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Effect of red emitting fluorescent pigment on fluorescent color of $SrAl_2O_4:Eu^{2+},Dy^{3+}$ phosphors

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Abstract: Green-blue fluorescence emitting $SrAl_2O_4:Eu^{2+},Dy^{3+}$ phosphors (SAOED) were coated by SiO_2 and a coumarin type red-emitting fluorescent pigment (FP). The effects of the FP on the morphology, crystal structure, photoluminescence properties and fluorescent color of the SAOED phosphors were systematically investigated by scanning electron microscopy (SEM), FT-IR, X-ray diffraction (XRD), photoluminescence spectra and CIE-1931 chromaticity coordinates characterization. Even though the surface of the SAOED phosphors became rough after being coated with SiO_2 and FP, crystal lattice of $SrAl_2O_4$ did not have any obvious lattice distortions. The photoluminescence spectra indicated that the SAOED phosphors could be used as the excitation light source to excite the FP to emit red fluorescence. The emission spectrum of the FP-coated SAOED consisted of a broad band with two emission peaks at 520 and 610 nm, and its fluorescence emission color was a mixed color of the SAOED phosphors and FP. The fluorescence color of the SAOED/SiO_2/FP composites tended to transfer to red area with the increase of the FP content varying from 0.1% to 0.9%.

Keywords: fluorescence; color; fluorescent pigment; coating; photoluminescence spectra; rare earths

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Phosphorescent compounds are a kind of energy absorption-storage-release luminescent material, which can absorb the energy of sun light and store this energy in the lattice[1,2]. Once the energy source is removed, the energy is gradually released in the form of bright visible phosphorescence and this process is cyclic. Several types of long lasting phosphorescent compounds have been prepared over the years, including aluminate, silicate and titanate doped with rare earth compounds[3–5]. $SrAl_2O_4$: Eu^{2+},Dy^{3+} (SAOED) for instance, is a representative blue-green emitting aluminate phosphorescent compound which functions after excitation by the sunlight and has high phosphorescence intensity, chemical stability, a simple synthesis process and can be obtained at a relatively low cost[6]. Specifically, the SAOED can phosphoresce for more than 10 h with bright blue-green color in a dark environment after being excited by the sunlight for 10 min. As a consequence, it is an optimal additive for production of luminous fibers. Recently, Ge et al. successfully prepared several kinds of luminous fiber by adding specific SAOED phosphorescent compounds into polyethylene terephthalate spinning solution in the melt-spinning process[7–10]. This novel luminous fiber shows significant application prospect in recreational and decorative textiles. However, as the emitted color of the SAOED phosphorescent compounds is blue-green, which is too monotonous and thus the wider application of the SAOED phosphorescent compounds and fibers are somewhat restricted. Therefore, in recent years an increasing number of researchers have focused on synthesizing red-emitting long lasting phosphorescent compounds that possess strong intensity and high chemical stability[11,12]. However, most of the red-emitting compounds do not satisfy the necessary requirements for production of luminous fibers because of their low phosphorescence intensity and short decay time, as well as having very complex preparation processes.

According to the subtractive trichromatic theory applicable to conventional coloration of textiles, any color could be obtained by combining the three primary colors cyan, yellow and magenta[13]. In order to save production costs often yellow, blue, and red colorants are used. In the case of light emitting material, however, additive colors, i.e. red, green and blue are combined to develop all other colors. As known to all, FP can emit a bright fluorescent light with a specific color after being excited by another specific light source. The chromophore and auxochrome groups in the structure of these compounds include carbonyl, azo and carbon-nitrogen bonds that enable the absorption of energy at higher waveband and the release of energy at longer wavebands[14]. Therefore, if there is an overlap between the emission spectrum of

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SAOED phosphorescent compound and the excitation spectrum of the FP, it could enable the use of SAOED compound as the excitation source for the FP.

On the basis of the assumption mentioned above, in this study, we focused on coating the SAOED phosphorescent compound with a coumarin type red emitting FP by chemical coating method and researching the effect of the red emitting FP on the fluorescent color of the SAOED phosphorescent compound. Usually, the sol-gel method is the most common way to prepare organic coating layer or organic-inorganic hybrid fluorescent materials for its advantages of fast reaction time, low processing temperature and controllable coating composition. For instance, Franville et al. prepared the rare-earth complexes/SiO_2 hybrid fluorescent material by adding the rare-earth ions into the sol-gel solution of tetraethylorthosilicate (TEOS), and the results indicated that this hybrid fluorescent material has an excellent fluorescent efficiency and its thermostability increased significantly compared with the rare-earth complexes[15]. Liu et al. successfully enhanced the moisture resistance and thermal stability of the $Ca_2BO_3Cl:0.02Eu^{2+}$ phosphors via hydrolysis of TEOS to form SiO_2 coating on the surface of the $Ca_2BO_3Cl:0.02Eu^{2+}$ phosphors by sol-gel method[16]. Xia et al. successfully coated the carbon fibers with SiC/SiO_2 layer via vinyltriethoxysilane hydrolysis sol-gel method, and the anti-oxidative properties of the carbon fibers were significantly improved[17].

In this work, we selected TEOS as silicon coating reagent to form the SiO_2 layer and encapsulated the SAOED phosphor particles and red-emitting FP via the sol-gel process. The effects of the FP on the morphology, crystal structure, photoluminescence properties and fluorescent color of the SAOED phosphors were also systematically investigated.

1 Experimental

1.1 Materials

The main materials are tetraethyl orthosilicate (TEOS), concentrated nitric acid (HNO_3), ethanol (C_2H_5OH), hydrogen peroxide (H_2O_2) and concentrated sulfuric acid (H_2SO_4), all of them are analytical grade and are offered by Sinopharm Chemical Reagent Co., Ltd. The red emitting FP was prepared by ourselves on the bases of other's research results[18–20], and the molecule structure of the FP is illustrated in Fig. 1.

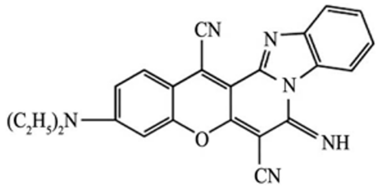

Fig. 1 Molecule structure of the FP

1.2 Preparation of the samples

The SAOED phosphorescent compounds were synthesized by the conventional high temperature solid state method, and the specific stoichiometric proportions of every original materials were determined by the reported references[21]. Firstly, the above prepared SAOED phosphorescent compounds were acidized by a mixture of H_2O_2 and H_2SO_4 (V_{H2O2}/V_{H2SO4}=3/7), and then dried at 200 ºC for 2 h. Secondly, 3.47 g of TEOS was added into the mixture of C_2H_5OH and deionized water, and the molar ratio of TEOS to C_2H_5OH and water is 1:15:35, then the mixed solution was transferred into a three-necked flask, and stirred for 30 min in water bath at 60 ºC, pH value of the mixed solution was adjusted to 2 by the HNO_3. Finally, 10 g of as-prepared SAOED phosphorescent compounds and a certain amount of FP (0.1 wt.%, 0.3 wt.%, 0.5 wt.%, 0.7 wt.%, 0.9 wt.%) were added into the above three-necked flask, and stirred at 60 ºC. When the mixture of SAOED phosphorescent powders and FP in the flask swelled and gave a wet gel-like look, the stirring was discontinued and the mixture was left untouched in an oven at 60 ºC for 12 h, then the final FP-coated SAOED phosphors with various FP contents were obtained.

1.3 Characterization

The morphology of the samples was inspected using a scanning electron microscope (SEM, SU1510, Hitachi, Japan). The FT-IR spectra were measured with a NICOLET Is10 infrared spectrophotometer (Thermo Fisher Scientific Co., Ltd) with the KBr pellet technique. The X-ray diffraction (XRD) measurements were carried out on an AXS-D8 diffractometer operating at 40 kV, 20 mA with Bragg-Brentano geometry using Cu Kα radiation (λ=0.15405 nm). The photoluminescence performances (excitation and emission spectrum) were measured by a Hitachi F-4600 spectrophotometer equipped with a 150 W xenon lamp as the excitation source. The chromaticity coordinates of samples was performed using an FS-5 spectrofluorometer (Edinburgh Instruments).

2 Results and discussion

2.1 Morphology

Fig. 2 gives the SEM images of the prepared SAOED phosphor particles and SiO_2/FP-coated SAOED phosphorescent compounds with various FP contents. As can be seen from the Fig. 2, the uncoated SAOED phosphor particles present irregular shapes with an average diameter of 8 μm, and show smooth and clean surfaces compared with the rough surface of SiO_2/FP-coated samples, which is caused by the deposition of the SiO_2 and FP nano particles. Besides, the surface of SiO_2/FP-coated