Preparation and characterization of dual-functional coatings of nanofibrillated cellulose and modified SrAl2O4: Eu, Dy phosphors

Longfei Zhang, Shaoyi Lyu, Zhilin Chen, Siqun Wang

PII: S0257-8972(18)30556-5
DOI: doi:10.1016/j.surfcoat.2018.05.071
Reference: SCT 23446
To appear in: Surface & Coatings Technology

Received date: 20 February 2018
Revised date: 23 May 2018
Accepted date: 30 May 2018

Please cite this article as: Longfei Zhang, Shaoyi Lyu, Zhilin Chen, Siqun Wang, Preparation and characterization of dual-functional coatings of nanofibrillated cellulose and modified SrAl2O4: Eu, Dy phosphors. Sct (2017), doi:10.1016/j.surfcoat.2018.05.071

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.
Preparation and characterization of dual-functional coatings of nanofibrillated cellulose and modified SrAl$_2$O$_4$: Eu, Dy phosphors

Longfei Zhang $^{a,b}$, Shaoyi Lyu $^{a,b}$, Zhilin Chen $^{a,*}$, Siqun Wang $^{b,a,*}$

$^a$ Research Institute of Wood Industry, Chinese Academy of Forestry, Beijing, 100091, China

$^b$ Center for Renewable Carbon, University of Tennessee, Knoxville, TN 37996, USA

*Corresponding author. E-mail: chenzhilin@caf.ac.cn (Z. Chen), swang@utk.edu (S. Wang)

Abstract: To prepare luminescent and superhydrophobic dual-functional coating materials, SrAl$_2$O$_4$: Eu$^{2+}$, Dy$^{3+}$ (SAOED) phosphors were modified with tetraethyl orthosilicate and (3-aminopropyl)trimethoxysilane for enhancing the water resistance and surface activity. Dual-functional coatings were fabricated by blending nanocellulose, 1,2,3,4-butanetetracarboxylic acid (BTCA), and modified SAOED phosphors on the poly(vinyl alcohol) pretreated surfaces of wood substrates using a two-step process combining spraying and chemical vapor deposition. The surface morphology, chemical structure, and mechanical properties of the hybrid coatings were characterized by SEM, energy dispersive X-ray analysis, FTIR, X-ray photoelectron spectroscopy, and abrasion tests. Incorporation of the modified SAOED particles and ONFC induced surface roughness on the wood surface with simultaneous afterglow luminescence and superhydrophobicity after low-energy modification. The water contact angle of the coating could go up to 153° and the slide angle was only 8.5°. The emission spectra for hybrid films showed a slight blue shift (2.8 nm) at around 512 nm compared to the SAOED particles. The obtained superhydrophobic wood materials with long afterglow luminescence can find application in interior decoration, intelligent ceilings, night indicators, or luminous logos and labels.
Keywords: Cellulose; particle; surface modification; thin films; multifunctional composites

1. Introduction

In recent times, wood-based materials have become the material-of-choice for decorative panels because of their lightweight [1], unique texture, color, and good processing ability [2]. In order to broaden their applications and overcome some of the shortcomings of wood, functional materials such as flame retardants [3], photochromic ingredients [4], or luminous and moisture-resistance components [5, 6] are usually incorporated. These process designs are based on the rich hydroxyl groups in the wood surface and relatively easy process for post-modification. Generally, functional surface coatings can be deposited by several methods [7, 8], including sol-gel processes, dipping, spraying, vapor deposition, and electro-spinning. Of these, spraying and chemical vapor deposition (CVD) are relatively cheaper and most widely used [9]. As a new type of decorative materials, functional wood materials not only retain the natural characteristics of wood, but also exhibit an extra performance.

Rare-earth-doped aluminate luminescent micro- and nanoparticles (SrAl2O4: Eu2+, Dy3+, denoted as SAOED), which exhibit excellent luminescence with long afterglow time [10, 11], are widely used in luminous displays, warning signs, escape routes, and advertisement cards [12]. Generally, these phosphors are easy to hydrolyze and their crystal structure can be destroyed when exposed to high moisture or aqueous solution without modification. Therefore, they are blended with oil-soluble polymers [13], varnishes, or paints [14] to prepare luminescent coatings. However, most polymers used for varnishing are derived from petroleum-based materials, which are highly volatile, non-renewable, rarely biodegradable, and environment unfriendly. Unlike petroleum-based polymers, nanofibrillated cellulose (NFC) [15, 16] is a natural biomass material with low density, high...
mechanical strength, high crystallinity, as well as high surface chemical activity and light transmittance especially when subjected to 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation [17]. It is expected to be one of the most promising candidates to replace petroleum-based polymer materials as a good functional carrier.

Therefore, in order to equip the plain wood materials with an excellent afterglow luminescence of SAOED phosphors, and introduce the potential water-dispersed NFC suspensions as reinforced substrates. It is necessary to modify the hydrolysable SAOED phosphors to improve its water resistance and control the surface composition before incorporation in NFC systems. Thus far, several physical and chemical strategies have been employed to improve the hydrolytic resistance of phosphors, such as boracic acid [18], phosphoric acid [19] and SiO$_2$-coated modification [20]. It revealed that a SiO$_2$ coating on the surface of phosphor particles was an effective strategy to improve the water resistance. However, the surface activity of modified phosphors with inorganic surface or inactive terminal groups was failed to enhance, especially in water-based systems. This was further confirmed in the studies, where a mixture of cross-linked resins was used to improve the interface combination between inorganic particles and cellulose fibers [21], and APTMS-coated modification was liable to enhance the bonding strength of fiber/particles composites [22]. Furthermore, our group has successfully fabricated nanocellulose films with different modified phosphors and a better mechanical strength was obtained for the films with amino-coated phosphors comparing with SiO$_2$-coated particles [23]. To the best of our knowledge, there are no reports on the two-step modification of SAOED phosphor particles using silica and APTMS, or incorporating them in the NFC substrate in water medium for functional coatings. Hydrogen bonds and electrostatic attraction [24, 25] between the carboxylate groups (\(-\text{COO}^-\)) of ONFC and ammonium groups (\(-\text{NH}_3^+\)) of
modified SAOED phosphors under weakly acidic conditions may be the driving force for a good combination and ensure a high compatibility of homogeneous suspensions.

Meanwhile, more attention is being paid towards the development of dual-functional materials with both luminescence and intelligent properties [26], such as superhydrophobicity; the possession of such properties broadens the application of these materials in wet environments and improves their pollution-resistant performance [21]. Superhydrophobic surfaces with water contact angles (CAs) larger than 150° and slide angles lower than 10° have aroused considerable interest because of their excellent water repellency, easy-clean characteristics, and good antifouling characteristics [27, 28]. Furthermore, the CVD of fluorine-containing silanes [29] is widely accepted as an effective post-treatment way to prepare superhydrophobic surfaces with a combination of low surface energy and relatively high surface roughness.

In the current investigation, using a simple hydrophobic treatment, we intend to fabricate luminescent and superhydrophobic wood materials with long afterglow luminescence. Modified SAOED phosphors are used as functional fillers, while crosslinked nanocellulose is used as the reinforcing skeleton. A new silica modification method, based on TEOS and APTMS, is developed to improve the water resistance and surface activity of SAOED particles. The microstructured coating was fabricated using a spray of luminescent phosphors incorporated in nanocellulose suspensions and it was later modified by the chemical vapor deposition of fluorine-containing silanes. Furthermore, the luminescence and superhydrophobic properties of functional coatings containing modified SAOED and nanocellulose in different ratios are also analyzed.

2. Experimental section

2.1 Materials
The carboxylated nanocellulose (ONFC) suspension, prepared via TEMPO-mediated oxidation, was supplied by Hao Jia Nanocellulose Technology Co., Ltd., Tianjin, China. The nanofibers were 10–20 nm wide with an average length of 0.8–2.0 μm. The charge density was 1.5 meq/g. Tetraethyl orthosilicate (TEOS, 28%), (3-aminopropyl)trimethoxysilane (APTMS, 97%), oxalic acid (C$_2$H$_2$O$_4$), 1H,1H,2H,2H-perfluoroctyltrichlorosilane (CF$_3$(CF$_2$)$_5$(CH$_2$)$_2$SiCl$_3$, 97%) (FOTS), absolute ethanol (C$_2$H$_5$OH), 1,2,3,4-butane tetracarboxylic acid (BTCA, 99%), and sodium hypophosphite monohydrate (SHP, 98%) were analytical reagent (AR) and acquired from Sigma-Aldrich, Co. SHP employed in this study was used as catalyst for the reaction of BTCA with ONFC. Hydrochloric acid (HCl), sodium hydroxide (NaOH), and PVA ($M_w=1750$) were obtained from Sinopharm Chemical Reagent Co., Ltd. Beijing, China. SrAl$_2$O$_4$: Eu$^{2+}$, Dy$^{3+}$ (SAOED) phosphors were purchased from Lu Ming Luminous Technology Group Co., Ltd, Dalian, China. Commercial 9-ply poplar plywood was supplied by the Chinese Academy of Forestry (CAF), Beijing, China. The veneering plywood had a density of 510.0 kg/m$^3$ and a total thickness of 12.0 mm. Sample panels with dimensions of 40 mm × 25 mm were cut, sanded with 800 mesh sandpaper, ultrasonically cleaned using deionized water and ethanol, dried, and reserved for use.

2.2 Surface modification of SAOED phosphors

A dual-step method was used to modify the SAOED particles to obtain coated phosphors. TEOS was pre-used in the first step to form a SiO$_2$ coating and subsequently APTMS modification was carried out to alter the surface components of phosphors. Deionized water (4.2 mL) and 10 mL of TEOS were blended by stirring in a water bath at 60 °C. The molar ratio of TEOS to C$_2$H$_5$OH and water was theoretically calculated as 1:20:35 and the pH of the mixture was adjusted to 2.5 by using oxalic acid to form a homogeneous sol. Later, 2.0 g of SAOED were added into the prepared sol and...
stirred until the phosphors transformed into a gel-like precipitate. The precipitates were washed with ethanol and calcined at 500 °C for 2 h in an N₂ environment to obtain SiO₂ pre-modified particles (SiO₂@SAOED). Secondly, 1.0 g SiO₂@SAOED particles were blended with 178 μL of APTMS and 50 g of C₂H₅OH by sonication for 5 min and sealed to stir for another 8 h. Finally, the suspension was centrifuged and washed with ethanol three times and vacuum dried at 70 °C to obtain amino-modified phosphors; these modified particles are denoted as NH₂@SiO₂@SAOED.

2.3 Deposition of ONFC luminescent coatings on wood substrates

The ONFC aqueous suspension (0.3 wt%) was mixed with NH₂@SiO₂@SAOED modified phosphors at different mass ratios (ONFC/phosphor= 7/3, 6/4, 5/5, 4/6, and 3/7); the different mass fractions were based on the dry weight of ONFC. Later, 2.0 wt% BTCA and SHP (dry wt% of the ONFC) were added to the mixture as cross-linking modifiers to adjust the pH of the suspension (5.0–6.0). The suspensions were stirred and ultrasonically dispersed for 10 min. The PVA solution was prepared by dissolving 20 g of PVA in 500 mL of distilled water by stirring at 90 °C for 2 h. Subsequently, 2 mL of the PVA solution was uniformly paved on the cleaned wood surface and allowed to penetrate for 30 min at room temperature. ONFC luminescent suspensions were then sprayed onto the PVA pre-coated wood substrate and transferred to an oven (80 °C) for a set time period to remove excess moisture. Subsequently, samples with the pre-crosslinking coating were dried in a vacuum oven at 150 °C for 2 min to induce covalent crosslinking between ONFC and BTCA. The samples were then washed with ethanol to remove the SHP catalyst and dried in an oven at 60 °C for 2 h. At the end of this process, wood materials with a 20 μm-thick coating were obtained. Scheme 1. illustrates the SAOED surface modification and the preparation of luminescent and superhydrophobic dual-functional coatings for wood materials.
Scheme 1. Schematic illustration of SAOED surface modification and preparation of luminescent and superhydrophobic dual-functional coatings on wood materials.

2.4 Modification of luminescent coatings via FOTS-induced superhydrophobicity

The wood specimens deposited with the luminescent coatings were placed in a sealed container along with 0.6 g of FOTS, a low-energy modifier, in a smaller bottle; they were processed at 80 °C for 4 h to ensure adequate CVD reaction between ONFC and FOTS. Subsequently, all the samples were taken out and vacuum dried (80 °C) for 30 min to remove unreacted low-energy modifier from the surface and any by-products of the CVD process. Finally, dual-functional wood materials were obtained. For comparison, control wood samples without a luminescent coating and low-energy modifier were also fabricated using the same method.

2.5 Characterization and measurement

The morphologies were observed by scanning electron microscopy (SEM, Hitachi S-4800, Japan) at an acceleration voltage of 5.0 kV. The surface chemical composition was analyzed by energy dispersive X-ray analysis (EDS, JEM-2100). The average thickness of the coating layer on
phosphors was evaluated by transmission electron microscopy (TEM, Tecnai G2, FEI Corp., Hillsboro, USA). X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo Escalab 250xi system (Thermo Electron Scientific Instruments Co. Ltd., USA). The chemical composition was analyzed by Fourier transform infrared (FTIR) spectroscopy (Nicolet 6700, USA) in the wavenumber range of 1900 to 700 cm\(^{-1}\). The surface charge was evaluated with deionized water in the pH range of 4.0 to 10.0 using a Zetasizer Nano Series instrument (Nano ZS, Malvern Instruments Ltd., UK). Prior to testing, the pH of the suspensions was adjusted using HCl (0.01 mol/L) and NaOH (0.01 mol/L) at room temperature. The excitation and emission spectra were recorded using a spectrophotometer (Hitachi F-4500, Japan). The quality of the samples was theoretically assumed to be equal for the comparative analysis of spectral intensity. The afterglow decay curves were assessed using a fluorescence tester (excitation illumination: 1000 lx and excitation time: 15 min).

The surface colorimetric parameters of the wood specimens, including \(L^*\) (lightness index), \(a^*\) (red-green index), and \(b^*\) (yellow-blue index), were measured by a CR-400 Chroma meter (Konica Minolta Sensing, Inc., Japan). The color difference (\(\Delta E\)) was quantified to evaluate the apparent color effect because of the incorporation of modified SAOED. The formula to calculate the apparent color difference (\(\Delta E\)) is as follows,

\[
\Delta E = [(L^* - L_{0}^*)^2 + (a^* - a_{0}^*)^2 + (b^* - b_{0}^*)^2]^{1/2}
\]  

(1)

where \(L_{0}^*, a_{0}^*,\) and \(b_{0}^*\) are the values of the control wood sample and \(L^*, a^*,\) and \(b^*\) are the values corresponding to the functional wood materials after dual-functional coating.

The water contact angle (CA) and sliding angel (SA) were measured using a contact angle meter (Zhongchen JC200D System, China) to evaluate the wettability. A small droplet of distilled water (5 \(\mu\)L) was dropped for the CA test. The SAs were carried out using the provided sample
platform equipped with a precise angle gauge and the minimum tilt angle of a water droplet (10 μL) rolling off the sample was recorded as the SA value. The reported CA and SA values are the average values obtained from measurement at least five different positions. To characterize the self-cleaning performance, a few sawdust and dust powders with good wettability were naturally scattered on the surface of the sample, a slow trickle of deionized water (about 10 μL) was dropped on the dirty surface of the sample pre-set at an inclination angle of approximately 10°. A sandpaper abrasion test was carried out according to the method reported in literature [9]. As illustrated in Fig. 8a, the samples were placed against a sandpaper (1500 mesh) under an axial compressed load of 200 g (2 kPa), moved horizontally for 25 cm at a controlled speed of 1 cm/s. This entire process was denoted as one abrasion cycle.

3. Results and discussion

3.1 Microstructure and surface morphology of the modified phosphors

![Fig. 1. SEM and TEM micrographs of (a) uncoated SAOED, (b) SiO₂ coated SAOED phosphors (SiO₂@SAOED), and (c) APTMS coated SiO₂@SAOED phosphors (NH₂@SiO₂@SAOED). The]
insets show the corresponding EDS spectra.

The SEM micrographs along with the corresponding EDS results and TEM images of SAOED particles before and after modification are shown in Fig. 1. Compared to the smooth surface of untreated phosphors in Fig. 1(a), the morphology of the coated SAOED particles is obviously coarse (Fig. 1(b and c)). As shown in Fig. 1(b), a thin layer (20 nm thick) on the surface of the SAOED particles was clearly observed after silica modification, which was consistent with previously reported results [20]. In the case of APTMS-coated SiO₂@SAOED phosphors (Fig. 1c), the surface morphology was rougher compared to the SiO₂-coated phosphors (Fig. 1b). It was likely that the polymer segments of APTMS grafted on the surface of SiO₂@SAOED phosphors. Detailed EDS scans are shown in Fig. 1(b and c); energy dispersive peaks of Si and an additional signal of C were recorded in SiO₂@SAOED and NH₂@SiO₂@SAOED phosphors, respectively. The successful modification of SAOED particles was further confirmed by FTIR, XPS, and Zeta potential analyses.

Fig. 2. FTIR (a) and XPS wide scan spectra (b) of SiO₂@SAOED and NH₂@SiO₂@SAOED modified particles compared to uncoated SAOED phosphors.

The FTIR spectra of SiO₂-coated SAOED (SiO₂@SAOED), APTMS-coated SiO₂@SAOED (NH₂@SiO₂@SAOED), and uncoated particles (SAOED) are shown in Fig. 2(a). The characteristic absorption bands at 850, 770, and 642 cm⁻¹ are the stretching vibration modes of SrAl₂O₄; they can
also be seen in the spectrum of modified SAOED phosphors, which indicates that the main structure of SAOED was not affected by SiO$_2$ and APTMS modification. This observation is consistent with the XRD results (Fig. S1). Comparing to uncoated SAOED, the absorption bands near 3420 cm$^{-1}$ in the spectra of SiO$_2$@SAOED and NH$_2$@SiO$_2$@SAOED were significantly enhanced and can be attributed to the symmetric stretching of hydroxyl groups [30]. In the case of SiO$_2$@SAOED phosphors, the strong absorption band at 1079 cm$^{-1}$ is due to the asymmetric stretching of Si-O-Si groups, which implies that the coating observed in the TEM images consisted of SiO$_2$, which was successfully coated on the surface of SAOED particles. In the spectrum of NH$_2$@SiO$_2$@SAOED, besides the stretching vibrations of Si-O-Si groups at 1087 cm$^{-1}$ and 1050 cm$^{-1}$, the coated phosphors exhibited an additional absorption band at 2926 cm$^{-1}$ [30] corresponding to the stretching vibration of -C-H [31]. This result indicated that APTMS reacted with the hydroxyl groups of the SiO$_2$@SAOED particles and -NH$_2$ groups were successfully grafted onto the surface of phosphor particles. The successful grafting of SiO$_2$ and APTMS onto the phosphor to form particles with a core-shell structure was further confirmed by XPS (Fig. 2b). The peaks at binding energies of O (1s, 532.8 eV), Si (2s, 154.6 eV; 2p, 103.4 eV) in the case of SiO$_2$@SAOED and additional peaks at binding energies of N (1s, 401.6 eV) and C (1s, 284.8 eV) for NH$_2$@SiO$_2$@SAOED phosphors can be clearly seen. These results were consistent with previous report on SiO$_2$ encapsulated graphene oxide composites [32]. In addition, because the detection depth of surface element in XPS inspection is less than 10 nm, in the case of SiO$_2$@SAOED and NH$_2$@SiO$_2$@SAOED phosphors (Fig. 2b), the absence of Sr (3s, 358.6 ev), Sr (3p, 279.4 ev), Sr (3d, 140.8 ev) and Al (2p, 74.1 ev) belonging to SAOED particles also indicates that silica and APTMS layers uniformly coated on the outer shell of SAOED phosphors. Furthermore, the reverse Zeta potential values of the modified phosphors (Fig.
S2), shifted from −25.3 mV to +19.6 mV after APTMS modification, which also proves that APTMS was successfully grafted on silica-modified particles.

3.2 Microstructure of the modified SAOED/ONFC coating on wood surface

Fig. 3. Micrographs of wood substrate, ONFC and functional coatings: (a) Pristine surface of wood, (b) TEM image of ONFC, (c) Surface morphology of PVA coating on wood, and SEM images of wood surfaces decorated with coatings of different mass ratio of ONFC/phosphors (d) 7/3, (e) 6/4, (f) 5/5, (g) 4/6, and (h) 3/7. (i) Cross-sectional morphology of coatings with PVA on wood substrate.

Fig. 4. Schematic model of the cross-section of ONFC coating films containing different amount of modified SAOED phosphors.
As shown in Fig. 3(a), the surface of the wood substrate contained a large number of natural micro-pores and cracks caused by the veneer peeling process. After pre-processing with the PVA coating, the original micro-grooved structures of the wood surface were observed to be filled by a continuous adhesive layer (Fig. 3c). When further treated using ONFC/modified SAOED micro-nanocomposites of different mass ratios (7/3, 6/4, 5/5, 4/6, and 3/7), a particulate morphology was developed on the wood surface (Fig. 3(d–h)). The inset high-magnification image revealed dual-scale roughness patterns consisting of modified SAOED particles and nanocellulose were randomly superimposed on the micro-nano structures formed by uniformly dispersed luminescent particles. Upon increasing the content of modified SAOED, the surface of the three-dimensional network of ONFC/NH\textsubscript{2}@SiO\textsubscript{2}@SAOED composites changed to be rougher (Fig. 4). The primary reason for this observation can be attributed to the electrostatic adsorption [24] of partial nanocellulose (negative charge) and amino-modified SAOED particles (positive charge) before spraying (Fig. S3); irregular micro-nanostructures were formed as a result of nanocellulose attaching onto the rough surface of modified SAOED particles. The relatively uneven spraying process might be another reason for this result [9]. As the ONFC/phosphors suspension comes out of the nozzle, nanofibers in the suspension are sheared to form small mist droplets and shrinkage occurred due to the removal of moisture, resulting in irregular roughness after the coating process. Fig. 3(i) shows the cross-sectional morphology of the treated samples with ONFC luminescent coatings and PVA adhesive. The PVA adhesive played a significant role as a conjunction material between the interface of the wood substrate and ONFC luminescent coating. As depicted in Fig. 3(i), a part of the cellulose fibers and modified particles were embedded in the PVA adhesive layer. The modified SAOED particles were fixed well in the nanocellulose skeleton due to electrostatic adsorption and physical
cladding of nanofibers. Such good interface bonding performance is expected to provide strong adhesion and stability in luminescent hybrid coatings.

![FTIR spectra of ONFC coating layers before and after modification.](image)

**Fig. 5.** FTIR spectra of ONFC coating layers before and after modification.

The FTIR spectra of nanocellulose coatings before and after modification are shown in Fig. 5. The characteristic absorption peak near 1600 cm\(^{-1}\) in all the ONFC coatings corresponded to the C=O stretching frequency of carboxyl groups from nanocellulose or BTCA in its acidic form [33, 34]. The new absorption peak at 1052 cm\(^{-1}\) was assigned to the stretching vibration of Si-O, which was formed due to the reaction between FOTS and the \(-\text{OH}\) groups on the surface of nanocellulose. The absorption peaks at 1235 cm\(^{-1}\) and 1146 cm\(^{-1}\) in the spectrum of FOTS modified ONFC are assigned to the stretching vibration of C-F of the low-energy modifier. These results were consistent with previous report in our group on FOTS-modified nanocellulose spray coatings [9] and affirmed that CVD is an effective method to graft fluoride groups on the surface of nanocellulose. Furthermore, a new absorption appeared at 1715 cm\(^{-1}\) corresponding to the C=O stretching of ester carbonyl groups, which is consistent with that of reported literature [35]. These groups are formed as a result of the cross-linking reaction between nanocellulose and BTCA via transesterification.
between the –OH groups of cellulose and the –COOH groups of BTCA [35]. The formation of cellulose/polymer esters is significant and could potentially increase the toughness of dual-functional crosslinking cellulose coatings [36]. It can be also inferred that the hydrophobic wood surface consisted of a combination of coarse-structured nanocellulose, modified phosphors in the coating, and a water repellent surface modification formed by the FOTS low-energy modifier.

3.3 Photoluminescence and optical performance

![Fig. 6](image-url)

**Fig. 6.** Photoluminescence of phosphors and functional coating films with modified phosphors: (a) Emission and (b) excitation spectra of phosphor particles and ONFC functional coatings (ONFC/phosphor= 5/5). (c) CIE color coordinates of phosphors before and after modification and ONFC coating with NH$_2$@Si$_2$O$_5$@SAOED at a 5/5 mass ratio, (d) Decay curves of wood materials with composite coatings of different mass ratios (inset: digital pictures of wood in 2 min under dark). (e) Photographs of modified SADOED dispersed in ONFC and (f) light transparency of coatings with particles of different mass ratios. (g) Surface status of coatings without PVA adhesion in daylight and ultraviolet light and (h) a luminescent logo in daylight (left) and dark (right).

Fig. 6 (a, b) show the excitation and emission spectra of the modified SADOED particles and the hybrid ONFC coatings (NFC/phosphor= 5/5) before and after FOTS low-energy modification. As shown in Fig. 6(a), a single peak at about 512 nm was observed under the excitation of 363 nm for
both SAOED phosphors and composite coatings due to the characteristic 4f^65d^1 to 4f^7 transition of Eu^{2+} ions [37]. More precisely, the intensities of the emission spectra were 3.46% and 9.71% lower for SiO_2@SAOED and NH_2@SiO_2@SAOED, respectively, compared to that of the SAOED sample. This can be attributed to the effects of light scattering and reflection due to the SiO_2 coating layer, APTMS segments on the outer surface of the phosphors without destruction of the crystal structure of SrAl_2O_4 (Fig. S1). These results are in good agreement with previous reports [12], which showed that macromolecule structures might reduce the photoluminescence intensity of phosphor particles. For ONFC hybrid coatings (Fig. 6a), the emission spectra of the films were basically consistent with those of the coated phosphors and showed a slight blue shift (2.8 nm) at around 512 nm compared to the modified SAOED particles. This is probably due to the variation in the local microenvironment [38, 39], including the effect of nanocellulose, BTCA cross-linking, and the additional introduction of a little moisture during the preparation of coating films.

Compared to the spectrum of modified particles, the emission spectra of dual-functional films showed a slight blue shift (2.8 nm). However, the luminous color was basically the same and still belonged to the green category (Fig. 6c). As demonstrated in Fig. 6(b), the continuous wide band centered at 363 nm, which is typical of the 4f^7-transition of Eu^{2+} ions, slightly narrowed and showed a blue shift of 3.2 nm for the hybrid coatings. This result is consistent with the excitation spectra and also indicated that coating films could be effectively excited in the ultraviolet to visible light. Fig. 6(d) presents the decay curves of the composite coatings with amino-modified particles at different mass ratios. All the luminescent coatings exhibited a rapid decay in the first 2 min and a subsequent slow decay [21, 38]. Even though the initial afterglow brightness of the coating films increased gradually with an increase in the addition of phosphors, this tendency was not obvious in the
subsequent period, especially for the coatings containing phosphor ratios greater than 5/5. The brightness values of the luminescent films containing ONFC/phosphor at ratios of 5/5, 4/6, and 3/7 were 315.8, 374.8, and 417.4 mcd/m², respectively, after 2 min. This is mainly ascribed to the different depths of trap levels in the luminescent coatings [21]. Additionally, only the control ONFC coating without luminescent particles showed no afterglow performance under the same test conditions, as shown in Fig. 6(d). In order to further demonstrate the water resistance and surface activity of the modified particles in ONFC suspensions, different proportions of modified SAOED and nanocellulose (ONFC/phosphor) were blended and homogeneous suspensions were formed. Meanwhile, all the diffraction peaks of crystalline ONFC (2θ=16.5° and 22.5°) and SrAl₂O₄ were observed from the composite films (Fig. S4). Furthermore, the translucence of the corresponding hybrid coating films was evaluated; it exhibited a small decline with an increase in the addition of phosphors, but still showed good translucency with visible alphabets under the composite films (Fig. 6f). The primary reason for this observation was the formation of relatively homogeneous dispersions of modified SAOED particles in the nanocellulose skeleton (Fig. S5). On the other hand, light can be transmitted through the highly crystalline nanocellulose [25] and reflected between the gaps of SAOED particles. Fig. 6(g) demonstrates the surface status of the debonding failure of coatings without PVA pre-adhesion. Furthermore, with PVA pre-treatment on wood substrate, a luminescent logo (Fig. 6h) was prepared to exhibit its potential applications. As shown in Fig. 7, ONFC was partly located between the interface of SAOED phosphors and PVA substrate because of its pristine amphipathic property. Meanwhile, hydrogen bonding with PVA [40] played a crucial role on the interface adhesive performance and eliminated debonding and warping in luminescent ONFC films. Furthermore, the formation of cellulose ester between ONFC and BTCA reduced the number
of active hydroxyl groups and enhanced the toughness of the functional coatings [35].

**Fig. 7.** Schematic illustration of the bridging mechanism of the PVA pre-treated layer at the interface of the ONFC/\(\text{NH}_2@\text{SiO}_2@\text{SAOED}\) coating films and wood substrate before FOTS modification.

In order to further determine the color effect of the hybrid coatings on the wood surface, the apparent color difference (\(\Delta E\)) and colorimetric parameters of the functional wood materials with different contents of \(\text{NH}_2@\text{SiO}_2@\text{SAOED}\) phosphors are shown in Fig. 8. As shown in Fig. 8(a), the surface luminosity (\(L^*\)) of functional wood exhibited a slight increase with an increase in the phosphor content. It was mainly because the color of the SAOED particles itself was yellow-white, which was a little brighter than the wood surface, especially after pre-treatment on the poplar wood substrate with the PVA transparent coating. The \(a^*\) and \(b^*\) values in Fig. 8(b, c) demonstrate a similar decline with an increase in the content of modified SAOED, which indicated that the color of the coating surface slightly shifted to the blue-green direction and therefore obscured the light-yellow color of wood substrate. Correspondingly, the color difference (\(\Delta E\)) exhibited a small increase from 4.80 to 9.56 as the addition ratio of the phosphors rose from 0.3 to 0.7, which was far less than the value obtained with coating of thermochromic microcapsules [4]. This methodology also led to a smaller color impact on the wood surface. Moreover, both the color parameters and \(\Delta E\)
showed a linear positive correlation with increasing phosphor content, which demonstrated that the dual-functional coatings exerted a small effect on the wood color; it might be further slightly adjusted by changing the content of modified SAOED particles.

![Graphs showing correlations](image)

**Fig. 8.** Apparent color difference of dual-functional wood materials after hybrid coatings with different contents of modified SAOED: (a) lightness index, (b) red-green index, (c) yellow-blue index, (d) color difference ($\Delta E$). The addition ratio of modified SAOED refers to the proportion of phosphors with respect to the dry weight of total ONFC and modified particles.

### 3.4 Hydrophobicity and self-cleaning properties

Water CAs and SAs were carried out to evaluate the wettability of the ONFC hybrid coatings on wood substrates. As shown in Fig. 9(a), the CA value of the functional wood surface increased initially from 142° to 153° and then declined sharply to 143°; this was firstly due to the increase in the surface roughness of the composite coatings with an increase in the content of modified SAOED particles (Fig. 3 (d–h)). When the mass ratio of ONFC/phosphor increased from 4/6 to 3/7, there
were not enough nanofibers to cover the phosphor surface and a number of cracks occurred between SAOED particles due to the shortage of nanocellulose skeleton (Fig. 4). However, all the coatings with nanocellulose and modified particles exhibited high water repellency with a CA value more than 140°. Furthermore, good SA values (lower than 10°) were obtained and water droplets were also found to roll off the surface of the functional coatings with an increase in the phosphor addition. Combined with the luminescent properties, wood materials with dual-functional hybrid coatings at a 5/5 mass ratio also exhibit excellent superhydrophobicity after FOTS low-energy modification.

Fig. 9. Wettability of CAs and SAs, sandpaper abrasion resistance, and self-cleaning performance for the functional materials: (a) CAs and SAs of ONFC coatings on wood with modified SAOED at different mass ratios (ONFC/phosphor), (b) Sandpaper abrasion test and an illustration of abrasion-induced damage of wood with PVA coating, (c) SEM images of the wood surface with ONFC hybrid coatings at a 5/5 mass ratio after 6 abrasion cycles, (d) CAs and SAs of wood with ONFC coatings at a mass ratio of 5/5. Self-cleaning process (left) and optical photographs of water droplets (mixed with a dark blue ink) (right) on the wood surface with (e) and without (f) functional coatings.

Wood materials with functional coating usually need good abrasion resistance in practical applications; sandpaper abrasion test is a simple and effective method to evaluate the abrasion
durability of superhydrophobic coatings [7]. Under an applied load of 200 g (2 kPa), wood samples were moved against a sandpaper (1500 mesh) for 25 cm at a speed of 1 cm/s (Fig. 9b). This process was denoted as one abrasion cycle. Fig. 9(b) also illustrates the partial mechanical removal of coatings from the wood surface. Fig. 9(d) illustrates the CAs and SAs after each abrasion cycle of the wood material with ONFC hybrid coating at a 5/5 mass ratio. It was shown that the coated wood materials still maintain superhydrophobic properties with CAs around 150°, and SAs lower than 8.5°, after being processed for 5 abrasion cycles. What’s more, the CAs and abrasion performance of the as-prepared ONFC/NH$_2$@SiO$_2$@SAOED hybrid coatings were a little better than the results of Chang et al for superhydrophobic wood surface using modified silica nanoparticles [41]. On one hand, this is mainly due to the good adhesion of PVA at the interface of the wood substrate and ONFC coating. On the other hand, nanocellulose esters were generated via BTCA cross-linking, as shown in Fig. 5, which can also withstand the abrasion damage. It is observed that the microstructures with dual-scale surface roughness were still remained on the wood materials after 6 abrasion cycles (Fig. 9c) and they exhibited a good luminous performance in water (Fig. S6).

To characterize the self-cleaning property of dual-functional wood materials, a slow trickle of deionized water was dropped on the dirty surface of the coated sample pre-set at an inclination angle of 10°, as shown in Fig. 9(e and f, left). After spraying by ONFC luminescent coatings and being deposited by FOTS low-energy modification, the wood materials proved to be superhydrophobic and luminescent simultaneously. Water droplets rapidly rolled off on the surface and took away the dirt from the surface (Video S1), while the pristine wood was hydrophilic and water droplets remained on the surface in large blocks with dirt inside (Video S2); this observation is consistent with previous reports [28] and can be confirmed by the digital images of dropping and wiping ink drops on wood
surfaces, as shown in Fig. 9 (e and f, right). The surface with a superhydrophobic coating was completely clean after water dropping and wiping (Fig. 9e), while the surface without any coating (Fig. 9f, right) did not show any luminescence or self-cleaning performance.

The environmental stability and durability of the dual-functional surfaces were also investigated at 60 °C for 7 days (Table S1) or immersed in running water for 2 days (Table S2). The water CAs and SAs of wood materials with hybrid coatings hardly changed as a result of these treatments, indicating their good stability. Furthermore, the approach presented here also provide an effective way for applications on other substrates and require further demonstration in future work.

4. Conclusions

In summary, a dual-functional coating was successfully fabricated on a PVA-pretreated wood surface by an easy and efficient two-step process combining suspension spraying and chemical vapor deposition. The SrAl₂O₄: Eu²⁺, Dy³⁺ phosphors after SiO₂ and APTMS-coated modification yielded a complete nano-scaled layer on the surface of the phosphors and formed relatively stable and homogeneous suspension with nanocellulose substrate without destroying the crystal structure. The introduction of modified phosphors with a soft ONFC skeleton made the wood surface a long afterglow property and created adequate surface roughness combining with nanocellulose for low-energy modification. The resulting dual-functional coatings on wood also displayed good self-cleaning performance as well as a remarkable tolerance against sandpaper abrasion-induced mechanical damage. Importantly, the hybrid coatings showed good translucency and had less effect on the apparent color of the wood substrate after coating process. Overall, wood materials with a long afterglow luminescence and superhydrophobicity can find potential application in fields, such as interior decoration, intelligent ceilings, night indicators, or luminous logos and labels.
Acknowledgements

This work was supported by the National Nonprofit Institute Research Grant of CAF (CAFYBB2017ZX003) and USDA National Institute of Food and Agriculture (Hatch project 1012359). Thanks for the financial support of China Scholarship Council (CSC) Program. We also greatly appreciate the associate professor of Xiaoqing Wang and M. E. Lizhuo Kong at CAF for their kindly help on superhydrophobic tests, and Dr. Yun Lu at CAF for her valuable suggestions for enhancing this paper.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version.

References


[21] J. Li, Y. Zhao, M. Ge, S. Fu, T. Lin, Superhydrophobic and luminescent cotton fabrics prepared by dip-coating of APTMS modified $\text{SrAl}_2\text{O}_4$: Eu$^{2+}$, Dy$^{3+}$ particles in the presence of SU8 and fluorinated alkyl silane, J. Rare Earth 34 (2016) 653-660.


[38] J. Li, J. Wang, Y. Yu, Y. Zhu, M. Ge, Preparation and luminescence properties of rare-earth doped fiber with spectral blue-shift: \(\text{SrAl}_2\text{O}_4; \text{Eu}^{2+}, \text{Dy}^{3+}\) phosphors/ triarylsulphonium hexafluoroantimonate based on polypropylene substrate, J. Rare Earth 35 (2017) 530-535.


Graphical Abstract

The SrAl$_2$O$_4$: Eu$^{2+}$, Dy$^{3+}$ particles after SiO$_2$ and APTMS-coated modification yielded a nano-scaled layer with amine groups and formed a stable suspension with ONFC by electrostatic adsorption and hydrogen bond without destroying their crystal structures. The modified particles with a cross-linked ONFC/BTCA skeleton made the surface a long afterglow property and created adequate surface roughness for FOTS modification. The dual-functional hybrid coatings showed good translucency and had less effect on the apparent color of the wood after coating process.

Size (5×11 cm)
**Highlights**

- TEOS and APTMS modification improve water resistance and surface activity of phosphors.
- Functional coatings were fabricated by ONFC/BTCA/phosphor spraying and CVD process.
- The hybrid coatings with good luminescence, abrasive resistance, superhydrophobicity and self-cleaning properties.
文献由“学霸图书馆-文献云下载”收集自网络，仅供学习交流使用。

学霸图书馆（www.xuebalib.com）是一个“整合众多图书馆数据库资源，提供一站式文献检索和下载服务”的24小时在线不限IP图书馆。

图书馆致力于便利、促进学习与科研，提供最强文献下载服务。

图书馆导航：
图书馆首页      文献云下载      图书馆入口      外文数据库大全      疑难文献辅助工具