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Warm-toned, color-tunable, and highly emissive long lasting phosphorescent composite: PMMA/RECC@$SrAl_2O_4$:Eu^{2+}, Dy^{3+}

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ABSTRACT

Color-tuned long lasting phosphorescent composite PMMA/RECC@$SrAl_2O_4$:Eu^{2+},Dy^{3+} (SAOED) with warm-toned phosphorescent color and excellent afterglow properties were prepared by coating PMMA and a red light-emitting coumarin fluorescent dye color converter (RECC) and PMMA on the surface of the green emitting long lasting phosphor SAOED. X-ray diffraction (XRD) patterns show that the crystal lattice of the PMMA/RECC@SAOED samples are identical to the uncoated SAOED. The photoluminescence (PL) emission spectra of the PMMA/RECC@SAOED consist of two broad band ranging from 450 to 575 nm and 576–700 nm, and the spectra intensity in the range of 576–700 nm increased gradually with the increment of RECC. The CIE chromaticity coordinates and the luminescence images of the PMMA/RECC@SAOED samples indicate that the emitting color of PMMA/RECC@SAOED is composed of the phosphorescent color of SAOED and the fluorescent color of RECC, and it exhibits a reddish emitting color with color purity of 0.8726 when the concentration of the RECC was added to 0.9%. Even though the coating layer of RECC has a negative influence on the quantum yield (QY) and afterglow brightness of PMMA/RECC@SAOED, the afterglow curves of PMMA/RECC@SAOED are similar in shape with the uncoated SAOED, both of them are fitted well with a third-order exponential equation.

1. Introduction

Long lasting phosphors (LLPs) are a special kind of environmentally friendly PL material, which can absorb and store light energy and release it in the form of persistent, visible luminescence, especially in a dark environment [1–3]. The luminescence process is absolutely recyclable with no irradiation. Since the first report of the green light-emitting LLP $SrAl_2O_4$:Eu^{2+},Dy^{3+} (SAOED) discovered by Matsuzawa [4], persistent luminescent materials have drawn a great deal of attention because of their wide application prospect in the field of emergency illuminations, optical displays, luminescent paints and luminous textiles [5–8]. Usually, the application of the long-lasting luminescent materials in these fields have to satisfy several basic requirements, such as strong brightness, long luminescence duration and sub-micron particle size. However, it is hard to prepare long-lasting luminescent materials with sub-micron particle size using the present synthesis method, no matter the traditional solid-state method, sol-gel method or the new hydrothermal, co-precipitation, and combustion methods [9–12]. Therefore, the pre-prepared luminescent particles need to be milled to sub-micron size to satisfy the industrial application requirements. Nevertheless, the mechanical milling process would damage the crystallite structure of the luminescent particle, which would do significantly affect its luminescence brightness and duration time, and restrict its commercial application [13].

So far, the most successful commercialized LLP is the rare earth Eu^{2+} and Dy^{3+} ions doped $SrAl_2O_4$:Eu^{2+},Dy^{3+} (SAOED) LLP synthesized by solid-state method, which still shows a relative high luminescence intensity and long afterglow duration time even though after being milled to sub-micron size compared with other LLPs. However, as a result of the characteristic $4f\,^{6}5d^{1}$ to $4f^{7}$ transition of the Eu^{2+} ion, usually the phosphorescent color of the SAOED LLP is restricted to the cool toned color of green, which is too monotonous and limits the application of LLPs in fields where multi-colored fluorescence colors were required [14,15]. Furthermore, luminescent materials with multi-colored emitting color usually are more attractive to people than monotonous cool toned luminescent materials. So the incentive to broaden the luminescent color of the LLPs is promising and thus has attracted intensive research interests. After decades of efforts, several kinds of LLPs with warm tone emitting color have been reported, including the orange-emitting LLPs $Sr_{2.96-x}Ba_xSiO_5$: Eu^{2+} prepared by Xu et al. [16] in 2014; the orange-yellow-emitting Li_2SrSiO_4:Eu^{2+}, Dy^{3+} LLPs reported by Cheng et al. [17] in 2015; and the red long persistent

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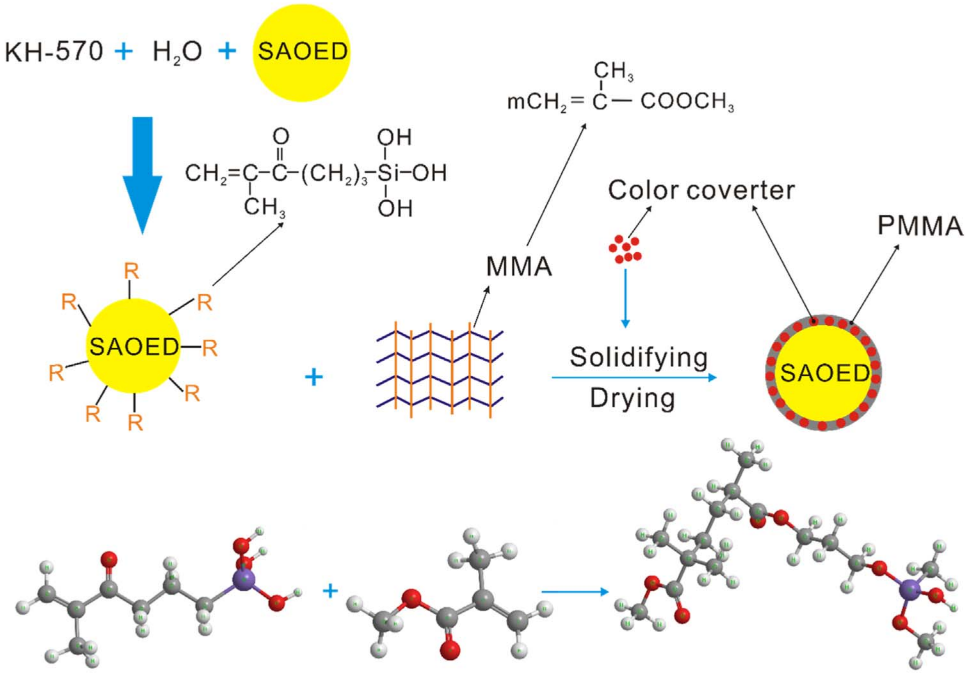

Fig. 1. Schematic diagram for the coating mechanism of PMMA and RECC on the surface of SAOED phosphor particles.

perovskite phosphor $Ca_3Ti_2O_7:Pr^{3+}$ proposed by Wang et al. [18] in 2015. Except for the above LLPs with single warm tone emitting color, LLPs with tunable luminescent color were also reported recently. In 2016, Wang et al. [19] proposed a color-tunable red persistent phosphor $NaCa_2GeO_4F:Mn^{2+},Yb^{3+}$ with a tunable luminescence color from red to green-yellow; In 2016, Xu et al. [20] reported a series of CaZnOS: xCe^{3+}, yNa^{+}, zMn^{2+} phosphors which can realize full-color emission by adjusting the x, y and z values; and in 2017, Zhu et al. [21] reported a novel Na_2MgSiO_4(NMSO): Tb^{3+}, Eu^{3+} phosphor with tunable emitting color from green to yellow and red. However, none are considered to be suitable to commercial application because of their relative weak luminescent intensity, and short afterglow decaying time.

In recent years, color converters have attracted considerable attention because of their narrow emission and high conversion efficiency. Based on the trichromatic theory that any needed color could be obtained by adjusting the primary colors, red, green and blue, color converters have been widely used in optical display devices, such as white LED, which use a blue LED chip to excite red and green color converters to produce white light [22–24]. As we know, the green light-emitting SAOED is the most successful commercialized and widely used LLP owing to its easy synthesis process, high luminescence brightness, long afterglow persistent time (over 1000 min) and improved chemical stability. Therefore, utilizing the red-emitting color converter and green-emitting LLPs SAOED to prepare warm-toned LLPs may be a better choice compared to the conventional solid state method or sol-gel method.

In this work, we chose a red-emitting coumarin fluorescent dye as the color converter (RECC) and the green light- emitting SAOED as the core phosphor, and prepared a warm-toned and color controllable LLP composite PMMA/RECC@ SAOED by coating the RECC and polymethyl methacrylate (PMMA) on the surface of SAOED. As a result of excellent transmittance of PMMA, the emission color and the fluorescence brightness of the PMMA/RECC@SAOED would not be affected by the coating layer of PMMA. In order to study the feasibility of this new method to prepared warm-toned LLPs, the XRD patterns, PL property, CIE chromaticity coordinate, color purity, real luminescence images, QY, afterglow decaying characteristic and luminescence process of the prepared PMMA/RECC@SAOED samples, which contain various concentrations of RECC, were systematically investigated.

2. Experimental

2.1. Preparation of samples

The selected green light-emitting LLPs SAOED were prepared by the solid state reaction method using $SrCO_3$ (A.R.), Al_2O_3 (99.99%), Eu_2O_3 (99.99%), Dy_2O_3 (99.99%) and H_3BO_3 (A.R.) as the starting raw materials (The detailed synthesizing process is given in the Supplementary Material S1) [25]. The RECC was prepared using the cyanide method by referring to previous research [26–29], and the synthesis process was illustrated in Fig. S2 (See Supplementary Material S2).

The PMMA/RECC@SAOED samples were prepared according to the following steps: (1) 10.0 g of the prepared green light-emitting SAOED phosphors were added into 60 g of absolute ethyl alcohol. After 30 min ultrasonic dispersing, 2.0 g of silane coupling agent KH-570 was added into the above solution for linking reaction with water bath (80 °C) and mechanic stirring condition, the pH value of the mixed solution had to be controlled around 1by using a dilute H_2SO_4 solution. After 4 h reaction, the obtained products were washed and dried for the next procedure. (2) 5.0 g of the pre-processed SAOED phosphors were added into a mixed solution composed of 40 mg of benzoyl peroxide and 40 g of methylbenzene; then the mixture was transferred into a three-necked flask and nitrogen was inputted continuously to exhaust the air in the flask. (3) A certain amount of RECC ($wt._{(RECC)}\% = 0.1\%$, 0.3%, 0.5%, 0.7%, 0.9%) was added into the flask, and stirred to make sure that the RECC dispersed uniformly in the mixed solution. In the meantime, a mixture consisting of 20 g of methylbenzene and 1 g of methyl methacrylate (MMA) were added gradually into the above flask and reacted in water bath (80 °C) with continual stirring for 2 h. The final products after the reaction finished were also washed and dried to obtain the PMMA/RECC@SAOED samples. The coating mechanism is illustrated in Fig. 1.

2.2. Characterization of the samples

The crystalline structure of the samples were characterized by XRD which carried out on an AXS-D8 diffractometer and operated at 40 kV, 20 mA with Cu-Kα radiation ($\lambda = 0.15405$ Å) at scanning steps of 0.02° ranging from 10° to 70°. The PL excitation and emission spectra were measured by the Hitachi F-4600 spectrophotometer equipped with a