Article

Flame-Retardant Wood Composites Based on Immobilizing with Chitosan/Sodium Phytate/Nano-TiO₂-ZnO Coatings via Layer-by-Layer Self-Assembly

Lin Zhou and Yanchun Fu *

College of Furnishings and Industrial Design, Nanjing Forestry University, Nanjing 210037, China;
z_zhoulin@163.com

* Correspondence: yanchunfu@njfu.edu.cn; Tel.: +86-25-8542-7793

Received: 15 February 2020; Accepted: 19 March 2020; Published: 22 March 2020

Abstract: Composite coatings of inorganic nanomaterials with polyelectrolytes are promising materials for wood modification. Endowing wood with flame retardancy behavior can not only broaden the range of applications of wood, but also improve the safety of wood products. In this work, chitosan/sodium phytate/TiO₂-ZnO nanoparticle (CH/SP/nano-TiO₂-ZnO) composite coatings were coated on wood surface through layer-by-layer self-assembly. The morphology and chemical composition of the modified wood samples were analyzed using scanning electron microscopy and energy dispersive spectrometry. The thermal degradation properties and flame retardancy of the samples treated with different assembly structures were observed by thermogravimetric analysis, limiting oxygen test, and combustion test. Due to the presence of an effective intumescent flame retardant system and a physical barrier, the CH/SP/nano-TiO₂-ZnO coatings exhibited the best flame retardant performance and required only approximately six seconds for self-extinguishing. The coated samples had a limiting oxygen index of 8.4% greater than the original wood.

Keywords: wood; flame retardancy; natural macromolecular polyelectrolyte; layer-by-layer self-assembly

1. Introduction

In recent years, the modification of wood surfaces with inorganic nanomaterials in order to improve or create new functional features has attracted intense research interests [1,2]. With the development of surface modification techniques based on layer-by-layer (LbL) self-assembly, the introduction of metal nanoparticles into polyelectrolyte multilayer coatings has proven to be feasible and promising [3–5]. The LbL self-assembly approach has been widely adopted in many fields for surface functionalization due to its advantages such as low cost, simple process, controllable coating thickness, and absence of limitations on the substrate size and shape [6,7]. Moreover, since Rennekar first found that polycations can be effectively attached to a wood surface by LbL self-assembly [8], it has been applied successfully in wood surface modifications, with many recent reports on the modification of wood with different materials via the LbL self-assembly process [9–11].

While many studies have investigated a polyelectrolyte/nanomaterials composite membrane, most of these have focused either on the fabrication of nanomaterials or on the performance of modified materials; therefore, a systematic study of the functional mechanism or the interaction between the different phases of the composite coatings has been lacking. In particular, due to its surface porosity and chemical heterogeneity, there has been relatively little research in this area for wood [12]. Furthermore, most of the studies performed to date have focused on nanocomposite coatings while

binary multicomponent have been rarely studied, most likely due to the greater difficulties involved in the experimental control of the combination of two or more phases [13]. To address these limitations, we analyzed multiple promising polyelectrolytes and nanomaterials for incorporation into thin-film systems through LbL self-assembly. This process proved to be adaptable to include three or more component quadlayers, and thus led to the possible combination of several different flame retardant action modes, for example, intumescence and an inorganic barrier, which are effective on wood surface [14–16]. Koklukaya et al. have confirmed the formation of a protective char layer along the cellulose surface [17,18].

Based on previously findings, it is well known that both nano-TiO₂ and nano-ZnO provide thermal stability, and to date several attempts have been made to endow wood with flame retardancy by using nano-TiO₂ or nano-ZnO as an effective inorganic barrier [19–22]. Additionally, natural polyelectrolytes such as chitosan, pectin, alginate, and xanthan gum have great potential for use in this area [23]. Chitosan is extracted from the shells of shrimp or crabs and sodium phytate is obtained from rice, making both of these materials highly environmentally friendly. Chitosan has been used as a natural biopolymer for surface modification in biomedical applications and textile treatment due to its unique properties, such as its polycationic nature, antibacterial characteristics, low cost, and accessibility [24–26]. Additionally, the high nitrogen content of chitosan makes it a potential flame retardant when combined with the phosphorus contained in sodium phytate [27–29]. The high negative charge of the sodium phytate surface makes it a potent chelator of divalent and trivalent cations in vitro, and it is most likely associated with Ca²⁺ or Mg²⁺ ions in vivo, so it has been widely used as a corrosion inhibitor and electrolyte in research studies [30–32]. The Carosio's group have successfully confirmed that the combination of chitosan and sodium phytate is a good assembly link in flame retardant modification in their recent research [17,18,22]. It is important to note that the superior properties of these materials are expected to compensate for the drawbacks of wood, such as flammability, that not only limit the use of wood but may also cause security risks, particularly for wood products and wood construction in public areas.

In recent years, LbL self-assembly for polyelectrolytes and/or nanoparticles has been proposed as an alternative and eco-friendly flame-retardant treatment for several substrates such as cotton, fabrics, pulp fibers, and PU foam [33–36]. The improvement of flame retardant properties including lower after-flame time, decreased total heat release, or self-extinction have been verified in these studies, and the individual components have also proven their potential in flame retardancy. Since the method here has been proved to be efficient on cellulose in flame retardancy, the point of this study was to evaluate different structural strategies and treatment steps. In the present work, a chitosan/sodium phytate/nano-TiO₂-ZnO composite was investigated by repeatedly adding one component at a time in order to explore its individual component effect. This kind of structure has not been reported previously and has achieved excellent results with relatively reduced processing time. Compared to traditional modification methods and the increased use of synthetic polymers which have raised serious recycling and environmental challenges, the environmentally benign building blocks of LbL assemblies and the natural macromolecular polyelectrolyte we used showed great positive significance [37].

Nanoscale anatase TiO₂ and hexagonal wurtzite ZnO were used in this work. Chitosan and sodium phytate served for bonding of nano-TiO₂-ZnO to fabricate binary nanocomposite films providing the flame retardant property on the wood surface. The adsorption interactions between each layer arose from electrostatic adsorption (positive and negative charge attraction), which was favorable for the LbL self-assembly process mentioned above. Since this study focused on the interaction of multiple phases, several groups with different film structures were fabricated. SEM and EDS were used to investigate the morphology and elements of the samples, and the flame retardancy of the films were examined by fire resistance tests [33]. Based on the results obtained by various characterization methods, the multi-component coatings showed relatively better performance than the single-component coatings and could prevent the combustion of the materials. Thus, we obtained an effective flame-retardant composite coating on a wood surface without changing the appearance

of the wood. The mechanism for these changes related to the individual components is discussed in detail below.

2. Materials and Methods

2.1. Materials

Balsa wood (*O. pyramidale*) formed into small blocks was supplied by Senyu Wood Industry Co., Ltd. (Dongguan, China). Sodium phytate (99.0% metals basis) was obtained from Hefei Bosf Biotechnology Co., Ltd. (Hefei, China) and zinc oxide nanoparticles (particle size of 30 ± 10 nm), titanium oxide nanoparticles (particle size of 5–10 nm), and chitosan (low viscosity: < 200 mPa·s) were all purchased from Shanghai Aladdin Biochemical Technology (Shanghai, China) and were used for multilayer coating compositions, as mentioned below. Hydrochloric acid (36.5%–38.0%, BioReagent) was obtained from Sigma-Aldrich (Shanghai, China). All aqueous solutions were prepared with distilled water.

2.2. Wood Substrate and Solution Preparation

Wood samples were cut into specimens with dimensions of $10 \times 10 \times 1$ mm³ and $120 \times 10 \times 4$ mm³ for characterization and evaluation of flame retardancy. Following that, the samples were rinsed twice with distilled water and dried in an oven at 60 °C for 1 h. They were then sorted into several groups and were weighed and measured prior to processing. The entire coating fabrication process was carried out at room temperature and pressure.

For the preparation of a mixed nano-TiO₂ and nano-ZnO solution, zinc oxide nanoparticles (1 g) and titanium oxide nanoparticles (1 g) at a mass ratio of 1:1 were added to distilled water (200 mL) under magnetic stirring, and the pH of the solution was adjusted to 2–3 using hydrochloric acid. The nano-TiO₂-ZnO solution was then positively charged by adjusting the pH below its isoelectric point. Solutions of pure nano-TiO₂ (positively-charged), pure nano-ZnO (positively-charged), chitosan (positively-charged), and sodium phytate (negatively-charged) were prepared, respectively, using the same procedure as that used for the preparation of the mixed nano-TiO₂ and nano-ZnO solutions. The concentration of each solution was set at 1%. Finally, the solutions were divided into groups for coating fabrication as described below.

2.3. Formation of Flame Retardant Coatings on Wood Surfaces via Layer-by-Layer Self-Assembly

In this experiment, the layer-by-layer self-assembly technique was used with mutual adsorption of polycation, polyanion, and metal oxide nanoparticles leading to the formation of composite coatings. In the deposition process, firstly, each set of negatively charged wood specimens was immersed in the corresponding positively charged chitosan solution for 90 min. The surface would then have a positive charge as the polycation ionized by the chitosan adsorbed onto the wood surface by electrostatic forces. Next, alternating negative and positive layers of sodium phytate and (or) nano-TiO₂-ZnO were deposited on the wood surface by immersing the specimens in the corresponding groups of solutions for 90 min, followed by rinsing twice with distilled water and 1-hour oven-drying between each layer. One layer of sodium phytate and one layer of nano-TiO₂-ZnO were considered to comprise a single deposition cycle. To ensure uniform coverage of the substrate, ten deposition cycles were used for each specimen (Figure 1). Thus, the as-prepared samples named CH/SP/nano-TiO₂-ZnO were obtained. For other samples as listed in Table 1, the nano-TiO₂-ZnO layer was replaced by pure nano-TiO₂ or pure nano-ZnO, and the obtained samples were named CH/SP/nano-TiO₂ sample and CH/SP/nano-ZnO sample, respectively. The wood treated with chitosan only, while the other conditions remain unchanged was called the CH sample. The wood treated with CH and SP was named the CH/SP sample.

Figure 1. Scheme of fabricating flame-retardant coating on a wood surface by layer-by-layer self-assembly.

Table 1. Assembly structure and invariants of coated samples.

Sample Name	Assembled Structure
CH	Wood/CH/CH/ ...
CH/SP	Wood/CH/SP/CH/SP/ ...
CH/SP/nano-TiO ₂	Wood/CH/SP/TiO ₂ /SP/TiO ₂ / ...
CH/SP/nano-ZnO	Wood/CH/SP/ZnO/SP/ZnO/ ...
CH/SP/nano-TiO ₂ -ZnO	Wood/CH/SP/TiO ₂ -ZnO/SP/TiO ₂ -ZnO/ ...
Invariants	
Soaking time: 90 min; Deposition cycle: 10; Chitosan, sodium phytate, nano-TiO ₂ , nano-ZnO, nano-TiO ₂ -ZnO concentration: 1%.	

2.4. Characterization

The surface morphology of the CH/SP/nano-TiO₂-ZnO coatings before and after wear, as well as their chemical compositions were characterized by scanning electron microscopy (SEM, Quanta 400 FEG, FEI Inc., Eindhoven, The Netherlands) equipped with an energy-dispersive X-ray spectroscopy (EDS) system. Each sample was coated with a 5–10 nm Au layer prior to SEM imaging. The mass change of the samples before and after the treatment was also recorded.

2.5. Thermogravimetric Analysis

Thermogravimetric analysis (TG209, Netzsch, Selb, Germany) under nitrogen atmosphere was performed to measure the thermal stability of the wood samples (0.5 mm thickness) before and after different kinds of treatment. The heating rate was 10 °C/min, and the temperature range was 30–800 °C.

2.6. Limiting Oxygen Index Test

The limiting oxygen index testing was conducted by oxygen index testing apparatus (PX-01-005, Phinix, Suzhou, China) according to standard GB2406.2-2009 [38] with 150 × (6.5 ± 0.5) × (3.0 ± 0.5) mm³ wood samples. The apparatus was set to standard conditions and the sample was placed vertically in the mixture of oxygen and nitrogen that had been adjusted to a specific value. After the airflow was stabilized, the sample was ignited. The minimum oxygen concentration required for the sample to maintain steady combustion for three minutes at 5 cm of the sample was identified as its oxygen index, expressed as a volume percent.

2.7. Combustion Test

Combustion testing was carried out by direct exposure to an alcohol lamp flame. Specifically, flame retardant trends were observed by exposing the wood samples ($120 \times 10 \times 4 \text{ mm}^3$) to the outer flame of the alcohol lamp, recording the combustion state and the time required for the flame to be completely extinguished. The entire burning process of every wood sample after ignition was videotaped for backup observation. After observing and comparing the combustion of all samples, we selected the most typical sample from each group as the representative to be discussed below. Each group had five replicates.

3. Results and Discussion

3.1. Surface Morphologies Analysis

In order to verify that the loading of films would not affect the wood's macroscopic characteristics, the weight of the coated wood samples before and after modification was recorded in Table 2. It is presented that the weight of all specimens after coating was hardly changed or only increased slightly. Figure 2a–d shows the representative SEM images of the original wood, CH, CH/SP, and CH/SP/nano-TiO₂-ZnO samples. It was observed that unlike the other three samples, the original wood had a smooth surface with clearly observed vessel holes, as indicated by the white arrow. Compared to the original wood sample, the samples shown in Figure 2b,c have more rough appearances, indicating that it is possible to absorb chitosan and sodium phytate on a wood surface. In Figure 2d, spherical particles densely covering the entire wood surface are clearly observed and identified as the immobilized nanoparticles. The corresponding plane scans of EDS spectrums for the CH/SP/nano-TiO₂-ZnO sample are presented in Figure 2e–h. In addition to the C (Figure 2e) and O (Figure 2f) elements derived from the wood chemical compositions, two new signals from Zn (Figure 2g) and Ti (Figure 2h) were observed in the corresponding EDS spectrums. This provides a further demonstration that the CH/SP/nano-TiO₂-ZnO coatings were successfully immobilized on the wood substrate, and that the hierarchical thin films were composed of two kinds of small nanoparticles.

Figure 2. SEM images of (a) original wood; (b) CH coated wood; (c) CH/SP coated wood and (d) CH/SP/nano-TiO₂-ZnO coated wood. Plane scan analysis of CH/SP/nano-TiO₂-ZnO coatings interface: (e) element C; (f) element O; (g) element Zn; and (h) element Ti.

Table 2. Initial mass and mass change after treatment of coated wood sample.

Sample Name	Initial Mass (g)					Mass Change (g)				
	1	2	3	4	5	1	2	3	4	5
CH	0.80	0.68	1.27	0.89	1.05	0.00	0.00	0.00	0.00	0.00
CH/SP	0.27	1.17	0.88	0.91	0.85	0.00	0.00	0.00	0.01	0.01
CH/SP/nano-TiO ₂	0.46	0.49	1.07	0.93	0.74	0.00	0.00	0.00	0.01	0.01
CH/SP/nano-ZnO	0.67	0.97	0.97	0.44	0.42	0.00	0.01	0.01	0.01	0.01
CH/SP/nano-TiO ₂ -ZnO	0.90	1.34	0.97	0.67	1.13	0.03	0.04	0.03	0.02	0.03

3.2. Thermal Stability and Fire Resistance Tests

To reveal the thermal degradation of uncoated and coated wood, TGA and DTG (Derivative Thermogravimetry) were carried out, and the curves are shown in Figure 3. With the introduction of the coatings, the thermal decomposition of wood changed significantly. The pyrolysis of the samples can be characterized by three stages. Before 250 °C, it is the drying and pre-decomposition stage. In this stage, the formed phosphoric acid and polyphosphoric acid produced by sodium phytate had a catalyzed effect on the thermal degradation of the wood. It resulted that the weight loss rates of the treated samples were higher than that of the uncoated wood, indicating that the coatings promoted the carbonization and dehydration of the material [39]. In addition, the treated samples came into the second stage at a lower temperature than the uncoated one, that is, holocellulose (cellulose and remaining hemicellulose) underwent violent pyrolysis at about 250 to 400 °C. In the third stage, at 450–800 °C, the residual weight of all samples remained stable. The residual weight rate of treated samples were higher than that of the uncoated one, and the samples in order of descending residual weight were: CH/SP/nano-TiO₂-ZnO (red line), CH/SP/TiO₂ (blue line), CH/SP/nano-ZnO (yellow line), CH/SP (purple line), CH (green line), and uncoated wood (black line).

Figure 3. TG (a) and DTG (b) curves of the uncoated wood (black line), CH coated (green line), CH/SP coated (purple line), CH/SP/nano-ZnO coated (yellow line), CH/SP/nano-TiO₂ coated (blue line), and CH/SP/nano-TiO₂-ZnO coated (red line) samples.

The flame retardant properties of all the samples were evaluated by limiting oxygen index (LOI) tests. A high LOI value corresponded to a high oxygen content required for burning to occur, which meant a high flame retardancy. According to the Figure 4, the LOI values increased as the composition increased. It is increased dramatically to 33% after being coated with CH/SP/nano-TiO₂-ZnO films, which suggested significant improvement in the sample's flame retardancy. In order to investigate the effect of individual components, LOI results of different assembly structure samples can be clearly seen from the bars below. The CH/SP/nano-TiO₂ coated sample possessed a higher LOI value of 32.8% compared with the CH/SP/nano-ZnO coated sample's LOI

of only 29.5%, which indicated that nano-TiO₂ played a major role in flame retardancy. Overall, the results demonstrated the fire resistance of the coatings.

Figure 4. Limiting oxygen index (LOI) of the uncoated wood (black), CH coated (green), CH/SP coated (purple), CH/SP/nano-ZnO coated (yellow), CH/SP/nano-TiO₂ coated (blue), and CH/SP/nano-TiO₂-ZnO coated (red) samples.

The general flame retardancy of the original wood and five groups of samples (Table 1) was assessed by the direct exposure to an alcohol lamp flame. The process of flame initiation, spreading, and self-extinguishing time were recorded for the samples treated with different components and are shown in Figure 5. It is clear from Figure 5(a1,a2) that once the original wood was ignited, it burned quickly and fiercely with no indication of dying out, which is very reasonable since wood is known to be a flammable material. In particular, the wood used in this experiment was loose and had large pores, making it more flammable. Thus, eventually the whole strip of wood was burned out. By contrast, the coated wood burned slowly and was extinguished naturally after a time of 6–30 s, which was consistent with the results achieved above (Figure 5(b2,c2,d2,e2,f2)), that is, with a shorter extinguishing time indicating a better flame retardant property. Table 3 lists the data description of each group and the results of statistical analysis (one-way ANOVA). It is obvious that p -value < 0.05, indicating that different assembly structures did have a great impact on wood flame retardancy.

As observed from Figure 5(a1,b1,c1,d1,e1,f1), the burning flame of the coated wood samples is much smaller than that of the original wood within 6 seconds of ignition. The fire of the sample coated with chitosan extended only slightly from the ignition point, as observed from Figure 5(b1,b2). It was revealed that the chitosan layer was barely effective for obtaining flame retardancy, which is consistent with the limiting oxygen index in Figure 4. The flame-retardant properties improved after the addition of the sodium phytate layer. This was because the nitrogen in chitosan and the phosphorus in sodium phytate constitute a ‘nitrogen–phosphorus’ flame retardant system. During thermal degradation, the generated phosphoric acid and metaphosphoric acid dehydrated strongly into charcoal, leading to the appearance of a carbon protection layer quickly after burning. These two materials have been proven to likely form an intumescent flame retardant system that can help trap air and heat [40]. In this system, cellulose and chitosan serve as carbon sources, while sodium phytate acts as an acid source and –NH contained in chitosan makes it act as a blowing agent. The char formation in this system not only prevents continued burning but also provides a certain mechanical support, which is of vital importance in wooden parts due to the severe dangers of collapse in a burning wood structure.

Figure 5. Flame burning tendency of (a1,a2) original wood; (b1,b2) CH coated sample; (c1,c2) CH/SP coated sample; (d1,d2) CH/SP/nano-ZnO sample; (e1,e2) CH/SP/nano-TiO₂ sample; and (f1,f2) CH/SP/nano-TiO₂-ZnO sample.

Table 3. Correlation data of self-extinguishing time and one-way ANOVA.

Sample Name	Quantity	Mean	Std. Deviation	Variance		
CH	5	28.08	1.89	3.587		
CH/SP	5	22.96	1.64	2.683		
CH/SP/nano-TiO ₂	5	20.26	4.80	23.058		
CH/SP/nano-ZnO	5	7.52	0.73	0.532		
CH/SP/nano-TiO ₂ -ZnO	5	6.58	1.07	1.137		
ANOVA						
Sources	SS	df	MS	F	p-Value	F Crit
Between groups	1836.652	4	459.163	74.06571604	1.06047E-11	2.886081
Within groups	123.988	20	6.1994	—	—	—
Total	1960.64	24	—	—	—	—

“—” means no data.

As shown in Figure 5(d2,e2,f2), upon the introduction of nanoparticles, the wood required a relatively shorter time of 6–20 seconds to extinguish the flame, demonstrating better flame retardant performance. It is well-known that both nano-TiO₂ and nano-ZnO provide high stability, high melting point, and good thermal stability, and their flame retardant effects have already been discussed and applied. For this multilayer composite, the immobilized nanoparticle layer further improved the flame retardant properties [17,41]. The metal oxides can significantly affect the pyrolysis process of the intumescent system and improve the fire resistance of the film. Physically, the dense cover of the nanoparticles on the wood surface also hindered the ignition and spread of combustion. The flame retardant mechanism of this nanocomposite film is illustrated in Figure 6.

Due to both physical and chemical interactions, the coated wood obtained in this work showed flame retardant performance. Among all of the samples examined in our experiments, the CH/SP/nano-TiO₂-ZnO sample showed the best performance. As observed from Figure 5f, only approximately 6 seconds were required for the flame to be extinguished, the burning was difficult to maintain, and even ignition was difficult. It had a maximum limiting oxygen index of 8.4% greater than the original wood. Markedly, the nano-TiO₂ provided a stronger flame retardant behavior than nano-ZnO. With the introduction of nano-TiO₂, both of the self-extinguishing time and

ultimate oxygen index deviated greatly from before. According to all the results obtained above, the CH/SP/nano-TiO₂-ZnO system had an excellent flame retardant property, and the wood showed an enhanced performance with the immobilization of the coatings. Nevertheless, it is still necessary to further optimize the experimental protocol and film parameters, because nowadays it is of commercial interest to develop natural, sustainable, renewable, and functional films. It is also important to point out that the materials investigated in our work have many other superior properties, and may have thus endowed the composite film with UV resistance, antibacterial behavior, and wettability.

Figure 6. Flame retardancy mechanism of CH/SP/nano-TiO₂-ZnO composite film.

4. Conclusions

A novel chitosan/sodium phytate/nano-TiO₂-ZnO flame retardant system was coated on the wood surface using the layer-by-layer assembly method. Considering all of the above-described results, we conclude that the composite films had a dramatic flame retardancy effect on the wood, leading to higher thermal stability. The higher limiting oxygen index of coated wood showed fire resistant property with a self-extinguishing time of around 6 seconds in combustion tests. According to the research of different component assembly structures, it has been proven that an effective combined effect between the constituents of the coating gave rise to the superior flame retardancy of the coatings, that is, the presence of an effective intumescent flame retardant system and a physical barrier. The use of these coatings was a promising approach for wood modification and for endowing other materials such as fabrics with flame retardancy. Since the impact of material modification on the environment has been paid more and more attention, this new environmentally friendly flame retardant composite film on wood surface could have significant importance in academic research and practical application.

Author Contributions: Conceptualization, methodology, Y.F.; software, validation, formal analysis, investigation, resources, data curation, L.Z. and Y.F.; writing—original draft preparation, L.Z.; writing—review and editing, Y.F. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Youth Science and Technology Innovation Fund of Nanjing Forestry University, grant number CX2016016.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Papadopoulos, A.N.; Taghiyari, H.R. Innovative wood surface treatments based on nanotechnology. *Coatings* **2019**, *9*, 866. [\[CrossRef\]](#)
2. Papadopoulos, A.N.; Bikiaris, A.N.; Mitropoulos, A.C.; Kyzas, G.Z. Nanomaterials and chemical modifications for enhanced key wood properties: A review. *Nanomaterials* **2019**, *9*, 607. [\[CrossRef\]](#) [\[PubMed\]](#)
3. Wang, L.; Zhang, T.; Yan, H.; Peng, M.; Fang, Z. Modification of ramie fabric with a metal-ion-doped flame-retardant coating. *J. Appl. Polym. Sci.* **2013**, *129*, 2986–2997. [\[CrossRef\]](#)
4. Liu, Z.; Yan, Z.; Bai, L. Layer-by-layer assembly of polyelectrolyte and gold nanoparticle for highly reproducible and stable SERS substrate. *Appl. Surf. Sci.* **2016**, *360*, 437–441. [\[CrossRef\]](#)
5. Apaydin, K.; Laachachi, A.; Ball, V.; Jimenez, M.; Bourbigot, S.; Ruch, D. Layer-by-layer deposition of a TiO₂-filled intumescent coating and its effect on the flame retardancy of polyamide and polyester fabrics. *Colloids Surf. A Physicochem. Eng. Asp.* **2015**, *469*, 1–10. [\[CrossRef\]](#)
6. Srivastava, S.; Kotov, N.A. Layer-by-layer (LBL) assembly with semiconductor nanoparticles and nanowires. In *Semiconductor Nanocrystal Quantum Dots*; Springer: Vienna, Austria, 2008; pp. 197–216.
7. Malucelli, G. Surface-engineered fire protective coatings for fabrics through sol-gel and layer-by-layer methods: An overview. *Coatings* **2016**, *6*, 33. [\[CrossRef\]](#)
8. 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. [\[CrossRef\]](#)
9. Lozhechnikova, A.; Bellanger, H.; Michen, B.; Burgert, I.; Österberg, M. Surfactant-free carnauba wax dispersion and its use for layer-by-layer assembled protective surface coatings on wood. *Appl. Surf. Sci.* **2017**, *396*, 1273–1281. [\[CrossRef\]](#)
10. Rao, X.; Liu, Y.; Fu, Y.; Liu, Y.; Yu, H. Formation and properties of polyelectrolytes/TiO₂ composite coating on wood surfaces through layer-by-layer assembly method. *Holzforschung* **2016**, *70*, 361–367. [\[CrossRef\]](#)
11. Lu, X.; Hu, Y. Layer-by-layer deposition of TiO₂ nanoparticles in the wood surface and its superhydrophobic performance. *BioResources* **2016**, *11*, 4605–4620. [\[CrossRef\]](#)
12. Bellanger, H.; Casdorff, K.; Muff, L.F.; Ammann, R.; Burgert, I.; Michen, B. Layer-by-layer deposition on a heterogeneous surface: Effect of sorption kinetics on the growth of polyelectrolyte multilayers. *J. Colloid Interface Sci.* **2017**, *500*, 133–141. [\[CrossRef\]](#) [\[PubMed\]](#)
13. Rassam, G.; Abdi, Y.; Abdi, A. Deposition of TiO₂ nano-particles on wood surfaces for UV and moisture protection. *J. Exp. Nanosci.* **2012**, *7*, 468–476. [\[CrossRef\]](#)
14. Nine, M.J.; Tran, D.N.H.; 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. [\[CrossRef\]](#) [\[PubMed\]](#)
15. Nine, M.J.; Tran, D.N.H.; ElMekawy, A.; Losic, D. Interlayer growth of borates for highly adhesive graphene coatings with enhanced abrasion resistance, fire-retardant and antibacterial ability. *Carbon* **2017**, *117*, 252–262. [\[CrossRef\]](#)
16. Holder, K.M.; Huff, M.E.; Cosio, M.N.; Grunlan, J.C. Intumescent multilayer thin film deposited on clay-based nanobrick wall to produce self-extinguishing flame retardant polyurethane. *J. Mater. Sci.* **2014**, *50*, 2451–2458. [\[CrossRef\]](#)
17. Köklükaya, O.; Carosio, F.; Grunlan, J.C.; Wågberg, L. Flame-retardant paper from wood fibers functionalized via layer-by-layer assembly. *ACS Appl. Mater. Interfaces* **2015**, *7*, 23750–23759. [\[CrossRef\]](#)
18. Köklükaya, O.; Carosio, F.; Durán, V.L.; Wågberg, L. Layer-by-layer modified low density cellulose fiber networks: A sustainable and fireproof alternative to petroleum based foams. *Carbohydr. Polym.* **2020**, *230*, 115616. [\[CrossRef\]](#)

19. Zhao, Z.; Sakai, S.; Wu, D.; Chen, Z.; Zhu, N.; Huang, C.; Sun, S.; Zhang, M.; Umemura, K.; Yong, Q. Further exploration of sucrose–citric acid adhesive: Investigation of optimal hot-pressing conditions for plywood and curing behavior. *Polymers* **2020**, *12*, 216. [\[CrossRef\]](#)
20. Sun, Q.; Yu, H.; Liu, Y.; Li, J.; Cui, Y.; Lu, Y. Prolonging the combustion duration of wood by TiO₂ coating synthesized using cosolvent-controlled hydrothermal method. *J. Mater. Sci.* **2010**, *45*, 6661–6667. [\[CrossRef\]](#)
21. 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*, 479–484. [\[CrossRef\]](#)
22. Carosio, F.; Laufer, G.; Alongi, J.; Camino, G.; Grunlan, J.C. Layer-by-layer assembly of silica-based flame retardant thin film on PET fabric. *Polym. Degrad. Stab.* **2011**, *96*, 745–750. [\[CrossRef\]](#)
23. Decher, G.; Hong, J. Buildup of ultrathin multilayer films by a self-assembly process, I. consecutive adsorption of anionic and cationic bipolar amphiphiles on charged surfaces. *Makromol. Chem. Macromol. Symp.* **1991**, *46*, 321–327. [\[CrossRef\]](#)
24. Zhang, R.; Xie, J.; Yang, B.; Fu, F.; Tang, H.; Zhang, J.; Zhao, Y.; Zhang, Y.; Liu, L.; Zhu, Y.; et al. Self-assembly of chitosan and cellulose chains into a 3D porous polysaccharide alloy films: Co-dissolving, structure and biological properties. *Appl. Surf. Sci.* **2019**, *493*, 1032–1041. [\[CrossRef\]](#)
25. Tian, M.; Hu, X.; Qu, L.; Du, M.; Zhu, S.; Sun, Y.; Han, G. Ultraviolet protection cotton fabric achieved via layer-by-layer self-assembly of graphene oxide and chitosan. *Appl. Surf. Sci.* **2016**, *377*, 141–148. [\[CrossRef\]](#)
26. Rinaudo, M. Chitin and chitosan: Properties and applications. *Prog. Polym. Sci.* **2006**, *31*, 603–632. [\[CrossRef\]](#)
27. Li, Z.F.; Zhang, C.J.; Cui, L.; Zhu, P.; Yan, C.; Liu, Y. Fire retardant and thermal degradation properties of cotton fabrics based on APTES and sodium phytate through layer-by-layer assembly. *J. Anal. Appl. Pyrolysis* **2017**, *123*, 216–223. [\[CrossRef\]](#)
28. Carosio, F.; Alongi, J.; Malucelli, G. Layer by Layer ammonium polyphosphate-based coatings for flame retardancy of polyester–Cotton blends. *Carbohydr. Polym.* **2012**, *88*, 1460–1469. [\[CrossRef\]](#)
29. Laufer, G.; Kirkland, C.; Morgan, A.B.; Grunlan, J.C. Intumescent multilayer nanocoating, made with renewable polyelectrolytes, for flame-retardant cotton. *Biomacromolecules* **2012**, *13*, 2843–2848. [\[CrossRef\]](#)
30. Zhu, Y.; Gao, W.; Huang, H.; Chang, W.; Zhang, S.; Zhang, R.; Zhao, R.; Zhang, Y. Investigation of corrosion resistance and formation mechanism of calcium-containing coatings on AZ31B magnesium alloy. *Appl. Surf. Sci.* **2019**, *487*, 581–592. [\[CrossRef\]](#)
31. Zhang, R.F.; Shi, H.W.; Liu, Z.L.; Zhang, S.F.; Zhang, Y.Q.; Guo, S.B. Property of anodic coatings obtained in an organic, environmental friendly electrolyte on aluminum alloy 2024-T3. *Appl. Surf. Sci.* **2014**, *289*, 326–331. [\[CrossRef\]](#)
32. Liu, X.; Li, W.; Wang, W.; Song, L.; Fan, W.; Gao, X.; Xiong, C. Synthesis and characterization of pH-responsive mesoporous chitosan microspheres loaded with sodium phytate for smart water-based coatings. *Mater. Corros.* **2018**, *69*, 736–748. [\[CrossRef\]](#)
33. Li, J.; Ren, D.; Wu, Z.; Xu, J.; Bao, Y.; He, S.; Chen, Y. Flame retardant and visible light-activated Fe-doped TiO₂ thin films anchored to wood surfaces for the photocatalytic degradation of gaseous formaldehyde. *J. Colloid Interface Sci.* **2018**, *530*, 78–87. [\[CrossRef\]](#) [\[PubMed\]](#)
34. Carosio, F.; Alongi, J.; Malucelli, G. Flammability and combustion properties of ammonium polyphosphate/poly(acrylic acid)-based layer by layer architectures deposited on cotton, polyester and their blends. *Polym. Degrad. Stab.* **2013**, *98*, 1626–1637. [\[CrossRef\]](#)
35. Carosio, F.; Ghanadpour, M.; Alongi, J.; Wagberg, L. Layer-by-layer-assembled chitosan/phosphorylated cellulose nanofibrils as a bio-based and flame protecting nano-exoskeleton on PU foams. *Carbohydr. Polym.* **2018**, *9*, 479–487. [\[CrossRef\]](#)
36. Camino, G.; Costa, L.; Martinasso, G. Intumescent fire-retardant systems. *Polymer* **1989**, *23*, 359–376. [\[CrossRef\]](#)
37. Lazar, S.T.; Kolibaba, T.J.; Grunlan, J.C. Flame-retardant surface treatments. *Nat. Rev. Mater.* **2020**. [\[CrossRef\]](#)
38. GB2406.2-2009 *Plastics-Determination of Burning Behaviour by Oxygen Index-Part 2: Ambient-Temperature Test*; Standards Press of China: Beijing, China, 2009.
39. Liu, Y.; Wang, Q.Q.; Jiang, Z.M.; Zhang, C.J.; Li, Z.F.; Chen, H.Q.; Zhu, P. Effect of chitosan on the fire retardancy and thermal degradation properties of coated cotton fabrics with sodium phytate and APTES by LBL assembly. *J. Anal. Appl. Pyrolysis* **2018**, *135*, 289–298. [\[CrossRef\]](#)

40. Yuste, M.; Escobar-Galindo, R.; Benito, N.; Palacio, C.; Martínez, O.; Albella, J.M.; Sánchez, O. Effect of the incorporation of titanium on the optical properties of ZnO thin films: From doping to mixed oxide formation. *Coatings* **2019**, *9*, 180. [[CrossRef](#)]
41. Wang, Z.; Han, E.; Ke, W. Effect of nanoparticles on the improvement in fire-resistant and anti-ageing properties of flame-retardant coating. *Surf. Coat. Technol.* **2006**, *200*, 5706–5716. [[CrossRef](#)]

© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).