A self-healing and stretchable light-emitting device†

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A self-healing and stretchable phosphor sandwiched between two aligned carbon nanotube/polyurethane composite electrodes. The aligned carbon nanotubes may interconnect to recover the electrical conductivity while the polyurethane elastomer can recover the mechanical strength upon contact of the two broken parts. The wrinkled structure of the aligned carbon nanotube sheet and the use of the polyurethane elastomer further made the electroluminescent device stretchable. As a result, the self-healing and stretchable electroluminescent device maintained a stable luminescence after cutting and healing for 10 cycles and after repeatedly stretching and releasing for 350 cycles.

Displays, as a key tool for information dissemination and human–machine communication, are required for various portable or wearable electronic devices. A spectrum of display technologies based on light-emitting polymers,1,2 quantum dots,3 perovskites4 and nano-structured P–N junctions5 have been widely studied. For practical applications, these displays usually suffer from accidental damage caused by falling, colliding or squeezing etc. As a result, they may fail to work after the above irreversible mechanical damage, which remains a key challenge in the future development of light-emitting devices. Inspired by the regeneration process of human skin and other living organisms, a series of self-healing materials have been developed to heal the mechanical damage automatically with the help of micro-encapsulated healing agents,6 dynamic molecular interactions,7–9 solvent assistance10,11 etc. If the self-healing materials are used to make light-emitting devices, we may expect to solve the above challenge by self-healing the damage. Hitherto, a series of self-healing devices have been developed as energy storage devices,12 sensors,13 actuators14 etc. However, the realization of self-healing light-emitting devices due to the difficulty in finding matchable materials remains unaccomplished. On the other hand, it is also significant to know whether they are robust enough to endure some usual deformations like stretching and distortion. To this end, the light-emitting devices should be stretchable and may easily change shape with the applied force. The main components including an active layer and two electrodes must be stretchable.

ZnS phosphor-based electroluminescent (EL) devices have been extensively explored by dispersing these active inorganic materials in insulating polymer matrices as their EL layers in recent years.15–17 The unique dispersion structure opens up an effective avenue in the incorporation of the other functional components inside. Different from the carrier injection mechanism of light-emitting diodes, where indium tin oxide glass is commonly required as an electrode due to energy level matching and roughness less than a few nanometers,18,19 the alternative current activating mechanism of the ZnS phosphor broadens the way to select and design electrodes with accessional functions. Therefore, it may provide a general and effective paradigm in the fabrication of both self-healing and stretchable light-emitting devices based on the use of an active ZnS phosphor.

Herein, for the first time, a self-healing and stretchable EL device is developed from the ZnS phosphor layer sandwiched by two aligned carbon nanotube (CNT) sheet composite electrodes. For the EL layer, through the introduction of self-healing polyurethane (PU) as the polymer matrix, the continuity and mechanical strength of the EL layer can be recovered from the healing of the PU matrix by the interactions in disulfide metathesis of aliphatic disulfides.20 For the CNT sheet electrode where a wrinkled structure21,22 was designed on the self-healing PU, the aligned CNTs may recover the electrical conductivity due to the formed van der Waals forces among them,23 while the PU matrix recovered the mechanical strength (Fig. 1a). The wrinkled structure of the aligned CNTs and PU matrices also made the composite electrode and further the EL device stretchable. In this work, the novelty can be highlighted in the following...
aspects. (1) Self-healing light-emitting active layers were realized by compositing electroluminescent phosphors with self-healing elastomers. (2) Electrodes with high self-healing performances were achieved on the basis of van der Waals forces of CNTs. (3) Self-healing can proceed without high temperature and solvent assistance.

Self-healing, highly transparent PU was synthesized by polycondensation of poly(neopentyl glycol adipate) (PNGA) as a soft segment, isophorone diisocyanate as a hard segment and 2-hydroxyethyl disulfide as a self-healable component, which was verified by the Fourier transform infrared spectrum (Fig. S1, ESI†) and nuclear magnetic resonance spectrum (Fig. S2, ESI†). The self-healing process of PU occurred efficiently under heating at 60 °C (Fig. S3, ESI†). Ascribed to the metathesis of aliphatic disulfides, the elongation at break can be recovered by 97.7%, and the fracture strength may be recovered by 90.0% after heating at 60 °C for 2 h. Note that the resulting PU was highly transparent with the optical transmittance over 95% at the wavelength range of 400–700 nm (Fig. S4, ESI†), which made it promising for light-emitting devices.

The EL device was then made by an efficient solution-based process (Fig. S5, ESI†). For the healable and stretchable electrodes, the aligned CNT sheet drawn from the spinnable CNT array was paved on a 400% pre-stretched silicone substrate to form a wrinkled structure in advance, followed by coating with the PU solution to make a composite electrode. The healable EL layer was prepared by dispersing the ZnS phosphor into a self-healing PU matrix. The EL device was assembled by sandwiching the ZnS active layer with two CNT sheet composite electrodes under hot-pressing and heating. These materials were proved to be thermally stable during the whole fabrication process (Fig. S6, ESI†).

For the aligned CNT/PU composite electrode, the wrinkles of the CNT sheet ranged from hundreds of nanometers to a few micrometers (Fig. 1b). Owing to the solution-based process, PU permeated into the CNT sheet and formed an embedding structure, which was further verified by the cross-sectional SEM images (Fig. S7, ESI†). Besides, the density and size of the wrinkles can also be tuned by changing the pre-stretching length (Fig. S8, ESI†). For the EL layers (Fig. 1c), the micro-sized ZnS phosphors (Fig. S9, ESI†) were dispersed in the PU

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**Fig. 1** (a) Schematic illustration of the structure of the self-healing EL device. (b–d) SEM images of wrinkled CNT sheets, EL layers and the cross section of the EL device, respectively. (e–h) Photographs of an EL device being illuminated, cut, healed and re-illuminated, respectively. Scale bars in b, c, d and e–h, 5 μm, 100 μm, 500 μm and 1 cm, respectively.
matrix without fractures and holes. The cross-sectional image of EL devices (Fig. 1d, the interfaces of the electrode-EL layer-electrode laminated structure are indicated in red) revealed that the EL layer, with a thickness of about 100 μm, was integrated perfectly with the two electrodes after the hot-pressing and heating process, which was favorable for high mechanical stability. When an EL device (Fig. 1e) was cut (Fig. 1f), healed (Fig. 1g) and illuminated (Fig. 1h) again, no obvious differences were observed for the structure of the EL device, and the luminescent area remained homogenous without defects or dark spots.

To understand the details during the healing process, we systematically investigated the healing behavior of both the electrode and EL layers. The healable performances of the electrode (Fig. 2a–c) and EL layers (Fig. 2d–f) were firstly evaluated through visual inspection. The samples were prepared by cutting them into two separate parts and then bringing them into contact. The healing operation was carried out at 60 °C for 12 h. For the healed electrode, the aligned CNTs were connected with each other at the notch without gaps (Fig. S10a and b, ESI†). Besides, the connection between the CNT sheets at the notch was still kept at a high strain of 400% (Fig. S10c, ESI†). For the

Fig. 2 (a–f) Microscopic images of the aligned CNT sheet composite electrode (a–c) and the EL layer (d–f) before cutting, after cutting and after healing, respectively. (g) Dependence of electrical resistance on CNT thickness. $R_b$ and $R_a$ correspond to electrical resistances before cutting and after cutting and healing, respectively. (h) Dependence of electrical resistance on strain from 0% to 450% before cutting and after cutting and healing. (i) Dependence of electrical resistance on the number of stretching cycles. $R_0$ and $R$ correspond to electrical resistances before and after stretching, respectively. (j) Tensile stress–strain curves of original and healed EL layers. Scale bars in a–f, 400 μm.
healed EL layer, the cutting mark disappeared and the layer was recovered as a smooth film. Furthermore, the variations in electrical resistance for the CNT sheets with different thicknesses after healing were critical for the preparation of high-performance EL devices (Fig. 2g). After healing, the thicker CNT sheet electrode showed a lower increase in electrical resistance, e.g., 5.4% for a thickness of 54 nm. The more available CNTs can be better re-connected to more effectively recover the electrical conductivity after cutting and enable the two broken parts to contact. Accordingly, the optical transmittance of a thicker CNT sheet electrode was lower (Fig. S11, ESI†). Note that the optical transmittances can be increased to exceed 85% for applications after optimization. We chose the 54 nm-thick CNT sheets for the following EL devices.

The resistance variation of aligned CNT sheet electrodes against a strain from 0% to 450% was used to study the re-connection between the broken CNT sheets (Fig. 2h). The resistance almost stayed constant at strains of up to 350%, while it increased by three times at a higher strain of 400%, which was the pre-stretched elongation of elastic substrates.

![Fig. 3](image-url) (a) EL images of an EL device before cutting and after cutting and healing (the arrows indicate the position of the notch). (b) Dependence of luminance on the applied voltage before cutting and after cutting and healing. (c) Dependence of luminance on the number of cutting-healing cycles. L₀ and Lₐ correspond to luminances before cutting and after cutting and healing, respectively (cutting directions are vertical to the alignment of the CNT sheet). (d) Dependence of luminance on strain before cutting and after cutting and healing. (e) Dependence of luminance on the number of stretching cycles. L₀ and L correspond to luminances before and after stretching, respectively. (f) Photographs of illuminated EL devices: original, cut, healed and then stretched to 400%. Scale bar in a, 200 μm.
Then the resistance increased sharply after 400% strain due to the damage of CNT microstructures. Resistances of 200% and 300% pre-stretched electrodes also showed a similar tendency (Fig. S12, ESI†). The healed electrodes demonstrated high cycling stability during repeated stretching and releasing processes at a strain of 200%. The resistance increased to 106.2% after the electrode was stretched for 100 cycles in the original state and 250 cycles in the healed state (Fig. 2i). The healing of EL layers was also examined by a tensile test as shown in Fig. 2j, which showed that 96.3% of the original elongation at break and 80.4% of the original fracture strength were restored. The elongation at break of the sample healed for 3 h can reach 939.5%.

The influence of the self-healing process on the luminescence performance of EL devices was systematically characterized. If not specified, the EL devices were driven by a $V_{pp}$ of a 400 V sinusoidal signal at a frequency of 2.6 kHz, where the peak luminance was reached (Fig. S13, ESI†). The EL images were firstly recorded at the local cutting part before and after healing (Fig. 3a). The continuity of light emission at the notch was proved to be fully recovered. Moreover, the luminance of the EL devices as a function of applied voltage before and after healing was tested (Fig. 3b). With the increasing voltage, the emission intensity increased rapidly. According to the equation, i.e., luminance $L = L_0 \exp(b/V^{1/2})$, where the applied voltage $V$ is the only variation, and $L_0$ and $b$ are constants, the fitting curve matched well with the testing data and the maximum luminance was 121.2 cd m$^{-2}$ at 15 V $\mu$m$^{-1}$. The luminance can be further enhanced by increasing the mass ratio of the ZnS phosphor (Fig. S14, ESI†). More importantly, the luminance after healing was highly consistent with that of the original device with only 2.8% decrease at 15 V $\mu$m$^{-1}$. Furthermore, the reversible cutting and healing processes of the device could be repeated well after 10 cycles (Fig. 3c).

The reliability of healing for the EL devices was evaluated under deformations such as bending, twisting, and stretching (Fig. S15, ESI†). As Fig. 3d shows, the EL performance can be fully recovered even at 400% strain, which is also visually displayed in Fig. 3f. The luminance gradually increased when stretched to 400%, which was attributed to the following two reasons. Firstly, the thickness of the EL layers became thinner during stretching, resulting in an increase of electrical field strength. Secondly, the wrinkled CNT sheet smoothed out (Fig. S16, ESI†), causing a higher transmittance of CNT sheets (Fig. S17, ESI†). On the other hand, the current density–voltage performance also reflected the healing of the device. The increasing current density in the stretched state corresponded to the enhancement of luminance (Fig. S18, ESI†). Moreover, the lighting performances of the healed device were quite stable under the stretching and bending cycling test. The luminance can be maintained at 96.1% and 96.3% after 350 cycles at 200% strain (Fig. 3e) and 0.5 mm bending radius (Fig. S19, ESI†), respectively.

Due to the high self-healing performance, the self-healing display devices were demonstrated to overcome the breakage problems (Fig. 4a). A self-healing EL device displaying a smiley face was fabricated (Fig. 4b), where the patterned EL layer was prepared by embedding the designed EL layer into the PU matrix.

![Fig. 4](image-url)  
(a) Schematic illustration of the repair of the display of a cell phone based on the use of a self-healing EL device. (b–g) Photographs of a flexible self-healing EL device before breaking (b), after breaking (c), after healing (d), lighting without deformation (e), lighting after bending (f) and lighting after stretching (g). (h) Schematic illustration of multi-colored EL devices fabricated by healing building units. (i) Photograph of the multi-colored device before healing. (j) Photograph of the healed multi-colored device being illuminated. Scale bars in (b–g) and (i and j) 1 cm and 0.5 cm, respectively.
The device was then cracked into pieces (Fig. 4c) and reconstructed simply by putting these debris together (Fig. 4d). The healed “smiley face” functioned normally and can undergo various deformations such as bending and stretching (Fig. 4e-g). A pixel array display may be further achieved in the future when the AC electroluminescent devices are driven by matching control circuits.  

Thanks to the unique dispersion structure of the ZnS phosphor in the PU matrix, multi-color EL devices can be arbitrarily designed by using components with different colors and shapes (Fig. 4h). To construct light-emitting letters of “FDU”, the components, coming from green, blue and orange EL devices, were spliced, healed and illuminated as a whole device (Fig. 4i and j). This flexible multi-colored device can be wrapped on a finger (Fig. S20, ESI†).

In conclusion, a self-healing and stretchable EL device was developed for the first time by laminating ZnS-based self-healing EL layers in two self-healing CNT composite electrodes. The EL device can efficiently recover its luminance after multiple breaking and maintain its performance under deformations. The promising applications of self-healable display devices were demonstrated by repairing a broken display screen and fusing different colors and shapes of building EL parts into an integrated display system with designed patterns. This work provides a new and general platform for self-healing display devices which can also be customized personally.

Experimental section

Self-healing PU synthesis

10 g poly(neopentyl glycol adipate) in a three-neck vessel (M_w of 2000, Xinyutian Chemical Co., Ltd) was mechanically stirred and heated to 120 °C under vacuum for 1 h to remove moisture, and then cooled to 70 °C. 2.8 g isophorone diisocyanate (99%, Aladdin) and 0.07 g dibutyltin dilaurate (>95%, TCI) dissolved in 2 mL dried N,N-dimethylformamide (DMF) were added to a vessel dropwise and stirred for 3 h in an Ar atmosphere to obtain the prepolymer. Whereafter, when the prepolymer was cooled to 40 °C, 0.96 g 2-hydroxyethyl disulfide (99%, Sigma-Aldrich) dissolved in 3.5 mL dried DMF was added dropwise under stirring. Then 3 mL dried DMF was added to lower the viscosity of reactants after stirring for 1.5 h, and the reaction proceeded for another 1.5 h. Finally, 9 mL dried DMF was added and the products were vigorously stirred for 15 min to obtain a homogenous PU solution. The PU films were acquired by solution casting and solution evaporation at 60 °C for 12 h, 80 °C for 6 h, and 70 °C under vacuum for 12 h in turn.

Fabrication of self-healing EL devices

As Fig. S1 (ESI†) shows, for the preparation of stretchable and self-healing electrodes, the CNT sheet that had been drawn from a spinnable CNT array synthesized by chemical vapor deposition27-29 was drawn onto a 400% pre-stretched silicone film with the alignment of CNT sheets parallel to the stretching direction. Then the wrinkles of CNT sheets were formed by releasing the silicone film to the natural state, followed by coating with the PU solution to produce the composite electrode. The composite electrode was then peeled off from the substrate. The self-healing EL layers were obtained by solution casting and solvent evaporation of the mixture of ZnS phosphor (Obest Technology Co., Ltd) and PU solution at a weight ratio of PU to ZnS of 2/1. At last, the EL layer was laminated by two composite electrodes after hot pressing at 80 °C for 5 min, followed by heating at 60 °C for 6 h.

Conflicts of interest

There are no conflicts to declare.

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