PAPER

Self-repairing inorganic phosphors/polymer composite film for restructuring luminescent patterns

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Abstract

Practical applications of phosphor particles in light sources and displays generally require the adhesion and support of polymer materials. However, these phosphor/polymer composites suffer from the difficulty in self-repairing after fracture. Inspired by the development of self-healing polymers, herein, we prepared phosphor/polymer composite films with self-repairing and restructuring properties. The N,N-dimethylformamide dispersant was used to uniformly disperse the phosphor particles in the self-healing polymer, which is considered to the key process for obtaining self-repairing properties. The developed self-repairing composite films are particularly suitable for restructuring luminescent patterns to provide multidimensional light-emitting modes including photoluminescence, persistent luminescence and mechanoluminescence. These results are expected to provide new insights for designing multifunctional self-repairing and reconstructing composites for anti-counterfeiting, integrated optics, optical communications, and artificial skins.

1. Introduction

Inorganic phosphors emit light during the exposures of electrical, photo-, thermal and mechanical stimulation [1–7] and play an important role in different fields including solid-state lighting [8, 26], anti-counterfeiting [9, 10], phosphor thermometry [11], and mechanoluminescence (ML) imaging technologies [12–22]. In order to obtain the adhesion and support, phosphor particles need to be compounded with polymer materials in these applications to obtain adhesion and support [16, 23–25]. For example, in phosphor-converted white light-emitting diodes, the phosphor particles (such as Y₃Al₅O₁₂:Ce) were dispersed in silicone resin before being packaged on a blue InGaN chip [26]. In anti-counterfeiting displays, the phosphor particles (such as NaYbF₄:Er) combined with polymer were made into anti-counterfeiting ink for spraying [27]. In temperature measurement, the composites which were composed of phosphor particles such as (La₂O₂S:Eu) and polydimethylsiloxane (PDMS) were used for phosphorescence-intensity based on temperature measurement [11]. In addition, the ML phosphor particles (such as BaTiO₃-CaTiO₃:Pr, CaZrOS·Mn and CaZr(PO₄)₂::Eu) were combined with epoxy resin for stress excited luminescence imaging [28, 29]. However, after these phosphors/polymer composites are damaged or cut, it is difficult to repair themselves. With the well development of self-healing polymers, it is a feasible solution to use them as the support for phosphors. Self-healing of polymers can be achieved via a number of different mechanisms such as molecular interdiffusion, photo-induced healing, recombination of chain ends, self-healing via reversible bond formation, the intermediate-strength crosslinks formed via hydrogen and/or ionic bonding, and the ionic aggregation and melt flow behavior of copolymers [30]. However, combining inorganic powder with self-repairing polymers suffers from agglomeration effect. Therefore, developing a phosphors/polymer composite with the desired self-repairing and restructuring properties still faces a significant challenge.
In this paper, we prepared a self-repairing phosphors/polymer composite film. The properties of self-repair after fracture in the self-healing properties were taken as the main properties for restructuring luminescent patterns. The basic principle of self-healing is the combination of hydrogen bonds in polymers [31]. In order to solve the agglomeration problem between phosphor particles [32], we used N,N-dimethylformamide (DMF) as a dispersant to uniformly disperse the phosphors particles in the self-healing polymer. The adsorption between polar phosphor particles and strong polar DMF allows the DMF to occupy the weak interaction sites between the particles, thereby achieving the dispersion of the phosphor particles [33]. The uniform dispersion of phosphors particles in the self-healing polymer enhances the bonding efficiency between hydrogen bonds in polymers and improves the self-repairing properties. The developed composite films exhibited superior self-repairing, photoluminescence (PL), persistent luminescence and ML properties. This work will greatly promote the application of inorganic phosphors in anti-counterfeiting, integrated optics and artificial skins.

2. Experimental

The Eu$^{2+}$-doped SrAl$_2$O$_4$ and Pr$^{3+}$-doped NaNbO$_3$ samples were synthesized by the solid-state reaction. The Sr$_{0.99}$Al$_2$O$_{1.9}$Eu$^{2+}$ (SAOE) samples were sintered at 1400 °C for 3 h in 5%H$_2$/95%N$_2$ atmosphere among stoichiometric mixture of SrCO$_3$ (Aladdin, 99.99%), Al$_2$O$_3$ (Aladdin, 99.9%) and Eu$_2$O$_3$ (Aladdin, 99.99%) [34]. The Na$_{0.99}$NbO$_{2.003}$Pr$^{3+}$ (NNOP) samples were sintered at 1300 °C for 3 h in air among stoichiometric mixture of Na$_2$CO$_3$ (Aladdin, 99.99%), Nb$_2$O$_5$ (Sinopharm Chemical Reagent, 99.99%) and Pr$_6$O$_{11}$ (Aladdin, 99.99%) [1]. The as-prepared powders were sieved by using a 450-mesh sieve. The particle size of phosphor particles after sieving was about 20–30 μm. The self-repairing phosphors/polymer composite films were prepared by embedding the as-prepared powders in a self-repairing polymer (PDMPS–MPU$_{0.4}$–I U$_{0.6}$) [31]. First, the 0.6 g of Et$_3$N (Sinopharm Chemical Reagent, >99%) was added to a solution of 4.12 g of H$_2$N–PDMS–NH$_2$ (Gelest, Mn = 5000) in 30 ml CHCl$_3$ (Sinopharm Chemical Reagent, >99.5%). The weight ratio of the solution of Et$_3$N, H$_2$N–PDMS–NH$_2$ and CHCl$_3$ was 0.6:4:12:20. After stirring for 1 h, a mixture solution of 1.1 g of 4,4′–Methylenebis (Sigma Aldrich, 99%) and 1 g of Isophorone diisocyanate (Sigma Aldrich, 98%) was added and 1 g of phosphor particles and 5 ml of DMF (Sinopharm Chemical Reagent, >99.5%) were added at the same time. The weight ratio of the resulting mixture of 4,4′–Methylenebis, isophorone diisocyanate, the as-prepared solution, phosphor particles and DMF was 1.1:1:24.72:1:5. The resulting mixture was stirred for 1 h while the temperature was kept at 0 °C with ice water. At last, the viscous solution mixed with the particles was injected into the mold subjected to vacuum evaporation for 48 h to remove the solvent. The mold is a rectangular shape with a length of 3 cm and a width of 1 cm.

Field emission scanning electron microscopy (SEM) (JSM-7800F, Jeol) was used to measure the morphologies of samples. A fluorescence spectrometer (F-4600, Hitachi) was used to measure the PL spectra. The magnetic stirrer was used to stir the sample at a speed of 540 round min$^{-1}$. A materials testing machine (3400, Instron) was used to record the stress–strain curves with a sample width of 10 mm, a thickness of 0.2–0.3 mm, a length of 20 mm, and a loading rate of 10 mm min$^{-1}$. A handheld ultraviolet (UV) lamp (254 nm, 6 W) was used to irradiate the phosphors particles in composite films. Optical images were taken by the camera (α7RII SONY Japan, FE 2.8/90 MACRO GOSS). The vacuum was degassed by laboratory vacuum pump (T0103226, Fujiwara).

3. Results and discussion

Figure 1 shows the fabrication processes and the mechanical properties of the self-repairing phosphors/polymer composite film. Figure 1(a) shows the schematic of fabrication of self-repairing phosphors/polymer composite film. Compared with the previous works, our fabrication process is more convenient and the self-healing of the prepared composite does not require heat and pressurization [35]. Herein, the fabrication process without DMF dispersion were shown for the comparison with the fabrication process with DMF dispersion. As shown in figure 1(a)–(ii) the phosphor particles in the self-healing polymer were significantly aggregated and the SEM image shows the situation of the aggregation between microparticles. Such aggregation severely hinders the bonding between hydrogen bonds and therefore makes it difficult for the composite films to heal itself. In contrast, with the dispersion of DMF, the phosphor particles were uniformly dispersed in the self-healing polymer and the SEM image shows the excellent dispersion between phosphor particles in the polymer (figures 1(a)–(i)). To quantify the effect of adding DMF on the self-repairing properties of the composite film, we performed mechanical tests to the composite films with and without DMF dispersion (figure 1(b)). The DMF-added composite film was able to be stretched to 106% and the load at breaking point was 34.6457 N. The composite film without DMF dispersion ruptured at less than 57% strain and the load at breaking point was 11.0593 N (Table of figure 1(b)). In summary, the dispersion of DMF is critical to the self-repairing and
mechanical properties of the composite films. The self-repairing time is also important to the self-repair of the composite films. To demonstrate the effect of self-repairing time on self-healing properties, we put the DMF-added composite films to self-heal for 6 h, 12 h, 24 h at room temperature (Figure 1(c)). The composite films can self-repair completely after 24 h at room temperature and enabled to be stretched to 106% (Table of Figure 1(c)). Heating helps the bonding between hydrogen bonds to increase the efficiency of self-repairing [31]. When the film was healed at 50 °C for 3 h, the composite film was enabled to be stretched to 103% which was nearly the same extent of stretch as the composite film healed at room temperature for 24 h (Table of Figure 1(c)). Therefore, in the following demonstration experiment, we heated the composite films at 50 °C for 3 h to speed up the self-repairing and restructuring process.

Figure 2 shows the images of the self-repair and restructuring of the prepared composite films. The self-repairing SAOE/polymer and NNOP/polymer composite films were divided into several pieces (SAOE #1–3 and NNOP #4–6), respectively (figure 2(a)). In the following experiment, we respectively showed the self-repairing properties and the restructuring properties of composite films. As shown in figures 2(b) and 2(c), in self-repairing experiment, we combined the composite films of SAOE #2 and 3 and NNOP #4 and 5, it can be observed that the composite films achieved well healing. The SAOE/polymer composite films emitted green PL under UV irradiation due to the luminescence of the doped SAOE particles (figure 2(b)) [34]. The NNOP/polymer composite films emitted red PL under UV irradiation due to the luminescence of the doped NNOP particles (figure 2(c)) [1]. Furthermore, we used a fluorescence spectrometer to measure the PL spectra of the composite films. A green emission at 518 nm can be observed for SAOE/polymer composite films (figure 2(b) inset). A sharp red emission at 616 nm can be observed for self-repairing NNOP/polymer composite film

![Figure 1](image1.png)

**Figure 1.** Fabrication processes and the mechanical properties of the self-repairing phosphors/polymer composite film. (a) Schematic of fabrication, optical images and SEM images of self-repairing phosphors/polymer composite film. (i) Fabrication process of composite film with DMF dispersion. The insets show the optical image and SEM image of DMF-added composite film. (ii) Fabrication process of composite film without DMF dispersion. The insets show the optical image and SEM image of the composite film without DMF dispersion. (b) Stress-strain curves of the DMF-added composite film and the composite film without DMF dispersion after being cut and self-repair. The table shows the ultimate elongation, load at breaking point and the slope of the stress–strain curves of the DMF-added composite film and the composite film without DMF dispersion after being cut and self-repair. (c) Stress-strain curves of the DMF-added composite film healed for 6 h, 12 h, 24 h at room temperature and 3 h at 50 °C. The table shows the ultimate elongation, load at breaking point and the slope of the stress–strain curves of the DMF-added composite film healed for 6 h, 12 h, 24 h at room temperature and 3 h at 50 °C. Scale bars of optical images: 1 cm, Scale bars of SEM images: 1 μm.
In the restructuring experiment, we combined the composite films of SAOE #1 and NNOP #6. The composite films after restruction also achieved excellent healing and emitted green and red PL under UV irradiation (figure 2(d)).

Figure 3 shows the self-repair property, flexibility, and hydrophobicity of composite films after restructuring: (a) SAOE/polymer and NNOP/polymer composite films; (b) Restructure; (c) Bend; (d) Water-proof. Scale bars: 1 cm. Ambient light: , UV light.

Figure 2. Images of the self-repair and restruction of the prepared composite films. (a) Tailoring of self-repairing SAOE/polymer and NNOP/polymer composite films. (b) Optical images of self-repairing SAOE/polymer composite film after restruction. The inset shows the PL spectrum of the self-repairing SAOE/polymer composite film. (c) Optical images of self-repairing NNOP/polymer composite film after restruction. The inset shows the PL spectrum of the self-repairing NNOP/polymer composite film. (d) Optical images of self-repairing SAOE/polymer and NNOP/polymer composite films after restruction. Scale bars: 1 cm. Ambient light: , UV light.

Figure 4 shows the patterned restructuring display of self-repairing phosphors/polymer composite films. The multi-luminescence (PL, persistent luminescence, ML) under different stimulation of phosphor particles was applied to achieve the information encryption. On one hand, we obtained four rectangular SAOE/polymer composite films and one square NNOP/polymer composite films through cutting (figure 4(a)). On the other hand, the composite films were restructured to a cross-shaped pattern with SAOE/polymer composite films as the side and NNOP/polymer composite film as the center. The composite films after restruction can be observed as a white cross-shaped pattern under the ambient light (figures 4(a)–(i)). In dark fields, the center of
the cross-shaped pattern emitted red PL and the four sides emitted green PL under UV irradiation (figures 4(b)–(ii)). After the UV irradiation, due to the persistent luminescence of the doped NNOP and SAOE particles [1, 34], the cross-shaped pattern with four green sides and one red center can still be observed (figures 4(b)–(iii)). Furthermore, figure 4(b)–(v) shows the ML property of the composite films, after the persistent luminescence disappeared, we used a glass rod to rub the surface of the composite film, the composite films emitted green ML due to the stress excited luminescence property of the SAOE phosphor particles [34]. These three luminescent modes were applied to realize the anti-counterfeiting of the pattern.

4. Conclusion

In this work, we have developed a self-repairing inorganic phosphors/polymer composite film for restructuring luminescent patterns through uniformly dispersing the phosphors particles by DMF. We solved the problem of agglomeration between phosphors particles and it will promote combining inorganic materials with other self-healing mechanisms. The composite film is composed of phosphors particles and a polymer which can self-repair after fracture. The composite film enables self-repair and restoration after being cut and exhibits excellent luminescent properties including PL, persistent luminescence and ML. It can be expected that the proposed self-repairing phosphors/polymer composite films broaden the applications in various fields such as anti-counterfeiting and artificial skins.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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