Luminous properties of recycling luminous materials SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ based on luminous polyester fabric

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Abstract

The recycling luminous materials SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ is a kind of long afterglow phosphor, prepared based on the alcoholysis of luminous polyester fabric, which has excellent characteristics like high lightness and long afterglow time. However, for that the luminous materials SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ are recycling, and the process on the alcoholysis of luminous polyester fabric may affect its performance. Hence, in this study a couple of luminous materials SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ were recycled from luminous polyester fabric based on the method of alcoholysis, the phase structure and luminescent properties of the fibers were characterized by scanning electron microscopy (SEM), x-ray diffractometer (XRD), fluorescence spectrometer and afterglow luminance meter. The results deduced that under a certain condition, the luminous polyester fabric can be basically degraded, and the recovered luminescent materials can be obtained at a high purity. Our research supplies a strategy to recycle luminous phosphors as well as other functional materials, and hopefully it could inspire development for luminous materials and fibers.

1. Introduction

Polyester-based luminous fabric is manufactured by interweaving polyester yarn and luminous polyester yarn. However, the alcoholysis of luminous fiber is rarely reported. Persistent luminescent materials generally use polyester as the fiber matrix and are added with SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ particles and nanoadditive, and the glycolysis method can be used to degrade the luminous polyester fiber. Therefore, the design principle of the alcoholysis of luminous polyester fabric is similar to that of waste polyester [1].

Polyester, also known as polyethylene terephthalate, is a general term for the polymer obtained by polymerizing diol and dicarboxylic acid. The alcoholysis reaction equation is shown below in figure 1 [2, 3]:

The reaction equation shows that alcoholysis is based on the degradation of polyethylene terephthalate in the presence of excessive glycol, a transesterification catalyst, and nitrogen under a certain temperature to achieve the scission of the ester bonds that will be later replaced by hydroxyl terminals [4]. This reaction is reversible. The speed of the forward reaction can be accelerated by adding catalysts during the reaction and increasing the temperature under N$_2$ protection. In the filtered alcohol solution, BHET is present in the filtrate [5], and SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ becomes insoluble with a small amount of oligomers and other impurities on the filter paper. The yellow-green viscous objects on the filter paper was dried and ground to obtain the samples required for the experiment.

In this study, in order to obtain the luminous materials from luminous polyester fabric, alcoholysis has been used to degrade the luminous fabric, and the properties has been researched.
2. Experimental

2.1. Raw materials
Luminous polyester fabric for degradation was synthesized in the laboratory. Ethylene glycol (A.R. grade) and zinc acetate dehydrate were purchased from Sinopharm Chemical Reagent Co., Ltd, China. N₂ was obtained from Wuxi Shengma Gas Co., Ltd.

2.2. Glycolysis of luminous polyester fabric
The luminous polyester fabrics with different contents were washed, dried, and cut into finely chopped yarns.

A 500 ml four-necked round-bottom glass flask equipped with a thermometer, a reflux condenser, a nitrogen catheter, and a magnetic stirrer was charged with a certain quality of zinc acetate dehydrate and ethylene glycol solution. When the reaction started, the electric heating sleeve and stirring device were turned on, and nitrogen was slowly injected. After a certain temperature was reached, the shredded luminous polyester fabric was added and stirred at a constant temperature. The solution after a period of reaction will be vacuum-filtered to obtain the yellow-green viscous objects, which were dried in an oven, extracted, and ground to produce fluffy luminescent powder.

A recovery method of luminescent materials from luminous polyester fabrics was designed by adjusting the reaction temperature, reaction time, and catalyst dosage. The experimental device is as follows as shown in figure 2 [6]:

2.3. Preparation of luminous materials: SrAl₂O₄:Eu²⁺, Dy³⁺
Five samples of luminous materials: SrAl₂O₄:Eu²⁺, Dy³⁺ obtained from luminous polyester fabric, and the details are as follows:
A: The content of SrAl₂O₄:Eu²⁺, Dy³⁺ in the luminous fabric is 3%
B: The content of SrAl₂O₄:Eu²⁺, Dy³⁺ in the luminous fabric is 5%
C: The content of SrAl₂O₄:Eu²⁺, Dy³⁺ in the luminous fabric is 7%
Experimental procedure: 200 g of ethylene glycol was poured into a four-necked flask. The main operating parameters: reaction temperature, reaction time, and catalyst dosage were optimized by analyzing the purity of the recovered luminescent materials to design the most suitable alcoholysis scheme. The purity of the product recovered from luminescent polyester fabric was characterized by the following formula:

\[ R_s = \frac{M_{800°C}}{M_0} \]

where \( M_0 \) is the mass of the recovered luminescent materials, g; and \( M_{800°C} \) is the mass remaining after calcining the recovered luminescent materials at 800 °C, g.

The yellow-green viscous substance obtained after degradation was only dried in an oven at 60 °C; however, this process cannot completely remove the impurities. TGA analysis of the yellow-green viscous substance obtained after degradation was conducted at the temperature range of 60 °C–800 °C and heating rate of 20 °C min \(^{-1}\) to test the product purity. The results showed no heat loss in the recovered luminescent materials at high temperature, indicating its stable performance at temperature less than 800 °C. Therefore, TGA can be used to determine the content of the phosphors and consequently the purity of the samples obtained by the reaction under various conditions.

The main operating parameters: reaction temperature, reaction time, and catalyst dosage were optimized by analyzing the purity of the recovered luminescent materials to design the most suitable alcoholysis scheme.

### 3.1. Results of alcoholysis reaction

A certain amount of fabric was cut into pieces and analyzed by varying the catalyst concentration, reaction time, and temperature to establish the optimal working conditions and compare the luminescent powder yield.

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The main operating parameters: reaction temperature, reaction time, and catalyst dosage were optimized by analyzing the purity of the recovered luminescent materials to design the most suitable alcoholysis scheme.

### 3.1.1. Effect of reaction temperature

Experimental procedure: 200 g of ethylene glycol was poured into a four-necked flask, added with 0.05 g of \( \text{Zn(AC)}_2 \cdot 2\text{H}_2\text{O} \), stirred, and heated under nitrogen atmosphere. The condensing reflux unit was turned on to control the evaporation of glycol at high temperature. The reaction temperature was taken as the variable of the reaction process, that is, when the solution was heated to 150 °C, 170 °C, 190 °C, and 196 °C, the dried and shredded fabric were added to the reactor (the mass ratio with ethylene glycol is 1:20), and the temperature was kept constant until the fibers in the four-necked flask disappeared and the alcoholysis stopped. After 5 h of reaction, the temperature was lowered to 160 °C under nitrogen protection, and the unreacted yarn was filtered and removed. The recovered powder was dried in the oven at 60 °C for 12 h.

Figure 3 shows that with the increase in reaction temperature, the purity of recovered luminescent materials also increased. However, the growth trend slowed down when the temperature reached 190 °C, and the purity of luminescent materials reached the highest value when the temperature was 196 °C. Previous studies reported that temperatures exceeding 197 °C, which is above the boiling point of ethylene glycol, lead to an incomplete reaction due to glycol volatilization \[7–9\]. Hydroxyl groups are present in the alcoholysis system. If the temperature is extremely high, then the degradation products are oxidized, resulting in an irritating odor and brown color for the product, thus affecting the subsequent research.

Therefore, the optimal reaction temperature for alcoholysis was set to 196 °C to ensure the highest purity of recovered luminescent materials.

### 3.1.2. Effect of reaction time

Experimental procedure: 200 g of ethylene glycol was poured into a four-necked flask, added with 0.05 g of \( \text{Zn(AC)}_2 \cdot 2\text{H}_2\text{O} \), stirred, and heated under nitrogen atmosphere. The condensing reflux device was turned on to
control the evaporation of glycol at high temperature. Heating was stopped when the boiling point of ethylene glycol (196 °C), and 10 g of dried and shredded fabric was added to the reactor (the mass ratio with ethylene glycol is 1:20). The reaction was kept a constant temperature of 196 °C. Change the reaction time, the temperature was lowered to 160 °C under the protection of nitrogen, and the unreacted yarn was filtered and removed, and the recovered powder was dried in the oven at 60 °C for 12 h.

Figure 4 shows that when the reaction time was 2 and 3 h, the purity of the powder was only 68%−69%, indicating the poor quality of the alcoholysis product under these conditions. When the reaction time was further increased to 4–5 h, the purity of the sample still did not increase, and a small amount of unreacted fiber settled at the bottom of the flask after the 4 h reaction. Therefore, the reaction time should be controlled at 5 h. If the reaction time is excessively long, then the fabric will react at a high temperature for a long time. In this case, the alcoholysis rate will not be improved, and the product color will be affected. These phenomena will have a bad influence on the recovered product.

3.1.3. Effect of catalyst dosage
Varying catalyst dosages from 0.02 g to 0.06 g were used to examine its effect on the purity of recovered luminescent materials, and the results are shown in figure 5. With the increase in the catalyst dosage, the purity of the luminescent materials also increased slowly. The content of SrAl2O4:Eu2+,Dy3+ phosphors in the recovered powder reached 92.34% when the catalyst dosage was 0.5wt% of the mass of luminous fabric. When the dosage was increased to 0.6 wt%, the purity of the luminescent materials decreased. This phenomenon occurred because the excessive catalyst dosage could produce reaction by-products, resulting in excessive impurities and reduced sample purity. The results proved that the catalyst with a mass ratio of 0.5 wt% can
achieve a good catalytic effect. By contrast, adding an excessive amount of catalyst increases the production cost and the catalyst residue and by-products, thereby affecting the product quality. Therefore, the catalyst dosage was selected as 0.5 wt% of the mass of luminous fiber.

Three operating parameters, i.e., reaction temperature, reaction time, and catalyst dosage, were selected for optimization because of their effect on the reaction. Under the optimal reaction conditions: \( T = 195 \, ^\circ\text{C}, \ t = 5 \, \text{h}, \) and catalyst dosage of 0.5 wt% of the mass of luminous fiber, the luminous polyester fabric can be basically degraded, and the recovered luminescent materials can be obtained at a high purity.

### 3.2. Characterization of alcoholysis-recovered samples

#### 3.2.1. Micromorphology analysis

Figure 6 shows the SEM image of the original SrAl\(_2\)O\(_4\):Eu\(^{2+}\), Dy\(^{3+}\) powder and five samples with a magnification of 2000 times. (a), (b), (c), (d), (e), (f) in figure 6 represent the original powder and samples A, B, C, D, and E, respectively.

Figure 6(a) shows that the particles of the original powder of SrAl\(_2\)O\(_4\):Eu\(^{2+}\), Dy\(^{3+}\) have an irregular shape, and most have sharp edges and corners with different sizes in the range of 1−10 μm \([10]\). Compared with the original powder, the recovered samples have larger particle size, and the surface is not as smooth. The surface became rough because some oligomers are attached to the surface particles of SrAl\(_2\)O\(_4\):Eu\(^{2+}\), Dy\(^{3+}\) during alcoholysis. Agglomeration and clustering also occurred between the particles possibly due to the lack of grinding time. However, figures 6(b)–(e) show that some particles are similar to the original particles. When the powder particle size is small, its ability to emit light is strong due to the increased specific surface area of receiving light \([11, 12]\). SEM patterns showed that the single particle size of the recovered powder is relatively large, and the luminous intensity is weaker than that of the original powder.

#### 3.2.2. XRD analysis

Figure 7 shows the XRD diffraction pattern of the original SrAl\(_2\)O\(_4\):Eu\(^{2+}\), Dy\(^{3+}\) powder and five recovered samples. The spectrum of the SrAl\(_2\)O\(_4\):Eu\(^{2+}\), Dy\(^{3+}\) powder is relatively multi-peaked and sharp. The diffraction peaks of these five samples showed sharp peaks at 20.1°, 28.5°, 29.3°, 35.1°, and 2θ, which corresponded with the standard XRD pattern card (JCPDS #34-0379) of SrAl\(_2\)O\(_4\). On the basis of the above analysis, spinning and degradation did not destroy the phase of SrAl\(_2\)O\(_4\):Eu\(^{2+}\), Dy\(^{3+}\), and its luminescent properties remained intact.

#### 3.2.3. Excitation and emission spectrum analysis

Figure 8 shows the excitation and emission spectrum of raw SrAl\(_2\)O\(_4\):Eu\(^{2+}\), Dy\(^{3+}\) powder and five recovered samples. As shown in figure 8(a), the excitation spectrum of raw and recovered samples had a broad absorption band from 250 nm to 500 nm with the most intense excitation peak of the raw SrAl\(_2\)O\(_4\):Eu\(^{2+}\), Dy\(^{3+}\) powder located at approximately 320 nm. This finding is consistent with many literature reports \([13]\). However, the main excitation peaks of five recovered samples had red-shifted in different degrees because some oligomers were coated on the surface of SrAl\(_2\)O\(_4\):Eu\(^{2+}\), Dy\(^{3+}\) during degradation, thereby affecting the position of excitation peak. Studies showed that the main excitation peak of polyester is at 390 nm. Owing to the existence of the polyester materials, the excitation spectrum of luminous materials showed different degrees of red shifting.
SEM images also revealed that most of the particles of recovered samples are wrapped with a layer of other substances, making their surface rough and affecting the main excitation peak. The emission spectra of the SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ phosphors and recovered samples are illustrated in figure 8(b). The samples were excited by 365 nm UV light, and a broad emission band centered at 520 nm was detected in the emission spectrum assigned to the 4f$^6$5d$^1 \rightarrow 4f^7$($8S_{7/2}$) transition of Eu$^{2+}$ ions [14]. In addition, the emission intensity of the emission peak of SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ phosphors was higher than that of the five recovered samples possibly due to the different concentration of Eu$^{2+}$ in the recovered samples. The content of SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ phosphors varied in the five luminous polyester fabrics, and the sample recovered by alcoholysis also changed with the concentration. For luminescent materials recovered from different fabric contents, no trend was observed for the influence of
emission intensity and the content of SrAl₂O₄:Eu²⁺, Dy³⁺ phosphors in the fabric. Also it can be seen that sample E has the highest excitation intensity, but sample C has the best emission intensity, it may because the oligomers coated on the surface of SrAl₂O₄:Eu²⁺, Dy³⁺ had an effect on the spectrum of SrAl₂O₄:Eu²⁺, Dy³⁺ due to the excitation and emission spectrum. And it was thought that sample C was better than others relative to spectral properties.

The results obtained from the analysis above implied that the recycling luminous materials SrAl₂O₄:Eu²⁺, Dy³⁺ could be excited by the light from 300 nm to 450 nm and the peak was around 390 nm. After being excited, the SrAl₂O₄:Eu²⁺, Dy³⁺ could emit bright light and the emission peak was located at 520 nm, which was due to the emission center Eu²⁺.

3.2.4. Luminescent property analysis

Figure 9 shows the afterglow decay curve for the raw SrAl₂O₄:Eu²⁺, Dy³⁺ powder and five luminescent powders recovered from different luminous polyester fabrics. The six afterglow decay curves exhibited a typical tri-exponential decay, including rapid, intermediate and slow decaying [15]. Rapid decaying occurred due to the short survival time of the electro in Eu²⁺, intermediate decaying was caused by the Eu²⁺ ions trapped by shallow centers, and slow decaying transpired due to the deep trap energy center of Dy³⁺ [16].

As shown in figure 9, the initial brightness of the SrAl₂O₄:Eu²⁺, Dy³⁺ phosphors was stronger than that of A – E samples, and the ranking of the initial brightness is E > D > C > B > A. This finding indicates that when the content of SrAl₂O₄:Eu²⁺, Dy³⁺ phosphors in the fabric for alcoholysis is high, the initial brightness of the recovered samples is increased. During the slow decay, the original powder was always brighter than the recovered samples. Although the initial brightness values of the recovered samples were different, their decay curves were similar during this process. Therefore, the recovered powder has the same afterglow attenuation law.
as the raw SrAl₂O₄:Eu²⁺, Dy³⁺ powder, but its luminous intensity is weaker. When the luminescent materials content in the fabric is high, the afterglow initial brightness of the recovered luminescent materials is increased.

4. Conclusion

This study applied alcoholysis to recover luminescent materials from luminous polyester fabrics, and the following conclusions are drawn:

1. The optimal reaction conditions are $T = 195 \, ^\circ C$, $t = 5 \, h$, and catalyst dosage of 0.5wt% of the mass of luminous fiber. Under these conditions, the luminous polyester fabric can be basically degraded, and the recovered luminescent materials can be obtained at a high purity.

2. After spinning and degradation, the crystal structure and spectral properties of the luminescent materials recovered from the fabrics with different contents of SrAl₂O₄:Eu²⁺, Dy³⁺ phosphors remained unchanged, and their luminous intensity and afterglow brightness decreased.

3. The recovered sample E had better luminous properties compared to others.

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