retardants into wood is the most commonly used method at present. Also, the related fire retardants are mainly phosphorus, nitrogen, and boron element-containing inorganic salt compounds or inorganic (nano)particles. By impregnation treatment, the whole modified wood could possess excellent flame-retardant properties. However, the inorganic salts impregnated into the wood are usually hygroscopic and easy to leach when exposed to humid conditions.3 What is worse, some of the inorganic salts could even bring about adverse effects on the physical and mechanical properties of the modified wood.4 For inorganic (nano)particles, the usage of fire retardants is usually very high, which could increase the modification cost.5,6 Surface treatment methods such as the brushing method,7,8 spraying method,9 sol–gel method,10,11 or hydrothermal treatment12,13 were also applied to improve the flame resistance of wood by coating or building flame-retardant layers on the wood surface. Although the above treatments could endow wood with flame resistance, the flame-retardant
efficiency of the coating produced by the spraying or brushing method was not high, while the preparation process of the sol–gel method and hydrothermal treatments were relatively complex and difficult to realize on large wood samples. Moreover, the coating thickness and homogeneity produced by the above methods were difficult to achieve precisely, which could result in waste of flame retardants and poor fire-retardant effects.

Layer-by-layer (LBL) self-assembly is a simple and multifunctional surface modification method, which is carried out by LBL alternating deposition of polyelectrolytes with opposite charges at liquid/solid interfaces by electrostatic action. Due to its low cost, simple process, easy operation, controllable coating structures and thickness, and absence of limitations on the substrate size and shape, the LBL self-assembly approach has gradually become an important approach for surface functionalization modification of materials. In the field of flame resistance, especially in the field of textile and cotton fabric, the LBL self-assembly approach is the most extensively used approach. Li for the first time used LBL self-assembly technology to construct an intumescent fireproof coating composed of polyallylamine and polysodium phosphate on cotton fabric, realizing the self-extinguishing fireproof effect of cotton fabric. Subsequently, various self-assembled coating materials were applied to cotton fabrics, such as chitosan (CS), ammonium polyphosphate, sodium alginate, polyeleimine, phytic acid, and so on. However, not too many research studies on wood modification by the LBL approach are reported, let alone the field of wood fire retardants. It was first reported by Renneckar and Zhou, who deposited a nanoscale film on wood by the LBL self-assembly approach using polydiallyldimethylammonium chloride (PDDA) and polyeleimine (PEI) as the polyelectrolytes, without changing the microscopic and macroscopic texture of wood. Later, until recent years, LBL self-assembly technology was applied on wood surfaces for flameproof modification. Zhao constructed a CS/sodium phytate/MgO nanoparticle coating on wood substrates via electrostatic LBL self-assembly and endowed wood with certain fire retardancy, while Zhou used a similar method to load a CS/sodium phytate/TiO$_2$–ZnO nanoparticle coating on wood. However, both of these two coatings built using polyelectrolytes and metal oxide composite systems did not show satisfactory flame-retardant performance, and the limited oxygen indexes (LOIs) were only around 33.

Graphene oxide (GO) as a two-dimensional carbon material possesses a unique layered structure and a good specific surface area, making it a heat barrier to effectively prevent the flame diffusion and reduce the heat propagation, thus, it has much better fire-retardant performance than metal oxide, which has already been widely used in polymer flame resistance. In addition, the presence of plentiful carboxyl and hydroxyl functional groups on the surface of GO is also beneficial for the dispersion of GO in matrix. Therefore, in an effort to achieve an efficient fire-resistant coating on wood, in this study, GO was first dispersed in CS solution, which could provide plenty of carbon resources, and along with the most common fire-retardant ammonium polyphosphate (APP) solution, a composite coating was constructed on the wood surface by a LBL self-assembly approach. The morphology and structure of the coating on the wood surface were characterized by SEM and FT-IR, respectively. Also, the thermal stability and flame-retardant performances were further investigated by TG and LOI test. In addition, the flame-retardant mechanism was also explored by residue char characterization and cone calorimeter analysis. This work provides a feasible and effective approach for fabricating flame-retardant wood.

2. MATERIALS AND METHODS

2.1. Materials. A sapwood of Chinese Fir (Cunninghamia lanceolata) was cut tangentially into timber specimens of two different sizes: 60 specimens were 150 mm × 6.5 mm × 3 mm (L × T × R) for LOI tests, and 10 specimens were 100 mm × 100 mm × 10 mm (L × T × R) for cone calorimetry tests. CS (viscosity: 100–200 mPa·s and degree of deacetylation ≥95%), ammonium polyphosphate (APP, degree of polymerization (DP) > 1000), acetic acid (99%), and sodium hydroxide (NaOH, ≥ 98%) were purchased from Aladdin reagent (China). GO (diameter: 0.5–5 μm and thickness: 0.8–1.2 nm) was obtained from Nanjing XFNANO Materials Tech Co. Ltd.

2.2. Preparation of the Self-Assembly Solution. First, 10 g of CS was added into 990 g of 1 wt % acetic acid aqueous solution and magnetically stirred for 24 h until the CS was completely dissolved to form a 1 wt % CS solution. Then, 0.25 g of GO (0.025%) was added to the above CS solution to form the CS–GO complex solution. For the APP solution preparation, 10 g of APP was added to 990 g of deionized water, stirred, and ultrasonicated for 1 h to form a 1 wt % APP solution.

2.3. LBL Deposition of Fire-Retardant Coating on Wood. Prior to LBL deposition, the substrates were surface-activated. All the wood specimens were immersed in a 1% NaOH solution at 70 °C for 30 min, followed by rinsing with deionized water until the surface pH = 7, and then dried in an
oven at 60 °C for 12 h. After that, the wood specimens were alternately immersed into the positively (CS-GO) and the negatively (APP) charged solutions. After each adsorption step, the excess solution on the wood surface was removed by rinsing with deionized water and drying in an oven at 70 °C for 5 min. The immersion period for the first layer of CS-GO and APP was set at 30 min, which was defined as a bi-layer (BL), while the subsequent layers were obtained after 5 min of dipping. The CS-APP-coated wood without GO as the control was also prepared using a similar process. Before each immersion, the APP solution should be ultrasonicated for 2 min in order to avoid the APP precipitation. The alternative deposition process was repeated until 5, 10, and 15 BLs were built on each wood specimen (shown in Figure 1). Finally, all the specimens were dried in an oven at 70 °C for 4 h and 103 °C for 8 h. The CS-APP-coated wood without GO as the control was also prepared using a similar process.

2.4. Characterization and Measurements. Zeta potential of the solution of different polyelectrolytes was detected using a laser particle size analyzer (Zetasizer nano ZS90). The morphology and element content of the wood coatings were characterized by field-emission scanning electron microscopy (FE-SEM) (model SU8010, Hitachi) equipped with an energy-dispersive X-ray (EDX) detector. Fourier transform infrared spectroscopy (FT-IR) analysis of the samples was performed using a Nicolet 6700 spectrometer (Thermo-Nicolet, Japan) in the region of 4000–400 cm⁻¹ at a 4 cm⁻¹ resolution for 32 scans. Thermogravimetric (TG) analysis of samples was performed on a TGA-Q5000 apparatus (TA Co., USA) from 30 to 600 °C at a heating rate of 10 °C/min under nitrogen protection; for each test, 8–10 mg of sample was weighed. Both the samples for FT-IR and TGA tests were prepared similar to the LBL deposition of fire-retardant coatings on woods as described in 2.3. The difference was that the wood block was changed to wood powder (120 mesh), and after each deposition, the powder was washed and filtered and then dried at 70 °C for 5 min. In this way, different coated wood powders for FT-IR and TGA tests were prepared.

2.5. Durability Evaluation. Chemical durability experiments were carried out by immersing the 15-BL-coated wood samples into hot water (70 °C), sodium hydroxide solution (pH = 12), hydrochloric acid solution (pH = 2), and acetone, respectively, for 24 h. Then, the surface chemicals were removed by rinsing with deionized water. The abrasion resistance of the deposited CS-GO-APP was evaluated by sand paper sanding and glue tape stripping tests. The sand paper sanding treatment was conducted by using a piece of 1500 mesh sandpaper under 500 g weight in one direction with a speed of 1 cm/s. The contact area between the sandpaper and the underlying coating was 1.00 cm × 3.25 cm, and almost a pressure of 15 kPa was applied on the coating. For the glue tape stripping test, the glue tape was first pressed on the wood surface using fingers, and then, the tape was peeled off from the wood surface; the same process was repeated for different times.

2.6. Combustion Property Test. The LOI test was carried out according to the ASTM D 2863–17 standard with a JF-3 oxygen index apparatus (Jiangning Analysis Instrument Company, China). The combustion test was performed on a cone calorimeter (Fire Testing Technology Ltd., East Grinstead, U.K.) in the horizontal position according to ASTM E1354-17 under an external heat flux of 50 kW/m² (750 °C approximately). The burning behavior test was conducted based on a modified method reported in previous studies. Briefly, the specimen was fixed at an angle of 45° to the vertical plane with the testing surface facing down, while a propane gas burner was placed 3 cm away vertically toward the wood sample surface, and the flame length was adjusted to 5 cm and burning time was 60 s. The burning process of each specimen was recorded using a video camera. After 60 s, the flame was blown out and the mass loss was weighed. Furthermore, the carbonized surface was characterized using a camera and SEM analysis.

3. RESULTS AND DISCUSSION

3.1. Zeta Potential Analysis. Zeta potential is an important index to characterize the stability of colloidal dispersion systems, whose value is related to the stability of colloidal dispersion. The higher the absolute value (positive or negative) of zeta potential, the more stable the system while the lower the zeta potential (positive or negative), the more it is likely to coagulate or flocculate. Generally, the separation line between stable and unstable suspensions is taken from −30 to +30 mV. From Figure 2 we can see that the zeta potential of CS solution and GO solution is +9.66 and −23.5 mV, respectively, which means that the two solutions are unstable, while the zeta potential of the CS-GO complex solution is up to +58.6 mV, indicating the excellent stability of CS-GO complex solution, which is beneficial for the following wood surface deposition. The low zeta potential of APP solution of −28.03 mV shows that the APP solution system is unstable, and this is why the APP solution should be ultrasonicated every time before depositing on the wood samples.

3.2. Morphology and Elemental Composition of the CS-GO-APP-Coated Wood. In order to observe the morphological changes on the wood surface after self-assembly, the control and coated wood surfaces were characterized by SEM (Figure 3). It is clear that the surface morphology and elementary composition of the wood samples by different LBL self-assembly approaches are quite different. Without polyelectrolyte deposition, the vessels and pits or rays in the tangential section were clear without any blocking. When the CS and APP polyelectrolytes were deposited, some substances similar to the polymer or wax were found in or between the
Figure 3. SEM images and elemental composition of different wood samples: (a) uncoated wood, (b) (CS-APP)$_5$-coated wood, (c) (CS-GO-APP)$_5$-coated wood, (d) (CS-GO-APP)$_{10}$-coated wood, and (e) (CS-GO-APP)$_{15}$-coated wood.
vessels. Also, as the number of BLs increased, more and more polymer-like or wax-like substances were found, almost completely covering the vessels, and no voids appeared on the vessel surface. What is more, with an increase in the BL number, the content of the N and P elements on the wood surface was also greatly increased from the original 3.49 and 0.18% to 10.76% and 16.55%, respectively. All the abovementioned results indicate that the CS-GO and APP polyelectrolytes were successfully constructed on the wood surface by the LBL self-assembly method.

3.3. FT-IR Analysis. FT-IR spectra of the LBL self-assembly coated and uncoated wood samples are shown in Figure 4. The characteristic absorbance peak of uncoated wood at 3419 cm\(^{-1}\) is ascribed to the \(-\text{OH}\) stretching vibration, the peak at about 2924 cm\(^{-1}\) is attributed to the \(-\text{CH}_2\) stretching vibration, the peak at 1052 cm\(^{-1}\) is due to \text{C}−\text{O}−\text{C}\) stretching vibrations, and the peaks at 1255 cm\(^{-1}\) and 893 cm\(^{-1}\) are attributed to \text{C}==\text{O}\) and the benzene ring, respectively. After being coated with CS-GO-APP, the peak at 3419 cm\(^{-1}\) was shifted to a higher wavenumber (3437 cm\(^{-1}\)) with an increase in the number of deposited BLs, which could be attributed to the overlap of the \(-\text{NH}_2\) stretching vibration from CS and APP with the original \(-\text{OH}\) on the wood surface. What is more, the peak at about 1635 cm\(^{-1}\) assigned to the \(-\text{NH}_2\) bending vibration was also obviously increased compared with that of the control group. Because of the similar polysaccharide nature of cellulose and CS, the characteristic absorption peaks of CS were not obviously observed in coated wood samples. However, the typical absorption peaks of APP around 1252 cm\(^{-1}\) and 885 cm\(^{-1}\) attributed to \text{P}==\text{O}\) and \text{P}−\text{O}−\text{P}\) vibrational modes were clearly observed in the coated wood samples at round 1256 and 892 cm\(^{-1}\), respectively.\(^{31,32}\) All the above analysis showed that CS and APP were successfully deposited on the wood surface. What is more, as the number of BLs increased, the amount of CS and APP polyelectrolytes deposited on wood also increased and showed a linear positive correlation with the deposited BL numbers, which was proved by the relative absorbance intensity calculation method provided by Fei and Zhang as shown in the inset of Figure 4.

3.4. Thermal Stability. Figure 5 shows the TG and DTG curves of the control and CS-APP/CS-GO-APP-coated wood samples, and the corresponding data analyzed by TG analysis software are summarized in Table 1. As shown in Figure 5a, it is obvious that after modification, both the char residue and the \(T_{\text{max}}\) greatly changed, indicating that CS-GO-APP could significantly affect the thermal decomposition process of wood. To be specific, the thermal stability-related \(T_{10}\) and \(T_{\text{max}}\) changed. For control wood, the \(T_{10}\) was 284.1 °C, while for the CS-APP-coated wood, the \(T_{10}\) was reduced to 269.1 °C, indicating that the thermal decomposition process of the CS-APP-modified wood occurred, which was mostly due to the earlier degradation of APP and CS. Furthermore, when GO was incorporated, the \(T_{10}\) and \(T_{\text{max}}\) only slightly changed, which is quite different from a previous study by Chen.\(^{31}\) In his study, he used a similar LBL assembly method to coat cotton fabric with CS and APP; however, the \(T_{5\%}\) and \(T_{10\%}\) decreased obviously with the increase in the LBL numbers of APP and CS. This difference was mainly due to the introduction of GO, which could block the heat transfer and flame propagation, thus preventing the CS and APP from decomposing to some extent. Moreover, for the control wood, one maximum decomposition peak appeared in the DTG curve, while for the CS-GO-APP modified wood, two decomposition peaks were observed, and both the peaks shifted to lower temperature, also proving the earlier degradation of the modified wood. In addition, when GO was incorporated, the \(R_{\text{max}}\) of the CS-GO-APP-modified wood was significantly decreased compared with that of the pristine and CS-APP-modified wood, indicating the improvement in the thermal stability of the modified wood, which was beneficial for making the wood fireproof. After CS-APP modification, the char residue at 400 and 600 °C greatly increased from 25.61% and 17.79% in the uncoated sample to 55.17% and 46.40% in the modified one, respectively. The significant increase in the char

![Image](http://pubs.acs.org/journal/acsodf)
residue was mainly due to the polyphosphoric acid produced from the APP decomposition, which could catalyze cellulose into char, and the polyhydroxy CS could also promote the residual char formation. When GO was introduced, the char residue was further increased because of the excellent thermal stability of GO. All in all, the catalytic carbon formation effect of APP and CS together with the heat-blocking and flame-blocking effect of GO contributed to the thermal stability of the modified wood.

3.5. Combustion Properties. 3.5.1. LOI and Durability Analysis. LOI values of different CS-APP/CS-GO-APP-coated wood samples are shown in Figure 6a. The LOI value of pure wood is 22 and increases to 25 when coated with five BLs of CS and APP. Obviously, when GO was introduced, the char residue was further increased because of the excellent thermal stability of GO. All in all, the catalytic carbon formation effect of APP and CS together with the heat-blocking and flame-blocking effect of GO contributed to the thermal stability of the modified wood.

### Table 1. Thermal Properties of the Wood Samples Uncoated and Coated with CS-APP/CS-GO-APP Polyelectrolytes under Nitrogen Conditions

| samples                | $T_{10\%}$ ($°C$) | $T_{max1}$ ($°C$) | $T_{max2}$ ($°C$) | $R_{max}$ (°C/%) | residue at 400 °C (100%) | residue at 600 °C (100%) |
|------------------------|-------------------|-------------------|-------------------|------------------|--------------------------|--------------------------|
| control                | 284.1             | 366.4             | 12.11             | 25.61            | 17.79                    |                          |
| (CS-APP)$_5$           | 269.1             | 276.3             | 13.79             | 55.17            | 46.40                    |                          |
| (CS-GO-APP)$_5$        | 247.5             | 277.1             | 8.92              | 56.21            | 46.52                    |                          |
| (CS-GO-APP)$_{10}$     | 246.8             | 231.9             | 6.83              | 59.78            | 49.70                    |                          |
| (CS-GO-APP)$_{15}$     | 245.9             | 232.1             | 5.69              | 62.34            | 53.13                    |                          |

$T_{10\%}$: decomposition temperature when the weight loss was 10 wt %, $T_{max}$: decomposition temperature when the weight loss was at its maximum, and $R_{max}$: the maximum mass loss rate.

Figure 6. LOI of coated and uncoated wood samples before (a) and after (b) 24 h of different immersion treatments.

Figure 7. SEM images of the 15-BL CS-GO-APP-coated wood surface after different immersion treatments: (a) HCl solution, (b) acetone, (c) NaOH solution, and (d) hot water.
the coated wood still possessed good flame-retardant performance.

In addition to the chemical agent resistance of the deposited coating, the abrasion resistance was also investigated. Figure 8 shows the LOI of the 15-BL CS-GO-APP-coated wood after tape stripping and sand paper sanding tests. It was obvious that the LOI of the coated wood after abrasion treatments gradually decreased with the increase in the number of abrasion cycles, but the LOI was still higher than 30; even after 20-times tape stripping tests and sand paper sanding tests (under a pressure of 15 kPa) was 20 times, which indicated the excellent fire-retarding ability of the treated wood and proved the abrasion durability of the deposited CS-GO-APP. The difference is that the sand paper sanding treatment had much more serious adverse effects on the coating than those of the glue tape stripping-treated wood as shown in Figure 8.

3.5.2. Burning Behavior and Char Residue Characterization. The fire behavior of the coated and uncoated wood was assessed by exposing all the samples to a propane flame for 60 s at a vertical angle, and the burning process was captured using a digital camera. The combustion state at different burning times is displayed in Figure 9. For the control wood sample, it was ignited quickly once exposed to the flame, and the flame spread very fast and burned vigorously in 60 s without too much carbon formed. When it was coated with CS-APP, only after 30 s of burning, some carbon layers were formed on the wood surface, which increased as time increased to 60 s, indicating that APP and CS were favorable for carbon formation. The carbon layer formed on the wood surface could gradually block the flame spread and heat transfer, thus improving the fire resistance of wood. Furthermore, for the CS-GO-APP-coated wood sample, it became much harder to ignite and much more carbon formed during burning. After 60 s of burning, the wood nearly self-extinguished. This may be attributed to the excellent thermal barrier effect of GO, which could prevent the flame propagation and reduce the heat transfer into the wood, thus preventing the wood from burning.

The surface morphology of the burnt wood samples after 60 s of combustion was also recorded using a digital camera and is shown in Figure 10. It is observed that the morphology of various burnt wood samples is quite different. For the uncoated wood (Figure 10a), the burnt area was much bigger than that of CS-APP- and CS-GO-APP-coated wood samples and the char layer formed was rough and loose with many large cracks. By contrast, the char layers of CS-APP-coated (Figure 10b) and CS-GO-APP-coated (Figure 10c) wood samples after burning were much smoother and denser, which could provide effective thermal barrier layers between the flame and the wood substrate during combustion and improve the fire safety performance of wood. For quantitative comparison of the flammability properties, the burnt area and mass loss of coated and uncoated wood were determined and are shown in Figure 11. The mass loss of uncoated wood was 1.980 g while that of the CS-APP- and CS-GO-APP-coated wood was 0.920 and 0.895 g, respectively, only half of that uncoated wood samples, indicating that more carbon layers were formed on the coated wood sample surface instead of complete combustion into CO₂ in the air.

In order to further clarify the combustion mechanism, the char residues after flame tests were collected and analyzed by SEM as shown in Figure 10d–f. For the uncoated wood sample, after combustion, the pristine tangential section structure of wood was reserved with a gray fragile char layer being deposited on the surface (Figure 10d). Furthermore, as shown in Figure 10e, in the wood sample coated with CS-APP, the surface of the char residue is dense and compact, while obvious bubble shapes (marked with yellow arrows) can be observed on the char layer surface and some of them have even burst (marked with red circles), which may be due to the release of ammonia gas from APP during combustion. When GO was incorporated into the polyelectrolyte coating, much more small bubble-like structures were observed on the char layer surface after combustion, like a bunch of grapes (Figure 10f), which could be attributed to the heat barrier effect of GO. Due to the heat-blocking effect of GO, much more heat was accumulated on the wood surface, thus promoting the expansion of char by the volatile gas generated in the burning process. Also, the possible flame-retardant mechanism for wood treated with CS-GO-APP during burning is exemplified in Figure 12.

3.5.3. Cone Calorimeter Analysis. Cone calorimetry tests were conducted to analyze the combustion characteristics of
different wood samples. Also, the heat release rate (HRR), total heat release rate (THR), total smoke production (TSP), and smoke production rate (SPR) were obtained and are shown in Figure 13; the corresponding data are listed in Table 2. The HRR is an important parameter to characterize fire intensity. The higher the heat release rate, the greater the burning heat of the material and the greater the fire hazard. Figure 13a shows the HRR curves of different wood samples; it is clear that two HRR peaks were observed in the HRR curves of both coated and uncoated wood samples, which means two main heat release stages were present. The first stage occurred mainly due to the rapid ignition of the wood surface during the early stage of the fire due to the oxidation of volatile pyrolysis products. Also, with the continuous pyrolysis and carbonization of the wood surface, the carbonization layer formed could temporarily block the radiation heat source, which led to a decrease in the fire intensity and heat release rate. As time went on, the carbonized layer broke up and exposed the inner matrix. As a result, the fire intensity increased again and led to the appearance of the second exothermic peak. Figure 13a shows that the position of the second pHRR is obviously ahead compared with that of the uncoated wood, indicating the earlier combustion of the CS-APP-modified wood, which may be due to the dehydration of wood components catalyzed by CS and APP during the low-temperature stage, accelerating the degradation of organic compounds. What is more, after CS-APP coating, both the HRR and THR obviously decreased compared with those of the uncoated wood. The HRR and THR of the CS-APP-coated wood were decreased to 92.03 kW/m$^2$ and 54.42 MJ/m$^2$ from those of pristine 105.50 kW/m$^2$ and 62.43 MJ/m$^2$, respectively, which means that the fire intensity was decreased after CS-APP modification. This may be attributed to the increased carbonized layer formation due to the catalysis of CS and APP. Furthermore, when the GO was incorporated into the CS-APP coating, the HRR and THR of the modified wood were further decreased (Figure 13b), indicating a further decrease in fire intensity. This may be due to the excellent heat-shielding effect of GO, which could block the heat transfer and flame propagation into the wood matrix, thus reducing the wood combustibility.

The smoke release curves of coated and uncoated wood samples are shown in Figure 13c,d. Obviously, after CS-APP modification, the TSP was decreased and further significantly

---

**Figure 10.** Digital photographs and SEM images of wood after combustion test: (a,d) uncoated wood, (b,e) (CS-APP)$_{15}$-coated wood, and (c,f) (CS-GO-APP)$_{15}$-coated wood.

**Figure 11.** Burnt area and mass loss of coated wood and uncoated wood after the combustion test.

**Figure 12.** Schematic of a possible flame-retardant mechanism for wood treated with CS-GO-APP during burning.
When GO was incorporated into the composite CS-APP coating, the TSP was decreased by 44.9%, from the pristine 3.25 m$^2$ of the control wood sample to 1.79 m$^2$ (Table 2), indicating that CS and APP together with GO possess an excellent smoke suppression effect. What is more, from Figure 13d, it can be observed that the time to the peak of SPR was brought forward after modification, indicating that the carbon-forming process happened earlier than that of the control wood by CS-APP catalysis. In addition, from Figure 13a, it can be seen that the instantaneous concentration of flue gas (expressed as the SPR) is similar to the change law of the HRR, and the two are basically synchronous, indicating that the flue gas release and heat release are synchronized, that is, most of the flue gas is produced during the stage of flame combustion. When the flame combustion process was blocked by CS-APP or CS-GO-APP modification, the TSP and SPR were reduced correspondingly as shown in Figure 13c,f.

### 4. CONCLUSIONS

In this study, efficient and durable flame-retardant coatings of CS-GO-APP were successfully deposited on wood surfaces via the LBL self-assembly method. Also, all kinds of characterization were performed to examine the coated and uncoated wood. SEM–EDX and FT-IR analyses confirmed that the CS-GO-APP coatings were successfully constructed on wood, and the deposited amount of the composite polyelectrolytes was positively correlated with the number of the BLs, which also directly affected the thermal stability and fire-retardant performance of coated and uncoated wood. According to TG analysis, the $T_{\text{max}}$ of the wood samples was obviously decreased to lower temperature after CS-GO-APP modification, indicating that the decomposition process of the coated wood occurred earlier, which was mainly due to the earlier degradation of APP and CS. However, the $R_{\text{max}}$ was significantly decreased, indicating that the thermal stability of the modified wood was improved. The improved thermal stability could be attributed to the large amount of carbon formed on the wood surface, proved by the increased char residue by TG test and the heat barrier effect of GO, both of which could prevent the heat transfer to the wood matrix and reduce wood degradation. According to the LOI test, the LOI for the pristine wood is only 22, while for the 5-BL CS-GO-APP-coated wood, the LOI was increased to 32; furthermore, for the 15-BL CS-GO-APP-coated wood the LOI was increased to 42, which was almost twice of that uncoated wood, indicating the high fire-retardant performance of the coating. What is more, the cone calorimeter test results also proved the high fire-retardant efficiency and smoke suppression ability of the CS-GO-APP polyelectrolyte coating on wood. When 15 BLs of CS-GO-APP polyelectrolytes were deposited, the pHRR and THR were decreased by 21.4 and 28.2%.

### Table 2. Cone Calorimetry Data for Coated and Uncoated Wood

| samples          | pHRR (kW/m$^2$) | HRR (kW/m$^2$) | THR (MJ/m$^2$) | TSP (m$^2$) |
|------------------|-----------------|----------------|----------------|-------------|
| control (CS-APP) | 207.2 ± 4.5     | 105.5 ± 2.3    | 62.4 ± 0.7     | 3.25 ± 0.12 |
| (CS-GO-APP)      | 180.8 ± 2.5     | 92.0 ± 1.7     | 54.4 ± 0.4     | 2.80 ± 0.07 |
| (CS-GO-APP)      | 162.9 ± 3.1     | 57.5 ± 2.9     | 34.3 ± 0.6     | 1.79 ± 0.11 |
45.0% compared with those of uncoated wood, and the total smoke production was decreased by 44.9%. In addition, the 24 h immersion treatments and abrasion tests proved the excellent durability of the coatings. To further uncover the combustion mechanism, the char residues after flame tests were analyzed by SEM. Compared with the pristine wood, much denser and compact char residue was found on the CS-APP-coated wood surface, which was mainly due to the catalysis of polyphosphoric acid produced from APP degradation that could catalyze cellulose into char and the promotion effect of polyhydroxy CS in char formation, thus blocking the heat band flame spread. Moreover, the abundant bubble shape substance on the char layer surface produced during burning indicated the release of plenty of ammonia gas by APP degradation during combustion, which could dilute the oxygen and also suppress the spread of the flame. In addition, GO introduction could further improve the wood thermal stability and fire-retardant property due to its excellent heat transfer blocking effect. All in all, the excellent fireproof property of the modified retardant property due to its excellent heat transfer blocking effect. All in all, the excellent fireproof property of the modified retardant property due to its excellent heat transfer blocking effect. All in all, the excellent fireproof property of the modified retardant property due to its excellent heat transfer blocking effect. All in all, the excellent fireproof property of the modified retardant property due to its excellent heat transfer blocking effect. All in all, the excellent fireproof property of the modified retardant property due to its excellent heat transfer blocking effect. All in all, the excellent fireproof property of the modified retardant property due to its excellent heat transfer blocking effect.

**AUTHOR INFORMATION**

**Corresponding Authors**

Yutao Yan — School of Chemical and Material Engineering, Zhejiang A&F University, Hangzhou 311300, PR China; orcid.org/0000-0002-1616-1859; Email: yyttao1988@163.com

Chunde Jin — School of Chemical and Material Engineering, Zhejiang A&F University, Hangzhou 311300, PR China; Email: jincd@zafu.edu.cn

**Authors**

Sijie Dong — School of Chemical and Material Engineering, Zhejiang A&F University, Hangzhou 311300, PR China

Haochong Jiang — School of Chemical and Material Engineering, Zhejiang A&F University, Hangzhou 311300, PR China

Bohan Hou — School of Chemical and Material Engineering, Zhejiang A&F University, Hangzhou 311300, PR China

Zhe Wang — School of Chemical and Material Engineering, Zhejiang A&F University, Hangzhou 311300, PR China; orcid.org/0000-0002-5516-354X

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c03624

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The authors acknowledge the funding provided by the Natural Science Foundation of Zhejiang Province, China (no. LQ19C160014), and the Student Scientific Research Training Project of Zhejiang A&F University (no. 2021KK0031).

**REFERENCES**

(1) Dong, Y.; Wang, K.; Li, J.; Zhang, S.; Shi, S. Q. Environmentally benign wood modifications: a review. ACS Sustainable Chem. Eng. 2020, 8, 3532–3540.

(2) Gan, W.; Chen, C.; Wang, Z.; Song, J.; Kuang, Y.; He, S.; Mi, B.; Sunderland, P. B.; Hu, L. Dense, self-formed char layer enables a fire-retardant wood structural material. Adv. Funct. Mater. 2019, 29, 1807447.

(3) Vakhitova, L. Fire retardant nanocoating for wood protection. In Nanotechnology in Eco-efficient Construction; Elsevier, 2019, pp 361–391. DOI: 10.1016/b978-0-08-102641-0.00016-5

(4) Wen, M.-Y.; Kang, C.-W.; Park, H.-J. Impregnation and mechanical properties of three softwoods treated with a new fire retardant chemical. J. Wood Sci. 2014, 60, 367–375.

(5) Ylimaz Atay, H. Novel eco-friendly flame retardant wood composites reinforced by hunteite and hydromagnesite minerals. Wood Mater. Sci. Eng. 2021, 0, 1–11.

(6) Miao, D.; Chen, X.; Tian, X. Intumescent flame retardant coatings on cotton fabric prepared using layer by layer assembly: a review. Polym. Adv. Technol. 2012, 387–406.

(7) Sehrajapenrual, A. R.; Manohar, A.; Banerjee, A.; Varla, E.; Wang, H.; Oströkov, K. Thermally-insulating verniculite nanosheets-epoxy nanocomposite paint as fire-resistant wood coating. Nanoscale Adv. 2021, 3, 4235–4243.

(8) Gan, W.; Chen, C.; Wang, Z.; Pei, Y.; Ping, W.; Xiao, S.; Dai, J.; Yao, Y.; He, S.; Zhao, B.; Das, S.; Yang, B.; Sunderland, P. B.; Hu, L. Fire-resistant structural material enabled by an anisotropic thermally conductive hexagonal boron nitride nitride coating. Adv. Funct. Mater. 2020, 30, 1909196.

(9) Li, S.; Wang, X.; Xu, M.; Liu, L.; Wang, W.; Gao, S.; Li, B. Effect of a biomass based waterborne fire retardant coating on the flame retardancy for wood. Polym. Adv. Technol. 2021, 32, 4805–4814.

(10) Yona, A. M. C.; Žigon, J.; Matjaž, P.; Petrič, M. Potentials of silicate-based formulations for wood protection and improvement of mechanical properties: A review. Wood Sci. Technol. 2021, 55, 887–918.

(11) Mahr, M. S.; Hübter, T.; Sabel, M.; Schartel, B.; Bahr, H.; Militz, H. Fire retardancy of sol–gel derived titania wood-inorganic composites. J. Mater. Sci. 2012, 47, 6849–6861.

(12) Kong, L.; Tu, K.; Guan, H.; Wang, X. Growth of high-density ZnO nanorods on wood with enhanced photostability, flame retardancy and water repellency. Appl. Surf. Sci. 2017, 407, 477–484.

(13) Song, K.; Ganguly, I.; Eastin, L.; Dichiara, A. High temperature and fire behavior of hydrothermally modified wood impregnated with carbon nanomaterials. J. Hazard. Mater. 2020, 384, 121283.

(14) Richardson, J. J.; Cui, J.; Björnman, M.; Braunger, J. A.; Ejima, H.; Caruso, F. Innovation in layer-by-layer assembly. Chem. Rev. 2016, 116, 14828–14867.

(15) Qiu, X.; Li, Z.; Li, X.; Zhang, Z. Flame retardant coatings prepared using layer by layer assembly: a review. Chem. Eng. J. 2018, 334, 108–122.

(16) Li, Y. C.; Mannen, S.; Morgan, A. B.; Chang, S.; Yang, Y. H.; Condon, B.; Grunlan, J. C. Intumescent all-polymer multilayer nanocoating capable of extinguishing flame on fabric. Adv. Mater. 2011, 23, 3926–3931.

(17) Wang, B.; Lai, X.; Li, H.; Jiang, C.; Gao, J.; Zeng, X. Multifunctional MXene/Chitosan-Coated Cotton Fabric for Intelligent Fire Protection. ACS Appl. Mater. Interfaces 2021, 13, 23020–23029.

(18) Fang, F.; Zhang, X.; Meng, Y.; Gu, Z.; Bao, C.; Ding, X.; Li, S.; Chen, X.; Tian, X. Intumescent flame retardant coatings on cotton fabric of chitosan and ammonium polyphosphate via layer-by-layer assembly. Surf. Coat. Technol. 2015, 262, 9–14.

(19) Kumar Kundu, C. K.; Wang, W.; Zhou, S.; Wang, X.; Sheng, H.; Pan, Y.; Song, L.; Hu, Y. A green approach to constructing multilayered nanocoating for flame retardant treatment of polyamide 66 fabric from chitosan and sodium alginate. Carbohydr. Polym. 2017, 166, 131–138.

(20) Xiong, M.; Ren, Z.; Liu, W. Fabrication of UV-resistant and superhydrophobic surface on cotton fabric by functionalized polylethyleneimine/SiO2 via layer-by-layer assembly and dip-coating. Cellulose 2019, 26, 8951–8962.
(21) Fang, Y.; Sun, W.; Li, J.; Liu, H.; Liu, X. Eco-friendly flame retardant and dripping-resistant of polyester/cotton blend fabrics through layer-by-layer assembly fully bio-based chitosan/phytic acid coating. *Int. J. Biol. Macromol.* 2021, 175, 140–146.

(22) Renneckar, S.; Zhou, Y. Nanoscale coatings on wood: polyelectrolyte adsorption and layer-by-layer assembled film formation. *ACS Appl. Mater. Interfaces* 2009, 1, 559–566.

(23) Zhao, F.; Tang, T.; Hou, S.; Fu, Y. Preparation and synergistic effect of chitosan/sodium Phytate/MgO nanoparticle fire-retardant coatings on wood substrate through layer-by-layer self-assembly. *Coatings* 2020, 10, 848.

(24) Zhou, L.; Fu, Y. Flame-Retardant Wood Composites Based on Immobilizing with Chitosan/Sodium Phytate/Nano-TiO2-ZnO Coatings via Layer-By-Layer Self-Assembly. *Coatings* 2020, 10, 296.

(25) Fang, F.; Ran, S.; Fang, Z.; Song, P.; Wang, H. Improved flame resistance and thermo-mechanical properties of epoxy resin nanocomposites from functionalized graphene oxide via self-assembly in water. *Composites, Part B* 2019, 165, 406–416.

(26) Nine, M. J.; Tran, D. N.; Tung, T. T.; Kabiri, S.; Losic, D. Graphene-borate as an efficient fire retardant for cellulosic materials with multiple and synergetic modes of action. *ACS Appl. Mater. Interfaces* 2017, 9, 10160–10168.

(27) Jing, J.; Zhang, Y.; Fang, Z.-P.; Wang, D.-Y. Core-shell flame retardant/graphene oxide hybrid: a self-assembly strategy towards reducing fire hazard and improving toughness of polylactic acid. *Compos. Sci. Technol.* 2018, 165, 161–167.

(28) Shi, X.; Peng, X.; Zhu, J.; Lin, G.; Kuang, T. Synthesis of DOPO-HQ-functionalized graphene oxide as a novel and efficient flame retardant and its application on polylactic acid: thermal property, flame retardancy, and mechanical performance. *J. Colloid Interface Sci.* 2018, 524, 267–278.

(29) Chen, G.-G.; Hu, Y.-J.; Peng, F.; Bian, J.; Li, M.-F.; Yao, C.-L.; Sun, R.-C. Fabrication of strong nanocomposite films with renewable forestry waste/montmorillonite/reduction of graphene oxide for fire retardant. *Chem. Eng. J.* 2018, 337, 436–445.

(30) Pollastri, S.; Gualtieri, A. F.; Gualtieri, M. L.; Hanuskova, M.; Cavallo, A.; Gaudino, G. The zeta potential of mineral fibres. *J. Hazard. Mater.* 2014, 276, 469–479.

(31) Chen, H.-Q.; Xu, Y.-J.; Jiang, Z.-M.; Jin, X.; Liu, Y.; Zhang, L.; Zhang, C.-J.; Yan, C. The thermal degradation property and flame-retardant mechanism of coated knitted cotton fabric with chitosan and APP by LBL assembly. *J. Therm. Anal. Calorim.* 2020, 140, 591–602.

(32) Fang, Y.; Liu, X.; Tao, X. Intumescent flame retardant and antidripping of PET fabrics through layer-by-layer assembly of chitosan and ammonium polyphosphate. *Prog. Org. Coat.* 2019, 134, 162–168.

(33) Fei, P.; Liao, L.; Cheng, B.; Song, J. Quantitative analysis of cellulose acetate with a high degree of substitution by FTIR and its application. *Anal. Methods* 2017, 9, 6194–6201.

(34) Zhang, T.; Yan, H.; Peng, M.; Wang, L.; Ding, H.; Fang, Z. Construction of flame retardant nanocoating on ramie fabric via layer-by-layer assembly of carbon nanotube and ammonium polyphosphate. *Nanoscale* 2013, 5, 3013–3021.

(35) Liu, L.; Huang, Z.; Pan, Y.; Wang, X.; Song, L.; Hu, Y. Finishing of cotton fabrics by multi-layered coatings to improve their flame retardancy and water repellency. *Cellulose* 2018, 25, 4791–4803.

(36) Lu, J.; Jiang, P.; Chen, Z.; Li, L.; Huang, Y. Flame retardancy, thermal stability, and hygroscopicity of wood materials modified with melamine and amino trimethylene phosphonic acid. *Constr. Build. Mater.* 2021, 267, 121042.