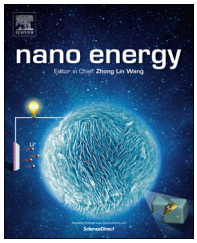
Nano Energy (▮▮▮▮) ▮, ▮▮▮–▮▮▮

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/nanoenergy



COMMUNICATION

Simultaneous dual-channel blue/green emission from electro-mechanically powered elastomeric zinc sulphide composite

Soon Moon Jeong*,[1], Seongkyu Song[1], Hyunmin Kim

Division of Nano & Energy Convergence Research, DGIST, Daegu 711-873, Republic of Korea

Received 3 November 2015; received in revised form 30 December 2015; accepted 15 January 2016

KEYWORDS
Mechanoluminescence;
Electroluminescence;
Color;
Dual-channel;
Composite

Abstract
Mechanoluminescent (ML) materials, which luminesce in response to mechanical stimuli, are attractive candidates in developing energy-sustainable technology and are widely used in sensors, ubiquitous light sources, and displays. Metal-doped zinc sulphide (ZnS) is considered a promising ML material because it produces intense and lasting luminescence under repeated mechanical stresses. Previous studies of ZnS luminescence have focused on single-channel emission by electroluminescence (EL) or ML generated by applied electric fields or mechanical stresses, respectively. Here, we report the simultaneous generation of EL and ML from an elastomeric ZnS composite embedded with silver nanowires and demonstrate the independent control of both EL and ML responses. We describe the tuning of the strength and color of the EL/ML emissions from a single ZnS-based structure by applying combinations of electrical and mechanical excitation forces. We also demonstrate a multi-color-patterned EL/ML emitting display using the ZnS-based composite; this application may provide a basis for the development of new optomechanical displays.

Introduction

Luminescence phenomena occur when the electronic states of a solid are excited by external energy and the excitations are released as light [1]. One such phenomenon, mechanoluminescence (ML), is defined as the generation of light by the application of a mechanical stress to a substance [2-6]. The demonstration of elastico-ML, in which tensile stresses produce photoemissions [7], has stimulated considerable interest in the study of ML; remarkable advances have been achieved in this field [8-10]. Zinc sulphide (ZnS) is considered a promising ML-producing material because of the intense and durable ML responses it displays under repeated stress applications [11-17].

*Corresponding author.
E-mail address: smjeong@dgist.ac.kr (S.M. Jeong).
[1]These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.nanoen.2016.01.012
2211-2855/

Recently, a ZnS-microparticle-embedded polydimethylsiloxane (PDMS) composite (ZnS+PDMS) has received increasing attention as an ML-generating source because it shows high durability, designability, and tunability under various mechanical deformations [6,11-13,18-19]. Notably, a PDMS-based structure of thick powder-based ZnS+PDMS films sandwiched between two electrodes exhibits alternating-current electroluminescence (ACEL) characteristics. The PDMS acts as both a dielectric material and a binder. The application of stretchable transparent electrodes [20-22] in such structures facilitates the development of intrinsically stretchable EL devices with good performance under large strain cycles [23]. Thus, the ZnS+PDMS composite can offer simultaneous EL and ML from a single material by combining different excitations of applied electric fields and mechanical stresses.

Luminescence is produced from ZnS by introducing lattice defects that deviate from the stoichiometric Zn/S ratio and by doping the material with impurity atoms called activators [24]. Most studies on ZnS ML have reported single-emission spectra with single colors determined by the types of dopants [11-13,16-19]. However, studies of EL have shown tunable emission colors by varying the applied electrical frequency [25-27]. The color of the EL from ZnS+PDMS composites can be changed by varying the electrical frequency applied to the composite. At high excitation frequencies, a blue-colored EL occurs because of the higher contribution from the deepest energy levels, or blue centers. In contrast, at low frequencies, the emission is dominated by energy levels emitting in the green range [13,18-19].

Based on blue EL generation from ZnS+PDMS composites at high-frequency electrical excitations, we have obtained blue-colored ML under harsh mechanical vibration conditions provided by strong winds, while weaker mechanical excitations produced green emissions [13]. This previous work suggested similar behaviors in EL and ML responses to applied electrical or mechanical frequencies. The relationship between EL and ML is not clearly understood, but it is generally accepted that two emission bands of blue and green exist in ZnS phosphors [28-29]. We previously proposed an explanation for ML color shifts [11] employing the mechanism of photoluminescence (PL) [30-33]. The green emission may arise from the transition between impurity-induced shallow donor states and the t_2 state of Cu [30-31], whereas the blue emission may relate to the e state [32-33]. Recently, Hao and co-workers provided an alternate explanation, ascribing blue emissions to the donor-acceptor (A) emission process of V_S (sulfur vacancies at shallow donor level) and Cu_{Zn} (Cu^+ substituted for Zn^{2+} at acceptor level) and green emissions to D-A pair recombination between Al_{Zn} (Al^{3+} substituted for Zn^{2+} at donor level) and Cu_{Zn} [18-19]. No uniform model exists yet concerning the color shift as well as the generation mechanism of ML in ZnS. However, according to previous reports [11-13,18-19], we note that mild mechanical excitation has been reported to emit green ML because it is insufficient to activate blue emission centers, whereas the application of high electrical frequency is sufficient to shift the excitation from the green to blue centers.

Here, we demonstrate the successful manipulation of dual-channel EL and ML emissions from a single ZnS-embedded PDMS composite by the simultaneous application of electrical and mechanical inputs. To our knowledge, this work reports the first demonstration of simultaneous EL and ML generation from a single system. The colors of the EL and ML can be independently regulated by controlling the excitation strength of each source. Under high electrical frequencies, the blue EL spectrum is reinforced, whereas the green ML is dominant in low-frequency conditions. We believe that this ML-based stretchable electronic light source could be applied to advanced systems such as wearable multifunctional sensors/displays, biomedical devices, and electronic skin, which are subjected to large body movements [34].

Materials and methods

Materials and EL/ML sample fabrication

To fabricate the EL/ML-emitting elastomeric ZnS composite, two Ag nanowire (AgNW)-embedded PDMS plates (~300 μm thick) were prepared using a transferring process from a glass substrate to PDMS. Initially, AgNW dispersed in ethanol (SLV-NW-35, Blue Nano Inc.) was spin-coated onto a pre-cleaned glass substrate at 500 and 100 rpm for the top and bottom plates, respectively, and subsequently dried at 100 °C for 1 min. Prior to spin-coating, part of the glass was screened with tape to form an electrode with an active emitting area of 1×2 cm^2 at the intersection of the bottom and top AgNW strips. Liquid PDMS (Sylgard 184, Dow Corning) with a curing agent at a weight ratio of 10:1 was cast on top of the AgNW film and subsequently cured at 100 °C for 35 min under Al mold pressure for uniform thickness. After peeling away from the glass, the AgNW film was buried at the surface of the cured PDMS to form a conductive and stretchable layer [21]. The electrical conductivity was realized by the two-dimensionally percolated AgNW networks. For the emitting layer (ZnS+PDMS composite), ZnS doped with a Cu-based phosphor (~25 μm average particle diameter, Figure S1, Supplementary Materials; (GG64, Global Tungsten & Powders Corp.) and liquid PDMS with a curing agent (weight ratio 10:1) were mixed at a weight ratio of 7:3 and subsequently sandwiched between the previously prepared AgNW-embedded PDMS layers at 100 °C for 35 min. More information regarding the EL and ML characteristics of the ZnS+PDMS composite used here, but arranged in different device architectures, is described in our previous reports [11-13]. The thickness of the ZnS+PDMS composite layer was determined by scanning electron microscopy (SEM, Hitachi SU8220). To fabricate the patterned bottom AgNW electrode, bird- and flower-shaped patterns were created using tape screening and spin-coating at 100 rpm of the AgNW solution. The detailed fabrication process of this device is provided in Figure S2 (Supplementary materials).

Electro-optical characterization

Electro-optical measurements of the ACEL devices were performed by applying a sinusoidal voltage of 150 V amplitude under frequencies of 10, 30, 50, 100, 200, 300, 500, 800, and 1000 Hz from a function generator (AFG3102, Tektronix) with a voltage amplifier (HAS4051, NF Corp.).

Please cite this article as: S.M. Jeong, et al., Simultaneous dual-channel blue/green emission from electro-mechanically powered elastomeric zinc sulphide composite, Nano Energy (2016), http://dx.doi.org/10.1016/j.nanoen.2016.01.012