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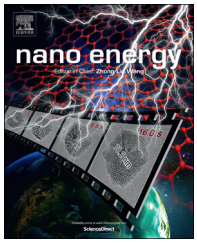

White and green light emissions of flexible polymer composites under electric field and multiple strains

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Abstract
The development of energy harvesting white light sources converted from multiple stimuli especially mechanical strain requires the search of new types of phosphors and devices. In this work, various flexible composites of single-phase metal ion-doped ZnS mixed to polydimethylsiloxane (PDMS) matrix have been prepared. The synthesized composites possess flexible, durable, easy fabrication, and compatible with arbitrary substrate characteristics. With the advantages of the flexible composite, we have fabricated two kinds of light-emission devices, namely flexible electroluminescence device with graphene electrode, and piezo-phototronic luminescence device composed of polymer phosphor layer coated on the top of piezoelectric actuator. Such composite phosphors and the related hybrid devices are capable of responding to different types of external stimuli, including electric field, uniaxial strains of stretch and mechanical writing, and piezoelectric biaxial strain, resulting in the observed white and green light emissions by the naked eyes. The stimulus excitation, resultant luminescence spectra, and their relations with color properties (color coordinates, color temperature, etc.) of the white light emission have been investigated. The observation is ascribed to the non-central symmetric crystal structure of wurtzite-type ZnS material, inherently producing piezoelectric effect under strain. Energy transitions of the observed white light emissions may originate from the donor-acceptor pairs recombination between $Al_{Zn} \rightarrow Cu_{Zn}$, as well as the radiation transition between $^4T_1$ and $^6A_1$ of Mn^{2+} ion. Our results show promise in constructing new types of flexible light source for applications in sustainable energy and so on.

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Introduction

Energy-saving solid-state lighting based on light-emitting diode (LED) has increasingly been used in our daily life, such as general illumination and backlight for liquid-crystal display [1]. Currently, white light is typically obtained based on a phosphor-converted method. In this technique, InGaN blue LED illuminates a phosphor (e.g., YAG: Ce) layer coated on the blue LED chip to emit yellow light, and then the white light is formed when the remaining blue light is mixed with the yellow light emitted from the phosphor [2]. Obviously, the commonly used inorganic white light source is consisted of p-n junction based blue LED and LED pumped inorganic phosphor, which are both rigid in nature. Therefore, it is fascinating to explore new strategies with the configurations beyond the existing semiconductor p-n junction based structure. Particularly, it would be more attractive if the light sources with flexible feature can be triggered by multiple stimuli, such as electric field and various mechanical stresses. Such flexible optical devices are promising for many applications, including self-powered and energy harvesting optical systems, remote sensing without making electric contact, smart skin, bio-labels in response to pressure and flow.

According to the type of excitation source, it is well-known that luminescence can be classified as photoluminescence (PL), electroluminescence (EL) and mechanoluminescence (ML), and so on. Compared to the PL and EL studies, ML has attracted much less attention so far. One of the reasons is that ML phosphors have suffered from destructive and poorly reproductive features. In order to make traditional ML phosphors useful in practical applications, it is essential to develop a so-called elastico-mechanoluminescence (EML) material which can emit luminescence during elastic deformation without fracture. The EML materials are expected to convert mechanical energy into light emission. Up to now, Xu's group has developed a series of EML phosphor materials with different emission colors by doping rare-earth-ions into silicates, titanates, aluminates as well as zinc sulphide (ZnS) [3]. These phosphor materials can be synthesized in several forms, including particle, thin film, ceramic disk, pellet, and composite. The characteristics of sensing various mechanical stresses have shown the potential in a range of applications, such as stress sensor, optical imaging, artificial skin, and structural health diagnosis [4,5]. Very recently, Jeong et al. presented the color manipulation by controlling the weight ratio of two different ML materials emitting orange and green colors in a soft polymer matrix under mechanical stress stimulation [6]. The color region can also be tuned by varying stress rate. Furthermore, a wind-driven ML system consisted of phosphor particles embedded in an elastomer has been demonstrated. The interesting results imply a potential use in harvesting wind power for illumination [7], although the gas flow simulated as wind requires a speed of 40–100 m/s which is within the range of hurricane or typhoon and therefore further improvement is needed to suit for more accessible mechanical stimulus.

On the other hand, Wang coined a new research field of piezo-phototronics. The piezo-phototronic effect is a three-way coupling among piezoelectricity, luminescence and semiconductor behavior [8]. It suggests that applying a strain to a semiconductor with piezoelectricity can tune the charge transport behavior and then improve the performance of optoelectronic devices [9]. One group of candidate materials applicable to the piezo-phototronic effect includes the semiconductors of ZnS, ZnO, and GaN with wurtzite non-central symmetric structure. The strain-induced piezoelectric potential is capable of turning and gating the transport properties of carrier in semiconductors [8,10]. By coupling piezoelectric, semiconducting, and photonic characteristics, the performances of optoelectronic devices such as LED and solar cell have been improved [9,11,12]. Inspired by this idea, we have previously reported the piezo-phototronic effect-induced dual-mode orange light and ultrasound emissions from ZnS:Mn thin film grown on piezoelectric $Pb(Mg_{1/3}Nb_{2/3})O_3$-$xPbTiO_3$ (PMN-PT) substrate [13]. However, the reported thin-film structure fabricated by pulsed laser deposition (PLD) is rigid, limiting the wide application of ZnS based phosphors. In this work, various flexible composites of metal ion-doped ZnS mixed to polydimethylsiloxane (PDMS) matrix have been prepared. Compared to our previously reported rigid thin-film structure by PLD, the synthesized composites are flexible, durable, easy, and cost-effective fabrication with no use of vacuum, and compatible with almost any type of substrate. With these merits of the composite phosphors, we have further designed and fabricated two types of light-emitting devices from the composite phosphor-based hybrid structures free of p-n junction. White and green light emissions are achieved under different external stimuli, including electric field, uniaxial strains of stretch and mechanical writing, and piezoelectric biaxial strain.

Experimental section

Synthesis of flexible phosphor composite

The flexible phosphor composite was made of metal ion-doped ZnS particles and PDMS. Single-phase metal ion-doped ZnS powders (green: ZnS:Al,Cu (GGS42) or white: ZnS:Al,Cu,Mn (GG73), Global Tungsten & Powders Co.) were homogenously mixed into a PDMS matrix. The PDMS consists of base and crosslink at a weight ratio of 10:1. Consequently, metal ion-doped ZnS based powders (70 wt. %) and the PDMS host (30 wt. %) comprise the flexible phosphor composite.

Fabrication of flexible EL device

A large-area single-layer graphene grown by chemical vapor deposition (CVD) was transferred on a polyethylene terephthalate (PET) substrate as the transparent conductive electrode. The composite layer with the thickness ranging from 100 to 150 μm was spin-coated on the graphene/PET substrate. And then the prepared sample was cured at 70 °C for 30 min. Finally, an Au film with a thickness of 100 nm was thermally evaporated on the surface of the flexible composite as bottom electrode.

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