

Supporting Information

Enhanced piezoluminescence in non-stoichiometric ZnS:Cu microparticles based light emitting elastomers

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FIGURES

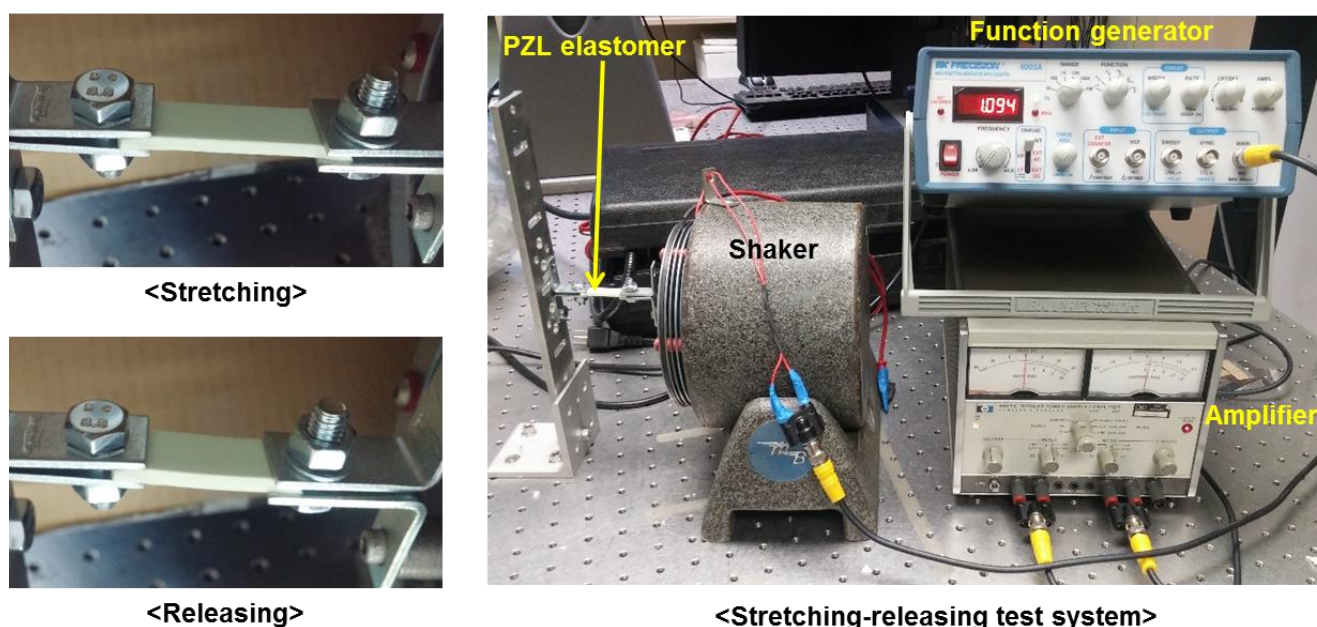


Fig. S1 Periodic stretching-releasing test system for applying cyclic stress on PZL composites.

Loading of PZL composite is shown to illustrate the measurement condition.

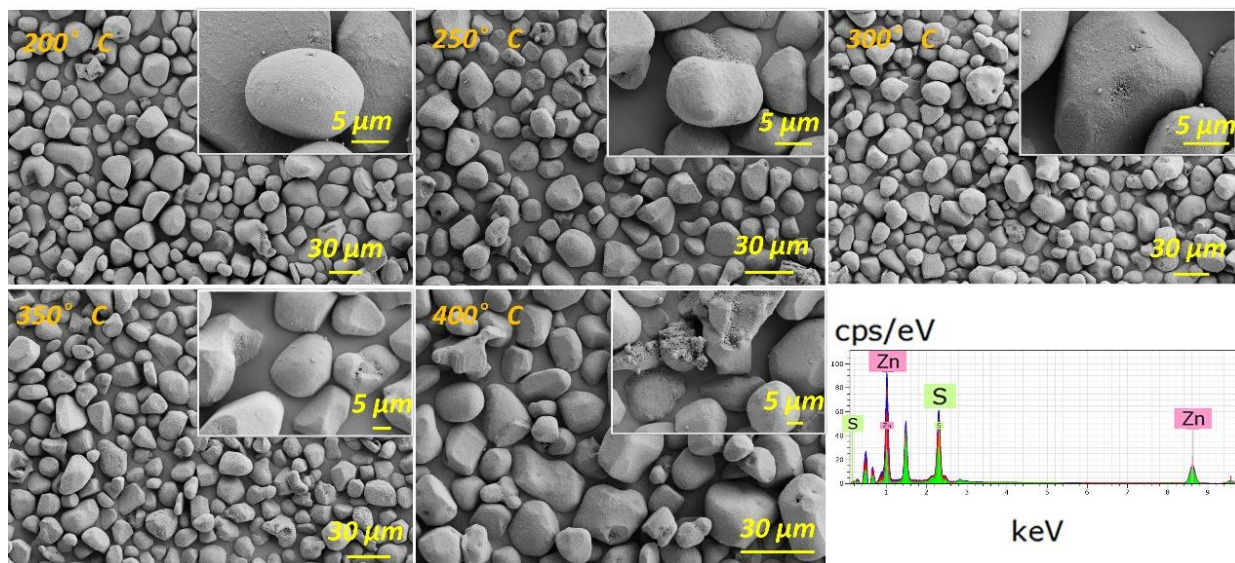


Fig. S2 SEM images of H-ZnS:Cu powder at different hydrogenation temperature and their EDS spectra.

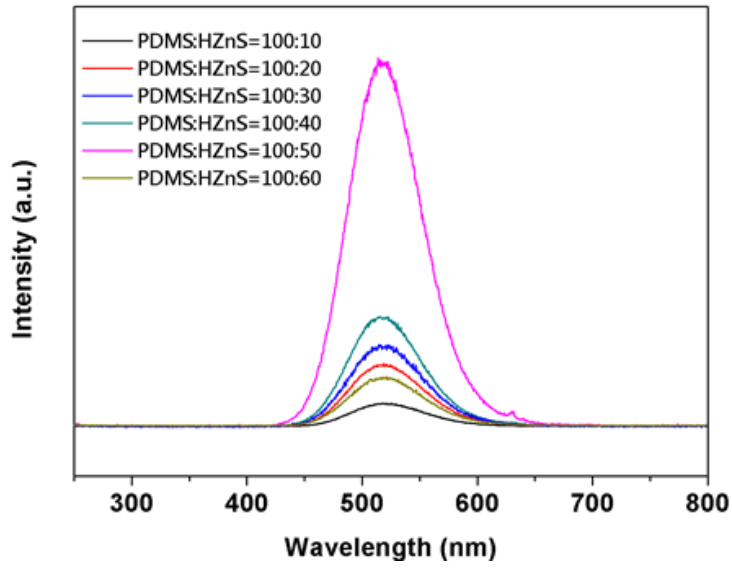


Fig. S3 PZL spectra of elastomer with different ZnS:Cu concentration.

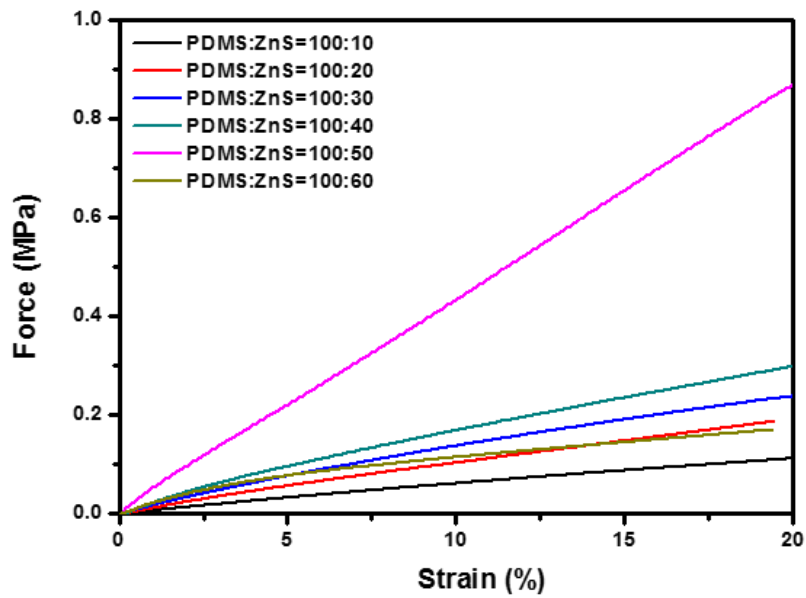


Fig. S4 Mechano-stiffness test on PZL elastomer samples with different PDMS:ZnS:Cu volume ratios (100:10 to 100:60). The measured size of each sample is 1 cm × 3 cm × 0.1 cm (width, length, thickness).

The intensity of PZL elastomer is strongly influenced by stiffness of the samples because different magnitude of stress is applied on ZnS:Cu particles under same strain. We found that the stiffness of elastomer is increased with increasing volume ratio of ZnS:Cu particles up to 100:50 composition and after that the stiffness starts to dramatically decrease to lower value (Figure S4). In case of high particle volume content (100:80, 100:90 etc.), the elastomer wasn't solidified after curing process. Significant difference in the intensity results corresponds well with different stiffness of the elastomer. We choose an optimum composition that has the highest stiffness leading to the highest PZL intensity in this study.

STUDY ON BASIC COUPLING MECHANISM IN PZL ELASTOMER

Besides the physical properties of ZnS that determines the PZL performance of elastomers, sample configuration is also important. Higher applied stress results in higher PZL intensity. To better understand the luminescence mechanism, we attempted to identify the relationship between applied stress and piezoelectric potential, as well as, the relationship between electric potential and luminescence.

Stress-Electrical potential

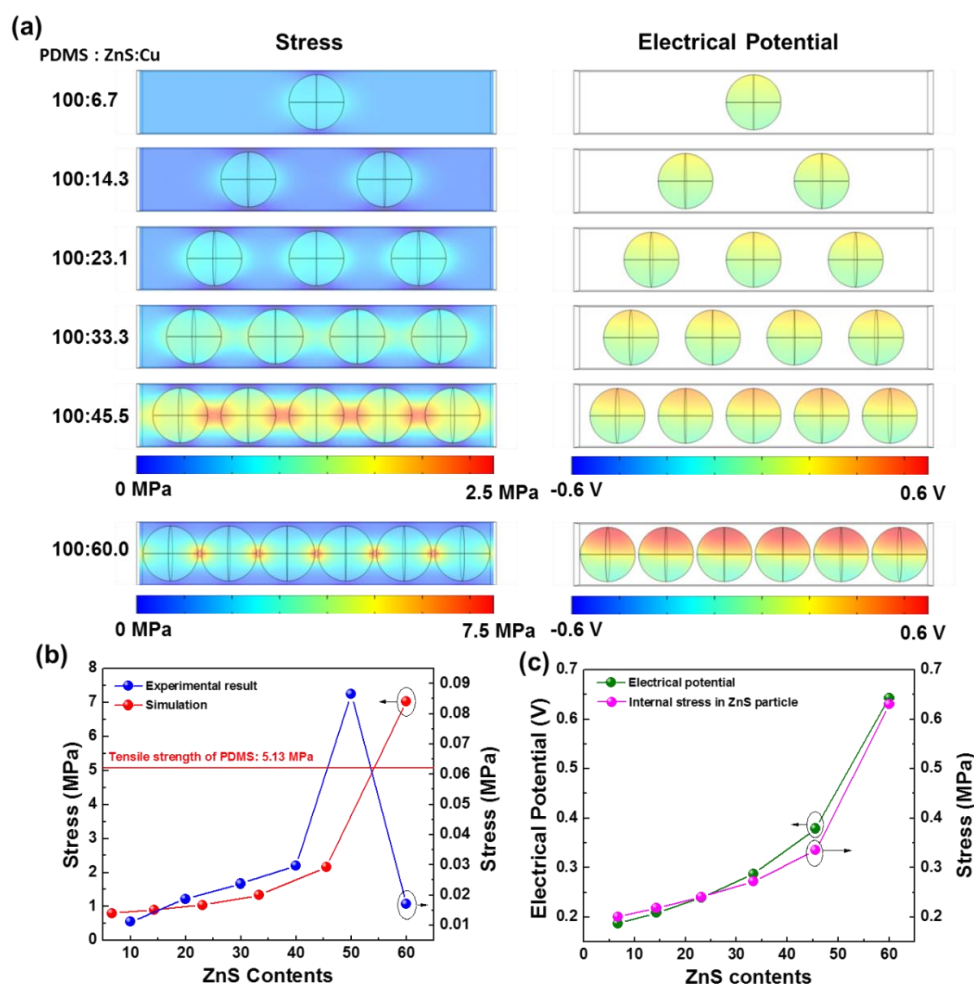


Fig. S5 Numerical simulation for stress induced electric potential in PZL elastomer with varying ZnS content.

To investigate the relationship between ZnS content and stress-induced internal electric potential in PZL elastomer, we performed numerical simulation using COMSOL. We assumed 25 μm -diameter ZnS particles are well-dispersed in the PDMS elastomer of $28.5 \mu\text{m} \times 28.5 \mu\text{m} \times 161.1 \mu\text{m}$ volume. The material properties of ZnS and PDMS were used from in-built material library. The internal stress profile and induced electrical potential were calculated when 10% strain was induced in PZL elastomer along length direction. Figure S5(c) shows internal stress (left) and electrical potential (right) profiles with different ZnS content. The stress and electric potential in PZL elastomer increases with increasing ZnS content. The trend of stress change between ZnS particles is very close to the experimental result in the mechano-stretch test under 10% strain (Figure S4 and S5). The induced stress exponentially increases near 100:45 composition in simulation, whereas it dramatically decreases near 100:60 composition according to the experimental result. This may be because the induced stress exceeds tensile strength of the PDMS (5.13 MPa) polymer near 100:60 composition leading to breakage of links between ZnS particles. These inside defects are generated in PZL elastomer after several stretching-releasing test cycle that decreases the stiffness of PZL elastomer as shown in Fig. S4. The induced electric potential, which is driving force for exciting trapped electrons, exhibits similar trend with applied stress in ZnS interior. This result is well aligned with piezoelectric theory, since the electric field and stress exhibit linear relationship following relation $E=gX$ where, E , g , and X are electric field, piezoelectric voltage constant, and applied stress, respectively.

Electric potential - luminescence

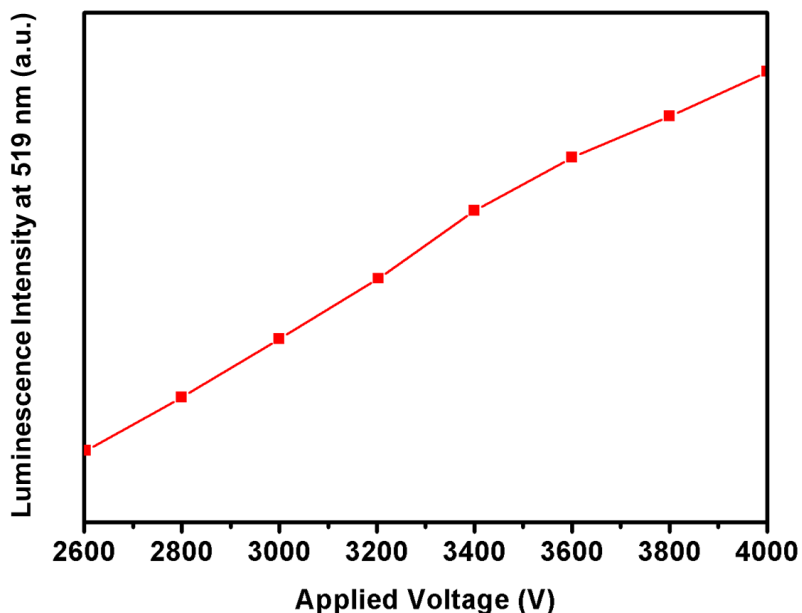


Fig. S6 Relative peak intensity from electroluminescence spectra at 519 nm as a function of applied voltage to the ZnS:Cu elastomer samples.

Figure S6 shows the relationship between applied voltage and the luminescence intensity at 519 nm. The result was obtained by collecting the peak intensity from spectrometer while changing the applied voltage to the elastomeric samples through a desktop size high power-high voltage power supply (Matsusada Inc, EPR). As PDMS has high resistance, we applied over 2 kV on the sample to enable bright light emission. The curve indicates that the brightness will increase linearly as electric voltage is increased. Similar trend was observed in Hurd's work[1].

Experimental condition – stiffness, strain, and strain rate

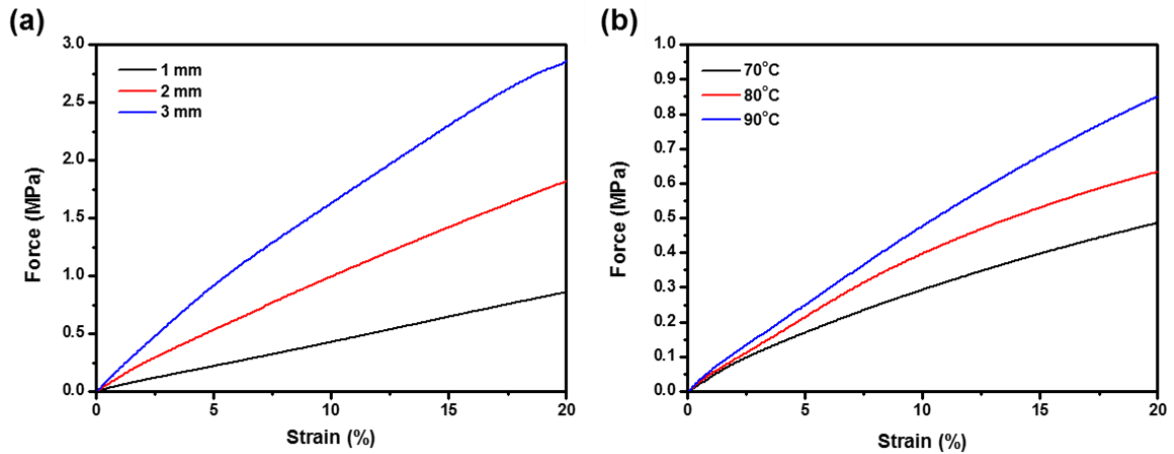


Fig. S7 Mechano-stiffness test on PZL elastomer samples of PDMS:ZnS:Cu (100:50). (a) sample thickness varying from 0.1 cm to 0.3 cm at the same curing temperature of 90 °C. (b) curing temperature varying from 70 °C to 90 °C for the same thickness of 0.1 cm.

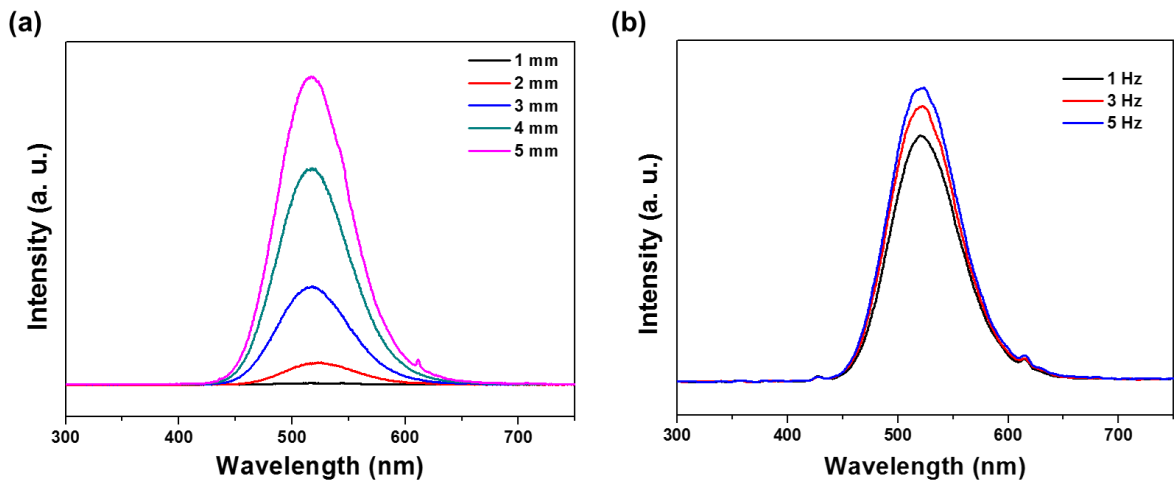


Fig. S8 PZL spectra of elastomeric sample of PDMS:ZnS:Cu (100:50) under a varying (a) extension length and (b) extension rate.

References

[1] Hurd, J. M.; King, C. N., Physical and Electrical Characterization of Co-Deposited ZnS-Mn Electroluminescent Thin-Film Structures. *J. Electron. Mater.* **1979**, *8*, 879-891.