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Photoluminescent spray-coated paper sheet: Write-in-the-dark

Tawfik A. Khattab[a,*], Hussein Abou-Yousef[b], Samir Kamel[b]

[a] Dyeing, Printing and Auxiliaries Department, National Research Centre, Cairo 12622, Egypt
[b] Cellulose and Paper Department, National Research Centre, Cairo 12622, Egypt

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ABSTRACT

A simple formulation of an organic-inorganic composite for spray-coating was adopted toward photoluminescent paper sheets. The coating composite layer was composed of a synthetic organic adhesive binder mixed with an inorganic lanthanide-doped strontium aluminate pigment. Such pigment-binder formula was applied effectively onto paper sheets via spray-coating followed by thermal fixation. The applied transparent photoluminescent coated layer exhibited optimal excitation wavelength at 365 nm and emission band at 517 nm resulting in phosphorescence of the paper surface with a substantial development of green-yellow, bright white, turquoise, and off-white colors as indicated by CIE Lab color coordinates under ultraviolet irradiation. The mechanical, decay and lifetime properties of the composite photoluminescent coated layer were described. The standard techniques of morphological properties and elemental analysis were explored by scanning electron microscope (SEM), wavelength dispersive X-ray fluorescence (WDXRF), and energy dispersive X-ray spectroscopic analysis (EDX). The spray-coated paper sheets demonstrated good fastness to light and reversible phosphorescence without fatigue.

1. Introduction

Cellulose is a highly abundant natural organic polymer, which is significant in the manufacture of different goods such as textile fibers and paper (Reddy & Yang, 2009; Khalil, Bhat, & Yusra, 2012). In industry, paper is manufactured with a broad variety of properties according to the end use application such as banknote, security paper, information storage, communication, packaging, electrical insulator, and filtration (Abou-Yousef, Khattab, Youssef, Al-Balakocy, & Kamel, 2017; Boufi et al., 2016; Elegir, Kindl, Sadocco, & Orlandi, 2008; Hill, Le, Darveniza, & Saha, 1995; Shen, Song, Qian, & Yang, 2010). Long-lasting photoluminescence is an attractive phenomenon in materials which is able to glow-in-the-dark upon the removal of an excitation source with UV or visible light. The excitation energy is stored by the long-lasting luminescent material and then progressively released, after the excitation source is turned off, over some minutes or even hours via slow de-trapping and radiative recombination of carriers at a particular wavelength (Bessiere et al., 2014; Jia, Wang, Kolk, & Yen, 2002; Xu et al., 2013). Long-lasting luminescent materials such as dysprosium and europium doped strontium aluminate have been employed in a variety of applications such as emergency signs during blackout circumstances, safety protective garments, night work goods, and decoration purposes (Han et al., 2008; Kshatri & Khare, 2014; Sahu, Bisen, Brahme, Tamrakar, & Shrivastava, 2015; Khattab, Rehan, & Hamouda, 2018). Various long-lasting photoluminescent substances have been developed to afford various phosphors of different colors such as $CaAl_2O_4$:Eu^{2+}/Nd^{3+} for blue, $SrAl_2O_4$:Eu^{2+}/Dy^{3+} for green, and Y_2O_2S:Mg^{2+}/Ti^{4+} for red color emitters (Yamamoto & Matsuzawa, 1997; Kang, Liu, Chang, & Lee, 2003; Rojas-Hernandez, Rubio-Marcos, Rodriguez, & Fernandez, 2018). Strontium aluminate-based long-lasting luminescent materials are the most well-known phosphors due to their non-radioactivity, thermal stability, high quantum efficiency, and high chemical stability (Damrauer, 2004; Yamazaki & Kojima, 2004; Zeng et al., 2011; Sun, Pan, Piao, & Sun, 2014; Komatsu, Nakamura, Kato, Ohshio, & Saitoh, 2015; Guo et al., 2016).

Recently, the spray coating approach has been presented as a new, simple, cost-effective, and non-contact method to coat paper with high speed, negligible agglomeration, and at a reduced amount of excess coating paste aerosol (Moridi, Hassani-Gangaraj, Guagliano, & Dao, 2014; Pham et al., 2010). To the best of our knowledge, the simple production of photoluminescent paper sheets employing spray-coating of only an aqueous binder and lanthanide-doped strontium aluminate phosphor has not been described yet. Herein, we develop phosphorescent paper sheets which can function as excellent hosts for luminescent pigments. A dysprosium and europium doped strontium aluminate phosphor was applied in a luminescent layer on paper sheets. Such

* Corresponding author.
E-mail address: tkhattab@kent.edu (T.A. Khattab).

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phosphorescent cellulose sheets are readily visible and writable at night without need for external light. Morphological analysis, elemental composition, mechanical performance, fastness to light, and luminescence properties of the spray-coated paper sheets were discussed based on a number of measurements.

2. Experimental details

2.1. Materials and methods

All the raw materials employed in the synthesis of dysprosium and europium doped strontium aluminate phosphor were supplied by Sinopharm Chemical Reagent Co. Ltd. Printofix Binder MTB-01 liquid (binding agent based on self-crosslinkable acrylate copolymer, Clariant). Wahttman cellulose filter sheets with 240 mm diameter qualitative filters, 180 μm Thickness, 87 g/m^2 basis weight, and 11 μm pore size; were purchased from Sigma-Aldrich and used as a model. This type of paper sheets has an off-white color.

2.2. Apparatus and measurements

Both of emission and excitation of the coated paper sheets were recorded on a Spectrofluorometer JASCO FP-6500, Japan; equipped with phosphorescence accessory for phosphorescence lifetime measurements. All phosphorescence measurements were performed at room temperature and at the same geometrical conditions. The light source was Xenon Arc Lamp 150 W with slit bandwidth 5 nm for both of excitation and emission monochromators. The samples were irradiated with UV radiation source at 365 nm using the instrument source. The ultraviolet light lamp (λ = 365 nm) with a power of 6 W was used as ultraviolet irradiation source. Before and after exposure to ultraviolet irradiation, the color characteristics of the coated cellulose papers were recorded on a Texflash ACS/Datacolor with a Spectraflash 600 spectrophotometer. The color changes were expressed using the colorimetric parameters (L^*, a^*, b^*, *K/S*, and absorption spectra) which were measured on an Ultra Scan PRO spectrophotometer (Hunter Lab, United States) with a D65 illuminant and a 10° standard observer. Fourier-transform infrared spectra (FTIR) were measured on an FTIR spectrophotometer (Nexus 670, Nicolet, United States) in the range of 4000–400 cm^{-1} with a spectral resolution of 4.0 cm^{-1}. The elemental analysis of the coated film was studied by Wavelength-Dispersive X-Ray Fluorescence Spectrometry (WDXRF) Axios advanced, Sequential WDXRF Spectrometer. The surface morphology and elemental analysis of the coated layer was examined by scanning electron microscope (SEM) on a Quanta FEG-250 (Czech Republic) cooped with Energy Dispersive X-ray Spectroscopy (TEAM-EDX Model). The EDX mapping measurements were recorded at 20 kV accelerating voltage and 21 mm working distance. Tensile strength, Young's modulus and strain percentage of paper sheets were recorded by Zwick Universal Test Instrument, equipped with a load Cell of 100 N. The samples were examined employing a crosshead speed 2 mm/min. At least five reads were recorded for each sample and the average was reported. The thermogravimetric analysis (TGA) was carried out on simultaneous thermogravimetric analyzer (Perkin Elmer thermal gravimetric analyzer, TGA7, the heating rate was 10 °C min^{-1}, USA). Colorfastness to light was carried out on a 'Weather-o-meter' (Atlas Electric Devices Co., United States) using AATCC standard procedure. The photographs of the coated paper sheets before and after UV-irradiation were taken by a Canon Power Shot A710 IS digital camera.

2.3. Synthesis of phosphor

The lanthanide-doped strontium aluminate ($SrAl_2O_4$:Eu^{2+},Dy^{3+}) was prepared according to literature procedure employing the high-temperature solid-state reaction (Khattab et al., 2018; Tang, Zhang, Zhang, Huang, & Lin, 2000). The $SrAl_2O_4$:Eu^{2+},Dy^{3+} complex was prepared by mixing strontium(II) carbonate ($SrCO_3$), aluminum(III) oxide (Al_2O_3), europium(III) oxide (Eu_2O_3), and dysprosium(III) oxide (Dy_2O_3), in the molar ratio Sr:Al:Eu:Dy = 1:2:0.01:0.02, and adding 5% boric acid (H_3BO_3; molar ratio 0.2). The mixture was then suspended in absolute ethanol (100 ml), followed by ultrasonic dispersion with 25 kHz for 20 min to acquire a homogeneous mixing. The produced mixture was dried at 90 °C for 24 h, grinded in a planetary high-energy ball-mill over 2 h and sintered at 1300 °C for 3 h with a heating rate of 10 °C/min in a reducing atmosphere of carbon power. The sintered product was re-milled and sieved to obtain the desired pigment activated by Eu^{2+}, Dy^{3+}.

2.4. Preparation of luminescent paper by spray-coating

The pigment-binder stock formula was prepared by homogeneous dispersion of ammonium hydroxide (NH_4OH; 0.05 wt%), diammonium phosphate ($(NH_4)_2HPO_4$; 0.05 wt%) and binder (20 wt%) in distilled water (79.9 wt%). The formula was then stirred using a magnetic stirrer for 15 min to allow full dispersion. Different formulations were prepared by adding different amounts of the pigment phosphor $SrAl_2O_4$:Eu^{2+},Dy^{3+} (conc. 0.1, 1–4 wt% which were abbreviated as Cell-0.1, Cell-1, Cell-2, Cell-3, and Cell-4 respectively) to the mixture with stirring for 30 min. We also included in this study the cellulose spray-coated by binder additive only and without pigment (Cell-B). All formulations were then applied to paper sheet using the spray-coating method. The final coated papers were left for 30 min to be air-dried at ambient conditions followed by thermofixation at 150 °C for 4 min in a thermostatic oven (Werner Mathis Co., Switzerland). The pristine cellulose (Cell-0) without binder or pigment was included in the study for comparison.

2.5. Reversibility and technical performance

The coated paper sheets were exposed to ultraviolet irradiation for 5 min and then kept in dark for 60 min to fade back to their pristine unexposed state. This ultraviolet irradiation and fading cycle was repeated over 15 cycles. The phosphorescence emission spectra were recorded after each cycle. In order to study the reversibility of phosphorescence emission spectra, the ultraviolet lamp (λ = 365 nm and a power of 6 W) was placed 4 cm above the paper sheet and the measurements were performed at ambient conditions.

2.6. Colorimetric measurements and fastness to light

The color of coated paper sheets before and after exposure to ultraviolet light was recorded by a Chroma meter Konica Minolta CR-400 with a D65 illuminant (daylight, color temperature 6504 K), a 2° standard observer function and an 8 mm diameter illumination area. The colorimetric measurements were recorded using color coordinates (L^*, a^*, b^*), which is a three dimensional color system, where L* (lightness), a^* (red/green) and b^* (yellow/blue); L^* supposes values from zero (darkest black) to 100 (brightest white), a^* indicates red when it is positive and green when negative, while b^* indicates yellow when it is positive and blue when negative (Khattab et al., 2017). In this test, paper sheets were exposed to ultraviolet light for 3 min using an ultraviolet lamp (λ = 365 nm and a power of 6 W) placed 4 cm above. The UV lamp was removed and the colorimetric values were recorded directly. The color strength (*K/S*) was assessed by high reflectance approach and Kobelka Munk equation. The colorfastness to light was tested according to ISO standard methods (Khattab, Haggag, Elnagdi, Abdelrahman, & Abdelmoez Aly, 2016, 2018).