Piezoluminescent devices by designing array structures

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\begin{abstract}
Mechanoluminescence has attracted increasing attentions because it can convert the kinetic energy during human daily motions into light to be used in sensors and displays. However, its practical applications are still hindered by the weak brightness and limited color while under large forces. Herein, we developed novel piezoluminescent devices (PLDs) which could effectively emit visible light under low pressing forces through the stress-concentration and enhancing deformation on the basis of carefully-designed array structures. The emitting colors were also tunable by using bilayer luminescent film under different pressures. This work not only provides a new strategy to effectively harvest mechanical energy into light, but also presents a scalable, low-cost and color-tunable PLD which shows great potentials in various applications such as luminescent floors, shoes and stress-activated displays.
\end{abstract}

1. Introduction

Light-emitting devices are indispensable for both industry and our life and have been widely explored for decades. Among them, electroluminescent devices such as inorganic and organic light-emitting diodes are generally explored to convert electricity to light\textsuperscript{[1–5]}. With the requirement to develop green energy, it is highly desired to more efficiently take use of other energy sources such as mechanical energy that can be produced by our body movements every day and is typically released to the environment without harvesting\textsuperscript{[6–8]}. Recently, there were some reports in regard to realizing mechanically light-emitting devices under pressing, stretching, vibrating and magnetic field by incorporating the rigid inorganic phosphors particles into elastomers\textsuperscript{[9–17]}. However, the mechanoluminescent materials generally exhibited weak brightness and limited color\textsuperscript{[18–20]}. In addition, it was hard to achieve tunable colors by changing pressure instead of frequency of applied electricity/magnetic field. Moreover, the press-induced light emission typically came out from where it was pressed, thus hindering the visualization.

In this communication, we have developed a new type of piezoluminescent devices (PLDs) that efficiently emit light under pressing by designing patterned array structures. The micro-structured array between the substrate and the piezoluminescent layer offered the designated sites for stress concentration and transfer, and the mechanical energy was thus efficiently converted to light in the above sites. The luminescent intensity could be varied by tuning the contact area, and the luminescent colors could be controlled by tuning the pressing force through the use of bilayer luminescent film. These novel PLDs were fabricated by solution processes and can be easily scaled up to meet practical applications, such as luminescent floors.

2. Materials and methods

2.1. Preparation of pressure-responsive luminescent films

Polydimethylsiloxane (PDMS) precursor solution was prepared by mixing the prepolymer and the curing agent (Wacker Chemical Co. Ltd., German, RT601) with a volume ratio of 9:1 and ultrasonic treating for 5 min. Then 8.75 g of Al\textsubscript{2}O\textsubscript{3} coated ZnS:Cu phosphor (ZnS:Cu) (Shanghai Keyan Phosphor Technology Co., Ltd., China) was added to 3.75 g of PDMS precursor solutions to make the mixture and the air bubbles were removed in a vacuum oven at room temperature. Afterwards, the mixture was poured into a rectangular mold with a depth of 1 mm and cured at 80 °C for 1 h to obtain a pressure-responsive luminescent film. Other luminescent films derived from different phosphors such as Al\textsubscript{2}O\textsubscript{3} coated ZnS:Mn phosphor (ZnS:Mn) (Shanghai Keyan Phosphor Technology Co., Ltd.) were prepared by similar method.
2.2. Preparation of pressure-responsive color-tunable luminescent films

First, a mixture of ZnS:Cu and PDMS precursor solutions was poured into a rectangular parallelepiped mold with a depth of 0.5 mm and then cured at 80 °C for 1 h. After demolding, the luminescent film was put in a rectangular parallelepiped mold with a depth of 1 mm. Later, the mixture of ZnS:Mn and PDMS precursor was poured into the mold with the layer of a thickness of 0.5 mm at the top of the ZnS:Cu based luminescent film and cured at 80 °C for 1 h. After demolding, we obtained a pressure-responsive color-tunable luminescent film with bilayer structure.

2.3. Preparation of hard piezoluminescent devices

The template layer with the protruding structure was prepared by 3D printing of nylon, and the size and pattern of the protruding portion could be designed. In this work, we designed the “dot matrix” and the letter “F” patterned by cylinders with different sizes and densities. The hard piezoluminescent device was finally obtained by putting the luminescent film on the hard template.

2.4. Fabrication of flexible piezoluminescent devices

The bare PDMS film was first prepared by pouring the precursor into a mold with a depth of 1 mm, curing at 80 °C for 1 h and releasing from the mold. Then the mixture of ZnS:Cu phosphor and PDMS precursor solution was injected into a spring-shaped mold, and cured at 80 °C for 1 h to obtain a spring-shaped illuminating unit after demolding. The illuminating units were placed between two flexible transparent PDMS films and further cured by PDMS precursor solution to obtain a flexible piezoluminescent device.

2.5. ABAQUS simulations

Finite element method was used to simulate the deformation of PDMS composite film and estimate the stress distribution. In the computation, the elastic modulus and Poisson’s ratio of PDMS composite film were 8 MPa and 0.47, respectively. We selected the “softened” contact to describe the interaction between the film and arrayed cylinders, which has an exponential contact pressure-overclosure relationships. This type of contact avoided the discontinuity of pressure at the interface. Besides, to solve the difficulties in convergence, the pseudo-dynamic algorithm (a stabilized nonlinear resolution method in finite element software Abaqus) had been adopted to solve the nonlinear problems.

3. Results and discussions

The PLD consisted of two parts (Fig. 1a), one bottom layer of rigid nylon plate with a protruding array by 3D printing and one top layer of soft light-emitting film of PDMS-embedded metal-doped ZnS phosphor. Under pressing, the device would be luminous on the protruding points due to the stress concentration. The stress distribution of the PLD was simulated by ABAQUS simulations (Fig. 1b). It can be seen that the stress was concentrated at each point of the protrusions. Therefore, we could control the emitting patterns by designing different protruding array structures and applying pressure on PLD.

It can be seen from the cross section of the luminescent layer (Fig. 2a) that the size of the ZnS phosphor particles was ~27 μm and they were uniformly dispersed and embedded in the PDMS matrix. The energy dispersive X-ray spectroscopy (EDS) element mapping in Fig. 2b shows the element distribution of an individual ZnS:Cu particle. In addition to the Zn and S elements, the particle also contained a small amount of the doped Cu, and all the elements were uniformly distributed in the particle. The Al elements from EDS and transmission electron microscope (TEM) image of the particles indicated the Al2O3 layer on the surface of ZnS:Cu particles. The coating layer of Al2O3 was reported to improve the stability and the sensitivity of luminescent particles [21]. X-ray diffraction (XRD) spectrum of particles also showed a typical zinc blende crystal phase of ZnS (Fig. 2d) [17].

It has been reported that the mechanoluminescent phenomenon was mainly derived from electron detrapping electrofluorescence induced by piezoelectric effect within inorganic hybrid semiconductors [22]. Therefore, the effective transfer of impact force to the inorganic phosphors to generate piezoelectric effect was important for the luminescent intensity. When the whole device was subjected to an external force from the top layer, the stress was redistributed and mainly concentrated at the local sites of protruding points and transferred to the phosphors; when the stress exceeded the threshold of the excitation stress, the luminescent film would be excited to emit light mainly at the points of the protruding part. Therefore, the luminescent intensities and patterns of the PLD can be tuned by changing the total area of the protruding structures (diameter and density) due to the different abilities for stress redistribution. Moreover, if each protruding point was regarded as a luminescent pixel, a patterned display can be designed and achieved, which may open up a new type of stress-activated displays.

As a demonstration, four patterns of the letter “F” were printed on the bottom plate composed of dots or lines of different total areas (Fig. 3a). Under pressing, the stress distribution of the luminescent film in PLD was concentrated along with the “F” pattern to emit blue-green light. Under the same force to the four PLDs, the

Fig. 1. (Color online) Structure and stress distribution of the piezoluminescent device (PLD). (a) Schematic to the PLD. (b) Stress simulation of piezoluminescent (PL) layer in PLD under pressing with stress concentrated at each point of the protrusions.
luminescent intensity was increased to show the letter “F” more clearly (Fig. 3b), which was attributed to the decreased total area of the protruding part for contact and stress concentration from the left to the right. The width and total length of the line were 0.4 and 103 mm in the first pattern, respectively, and the spot diameters in the remaining three patterns were 0.75, 0.5 and 0.5 mm, respectively. Under the same applied force of 150 N, the pressure on the luminescent films in Fig. 3a and b from left to right were increased from 3.65, 5.94, and 11.73 to 15.92 MPa, which was consistent with the principle of stress induced luminescence [23,24]. It was expected that the applied force was decreased with the reduced cross-sectional area of the pattern due to the enhanced stress concentration effect, but the mechanical stability of the device should be balanced.

The luminescence occurred twice in PLD with the stress applied and removed in one cycle. As shown in Fig. 3c, the luminescence peaks of the PLD appeared in pair in the press and release process. This phenomenon may be related to elastic deformation of luminescent film and the energy conversion process. At the moment of pressing, the elastic luminescent film in the PLD was deformed, part of the mechanical energy in the process was stored in the elastic film and another part was transferred to the phosphors and converted into light energy [25]. After removal of the stress, the deformation of the luminescent film was recovered, and the stored
mechanical energy was again released in the form of light. In general, as shown in Fig. 3d, all the luminance of the PLD during press and release increased with the increasing external pressure within a certain range (0–16 MPa). In addition, embedding the phosphor in the elastic and transparent polymer also protected the phosphor during the stress process to achieve high repeatability of the stress luminescence [9,10,12,17]. As shown in Fig. 3e, we repeatedly applied the same pressure to the device, and the luminous intensity maintained stable after 1,000 cycles, indicating a good stability of the PLD.

For display devices, other than brightness, the regulation of the color is also a key parameter [26,27]. The color of the light from the ZnS phosphors could be changed by doping different elements [28], e.g., ZnS:Cu emitted blue-green light, ZnS:Mn emitted orange light, and ZnS:Cu/Cl emitted white light [28–30]. It was expected to obtain a variety of colors by mixing different kinds of phosphors in certain ratios and then embedding them in the elastic transparent PDMS matrix [14,30,31]. However, the resulting PLD could only emit light with a single mixed color even under increasing stresses, and the color change could not be achieved in one device [29]. It was also reported that the ZnS:Cu phosphor had a blue shift in color under a high-frequency stress, while a negligible shift was generated under the low frequency. [15,16]

If one PLD can emit different colors of light by changing the external force, it would be useful for stress indication and dynamic display. Based on the single-layer luminescent film in PLD, we carried out bilayer structural design for the luminescent film to achieve chromatism. As shown in Fig. 4a, the structure of the PLD was the same as before, but the luminescent film consisted of the bilayer of green luminescent ZnS:Cu/PDMS and orange luminescent ZnS:Mn/PDMS composite layers. With the orange luminescent layer at the top, the PLD changed the light from green to a mixture color and orange along with the increasing forces (Fig. 4a and b). The PLD emitted tunable light from orange to green under increasing forces (Fig. 4c and d) if the green luminescent layer was made at the top.

In order to know the dependence of the color on sequence of luminescent layer and pressure, the stress distribution of the luminescent film was simulated by ABAQUS simulations. Under pressure, the protrusion of the bottom hard template of the device caused deformation of the luminescent film, and the stress was mainly concentrated at the bottom layer of the bilayer luminescent

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**Fig. 3.** (Color online) Piezoluminescence performance of the PLD. (a) Schematic illustration and (b) photographs of PLDs under pressing based on different array structures with increasing stress concentration. (c) Luminescence curve of PLD under repeated press and release. (d) Dependence of the piezoluminescence intensity of the PLD on increasing pressure. (e) Evolution of the piezoluminescence intensity of PLD during pressing cycles.
film (Fig. 4e) which was closer to the protrusion to emit green light (Fig. 4b). Under a higher pressure, the stress distributed at the top layer would raise over the threshold (Fig. 4f) to realize the increasing orange luminescence to show a mixed color like yellow for PLD (Fig. 4b). Similarly, as shown in Fig. 4d, when the composite film was made by putting the green and orange luminescent layers at the top and bottom, respectively, the PLD emitted orange light first and then a mixed color with green as the pressure increased. The color mixing phenomenon was similar to the previous report with mixed phosphors in the same film [31], while here it could be tuned by changing applied forces on the bilayer film. In order to characterize the change of the illuminating color in this process, we measured the CIE (Commission Internationale de L’Eclairage) color coordinates of the mixed light color from the PLD under different stresses, and plotted the color coordinates as shown in Fig. 4g. The color of the light can be adjusted in the region as the pressure changed.

In order to meet the development trends and requirements of flexible wearable devices [5, 6, 32, 33], we had further realized the construction of fully flexible PLDs by redesigning the flexible array structure for emitting light. As shown in Fig. 5a and b, the top and bottom layers of the PLD were made from transparent and flexible PDMS films, spring-like illuminating units as illuminating pixel points were vertically arranged and sandwiched by two transparent PDMS films. When the PLD was subjected to an external pressure, the PDMS film at the corresponding position drove the surrounding light-emitting unit to deform together, leading to light emission from the spring spots as shown in Fig. 5c. The spring-like illuminating units could also be horizontally arranged between two PDMS films to be luminescent under press (Fig. 5d and e). We also found that the PLD with horizontally arranged illuminating units emitted a more bright light than that with vertical arrangement (Fig. 5f). The flexible PLDs were stable even after the bending and twisting treatments (Fig. 5g–i), exhibiting promising potentials for wearable applications.

Then the luminescent intensity was measured. Both flexible PLD could illuminate at a lower pressure (5 N) than the rigid ones, and the intensity of the luminescence increased as the pressure increased (Fig. 5j and k). This may be attributed to the design of flexible and spring structure that could provide larger deformation for effective transfer and storage of mechanical energy [22]. By normalizing the luminescent intensity in Fig. 5l, the flexible PLDs with horizontally arranged illuminating units showed much higher intensity than that of horizontally arranged illuminating units under the same condition. This should be due to the larger effective deformation and light-emitting area. Therefore, the design of the different light-emitting unit structures and assembly forms could make the PLD more sensitive to stress, which would provide a new way for enhancing the piezoluminescence.
4. Conclusion

To summarize, PLDs were realized through the design of a patterned protrusion structure of the bottom layer for stress concentration to enhance the luminescent intensity. Besides increasing the pressing force, the luminescent intensity could be controlled by varying the patterned structures. The PLDs could also change the luminescent color under increasing forces by using a bilayer luminescent film composed of different kinds of phosphors. Based on this, the fully flexible PLD was also realized by designing the spring-like flexible light-emitting unit, which could be excited to emit light under a low external force. These PLDs are promising for a wide range of applications, such as illuminated floors, illuminated shoes, and even stress-activated displays and other flexible wearable facilities.

Conflict of interests

The authors declare that they have no conflict of interests.

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Appendix A. Supplementary data

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References


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