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

Li Chen[a,b], Man-Chung Wong[a,b], Gongxun Bai[a,b], Wenjing Jie[a,b], Jianhua Hao[a,b,n]

[a]Department of Applied Physics, The Hong Kong Polytechnic University, Hong Kong, China
[b]The Hong Kong Polytechnic University Shenzhen Research Institute, Shenzhen 518057, China

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 polydimethyl- siloxane (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}-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.

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 mm was spin-coated on the graphene/PET substrate. And then the prepared sample was cured at 70 1C 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.

Fabrication of piezo-phototronic luminescence device

A PMN-PT single crystal oriented (001) (Hefei Kejing Material

Technology Co., Ltd.) with the dimension of 5 mm Â 5 mm Â 0.5 mm was used as the substrate. Au electrodes with different thickness of 100 nm and 200 nm were deposited by sputtering technique on the top and bottom surface of PMN-PT, respectively. The flexible phosphor composite was spin-coated on the PMN-PT substrate and cured at 70 1C for 30 min.

Luminescence spectra and color measurements

The luminescence spectra were recorded by an Edinburgh FLSP920 spectrophotometer or an Ocean Optics USB4000 CCD spectrometer. A spectroradiometer (PR-670, Photo Research Inc.) was used to measure color properties, including Commission Internationale de L'Eclairage (CIE) coordinates, luminance, and correlated color temperature (CCT). In the piezo-phototronic luminescence device, the PMN-PT substrate which can provide biaxial strain to the phosphor composite was polarized with a Keithley 2410 high-voltage source meter. When applying an external voltage, the ac voltage was amplified by a high voltage linear power supplies (KEPCO Inc.). The light-emitting images were captured by a digital camera (Sony Nex-5T). For the uniaxial strain measurement, a home-made stretching-releasing (S-R) system was used, which was composed of a stretch and release platform, as well as a step motor with variable stretching rate.

Results and discussions

Figure 1 shows a basic strategy for light-emissions from the flexible phosphor composite under different stimuli in this work. Various flexible composites of single-phase metal ion-doped ZnS mixed to PDMS matrix are served for the phosphor sample. It is known that ZnS is an excellent optoelectronic semiconductor. Furthermore, ZnS also exhibits piezoelectric effect due to its non-central symmetric wurtzite structure, resulting in piezoelectric potential when applying strain. PDMS chosen here works as a packaging material to encapsulate the metal ion-doped ZnS particles and transmit external stimuli to the luminescent centers. PDMS features high flexibility, high optical transparent,
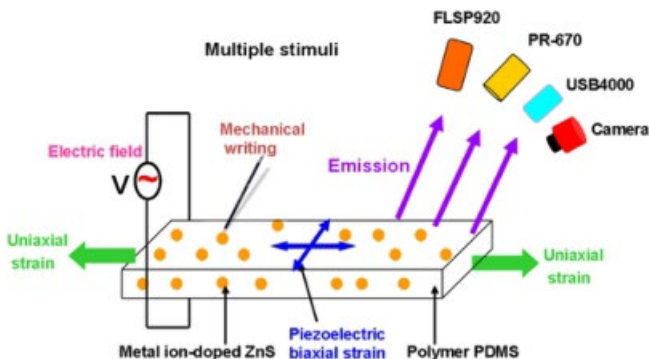

Figure 1 **Schematic strategy of light-emissions from the flexible phosphor composite under multiple stimuli.**

durable, and low cost characteristics, which has widely been used in the fields of flexible solar cell, biological sensor, and piezoelectric nanogenerators [14,15]. In our experiments, this metal ion-doped ZnS + PDMS flexible composite can be either used individually or coated on arbitrary substrates. Therefore, two types of devices with different hybrid structures, that is, flexible EL device with graphene electrode and piezo-phototronic luminescence device using PMN-PT wafer can be designed and fabricated. These structures will be simply triggered by various types of stimuli to generate light. Figure 1 shows four kinds of stimuli acting on the metal ion-doped ZnS + PDMS flexible composite, including electric field, uniaxial strains of stretch and mechanical writing, and piezoelectric biaxial strain. Light emissions can be recorded by a digital camera and various spectrometers as shown in Figure 1. Consequently, the fabricated composite can be employed as a basic component for multiple purposes which will be described as follows.

White light-emission of flexible EL device

Flexible materials and composites have widely been used in optoelectronic devices, including LED, photodetector, and touch-screen panel [16]. In this study, we demonstrate a flexible EL device based on the fabricated composite. The schematic structure of a flexible EL device is presented in Figure 2a. A single-layer graphene as a top electrode was transferred on a flexible and optical transparent PET substrate. The prepared flexible composite consisted of metal ion-doped ZnS (ZnS:Al,Cu,Mn) and PDMS was used as the phosphor layer, and the Au thin film was employed as the bottom electrode. Traditionally, indium tin oxide (ITO) film has commonly been used as transparent conductive electrode. However, the brittle property of ITO hampers its bending in flexible optoelectronic devices. In comparison to ITO film, the large-area CVD-grown graphene here possesses good flexibility, excellent mechanical properties, high electrical conductivity, and optical transmittance [17]. The configuration of our flexible EL device is simpler than that of traditional alternate current electroluminescence (ACEL) rigid device where inorganic dielectric layer is usually needed. When applying an ac voltage of 100 V at the frequency of 1 kHz, white light-emission was observed. Figure 2b exhibits the EL spectrum of the device. The inset photograph shows the bright white light-emission which can be observed by the naked eyes, even though the flexible device was greatly bent. Note that the white EL spectrum consists of two main peaks of 512 nm and 588 nm, plus one minor shoulder band located at around 460 nm. The feature of the measured EL spectrum can be understood by considering the energy transition as shown in Figure 2c. When an electric field is applied to the EL device, piezoelectric ZnS grains provide surface charges and lattice dislocations on the grains [18]. Then sulphur vacancies (V_S) will trap electrons to form shallow donor levels below the conduction band (CB), while Al_{3+} substitutionally occupies the Zn_{2+} site (Al_{Zn}) to generate another donor levels deeper in the CB, and Cu_+ substituted for Zn_{2+} (Cu_{Zn}) will create acceptor level above the valance band (VB) which can trap holes [19]. With an increase in piezoelectric field, the
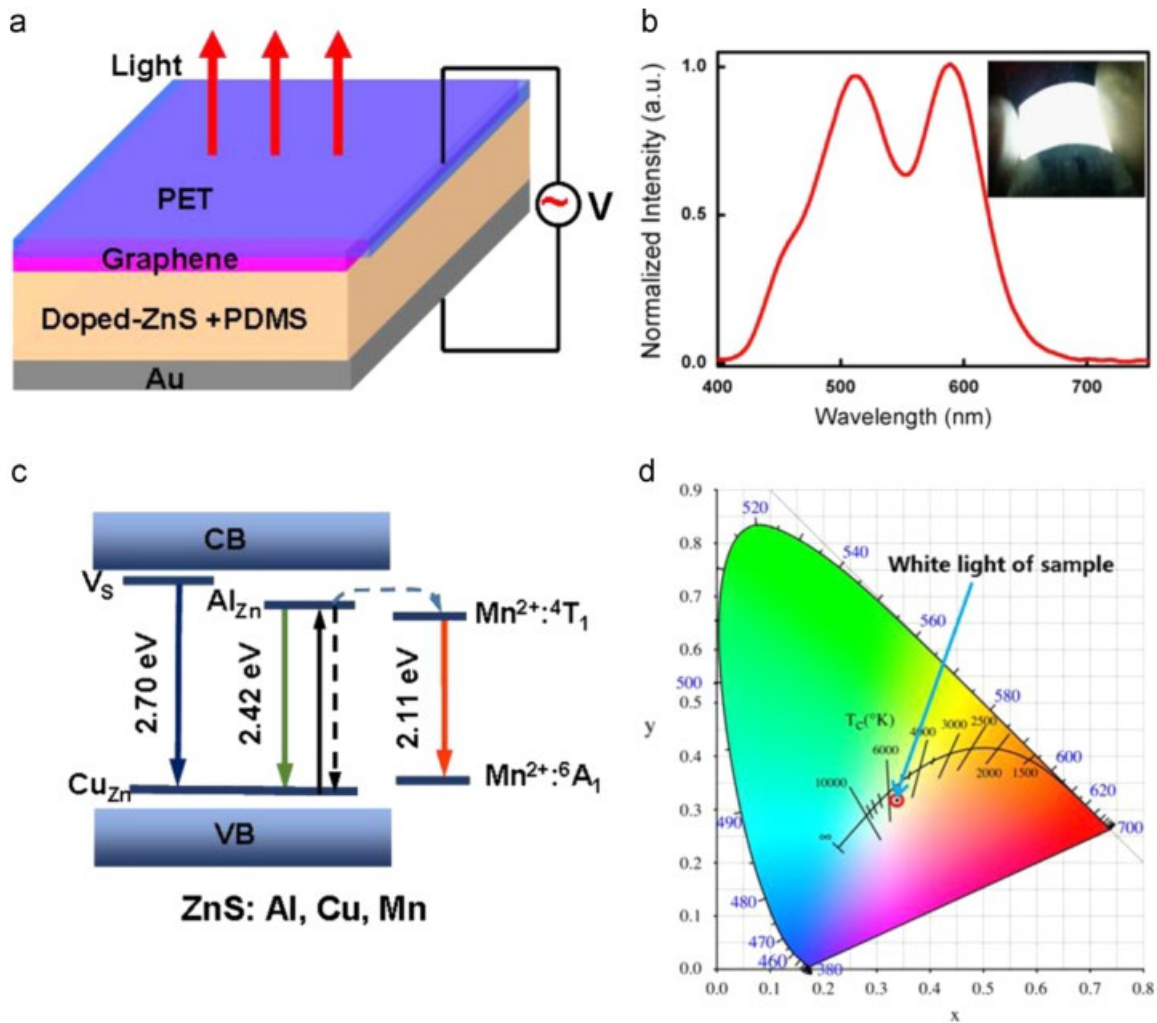
Figure 2 **Device structure and light-emission of the flexible EL device with graphene electrode. (a) Structure of the device. (b) Luminescence spectrum of the device biased at 100 V and 1 kHz. The inset shows the photograph of white light-emission. (c) Energy level diagram of ZnS:Al,Cu,Mn phosphor. (d) CIE diagram showing the white light of EL sample.**

carriers in the luminescent center are excited to a higher energy level because of the strong interaction. Subsequently, luminescence is induced by the electron-hole recombination. Considering previous report [20,21], the minor shoulder band of luminescence spectrum around 460 nm (2.7 eV) can be ascribed to the donor-acceptor (D-A) type emission process of V_S-Cu_{Zn}. In addition, the intense light emission at 512 nm (2.42 eV) originates from the D-A pairs recombination between Al_{Zn}-Cu_{Zn}, while another main band peaked at 588 nm (2.11 eV) is due to the radiation energy transition between $^4T_1$ and $^6A_1$ of Mn^{2+} ion [22]. The Mn^{2+} ion related emission is deduced to an effective nonradiation energy transfer from Al_{Zn}-Cu_{Zn} to Mn_{Zn}. For the measured spectrum overall, the three emission bands give rise to the observed white light-emission.

Accordingly, the CIE coordinates are determined to be (0.3386, 0.3167), and the CCT is 5165 K. Hence, this device emits a somewhat cool white color as shown in Figure 2d. It is interesting to compare this device with other types of devices emitting white light as follows, keeping in mind that the comparison is not clear-cut because the EL measurements were not made under identical conditions. In earlier year, Okamoto et al. reported white-emitting thin-film EL device with the phosphor layer of SrS:Sm,Ce, showing the CIE coordinates of (0.35, 0.38) at a sinusoidal applied voltage of 5 kHz [23]. In addition, the most widely used white LED as above introduced consists of InGaN blue LED and YAG:Ce yellow phosphor. Unfortunately, this type of white LED lacks red and green light, resulting in high CCT and low color rendering index. These drawbacks had motivitated some researchers to search alternative approaches, such as new system of non-rare-earth phosphors [24], and mixture of green and red phosphors instead of single YAG: Ce phosphor [25,26]. It is noticeable that such LED-based white light-source lamp originating from a small area can be precisely imaged and directed with downstream optics. However, these point-source lamps are difficult to achieve when "useful" amounts of light for general illumination are desired [27]. Differing from the point-source lamps of conventional white LED with rigid structure, our white light source shows a promise in terms of flexibility and planar structure with large-area. Certainly, it is much needed to reduce the operating voltage and increase white light emission efficiency through optimizing the design and fabrication process of the device for practical application in the future work.

Uniaxial strain induced luminescence

Compared to extensively studied PL and EL, there has been limited report on the white light luminescence triggered by mechanical strain, because most of the ML phenomena are weak and irreproducible. Fortunately, the introduction of EML materials allows us to develop novel phosphors which are capable of converting mechanical stress into light emission. In this work, the flexible composite layer consisted of metal ion-doped ZnS and PDMS was stimulated by uniaxial strain of stretch and release, resulting in the white and green light emissions. Figure 3a shows the flexible phosphor composite layer with the thickness ranging from 400 to 800 mm and an unstretched length of 4 cm mounted on the S-R system. It is known that the polymer thickness can affect the strength and endurance of the sample. When the step-motor is operated, the composite is first stretched to one direction and then returned back. Such a complete process is regarded as one cycle here. Then the step-motor would repeat the motion in a pre-set period. Luminescence can be observed by the naked eyes, as shown in Figure 3b. The blurred image is mainly due to the sample's motion.

Figure 3c shows white light emission spectra of the flexible phosphor composite at the S-R rate between 100 and 400 cycles per minute (cpm). Apparently, the white ML spectra consist of two main peaks at 525 nm and 588 nm, which are slightly different from the EL spectra composed of main peaks at 512 nm and 588 nm as shown in Figure 2b. Furthermore, a minor shoulder band located at around 460 nm in the EL spectrum is not apparent in the ML as shown in Figure 3c. It is speculated that the frequency of S-R system is not high enough to activate the blue emission peaked at 460 nm sufficiently [7], as the maximum rate of 400 cpm used in our test is approximately equivalent to 6.7 Hz, which is far less than the voltage frequency of 1 kHz on EL device. Noticeably, ML intensities at both two peaks increase linearly with the increasing S-R rate. It can be explained that more charge carriers are detrapped with increasing S-R rate, resulting in the enhancement of electron-hole recombination [28]. It seems that luminescence intensities at two peak wavelengths are increased with different slope as the S-R rate ranges from 100 to 400 cpm (Figure 3d). As above discussed for the energy transition mechanism of the EL sample, the emission peak at 525 nm is due to the D-A pairs recombination between Al_{Zn}-Cu_{Zn}, while the radiation transition $4T_1$- $6A_1$ of Mn_{2+} ion dominates the emission peak at 588 nm. At the same S-R rate, the spontaneous transition probability of Cu and Mn ions may differ, leading to different enhancement factor in luminescence. Besides, another possible reason is associated with the green emission at 525 nm which might be more scattered by PDMS layer.

It is helpful to understand the color characteristics of the sample by measuring the CIE coordinates. The CIE and CCT of the composite under uniaxial strain were measured to be (0.3397, 0.3466), and 5196 K, respectively. The results indicate that the ML emitted from the flexible composite can be regarded as a cool white light. Jeong et al. have
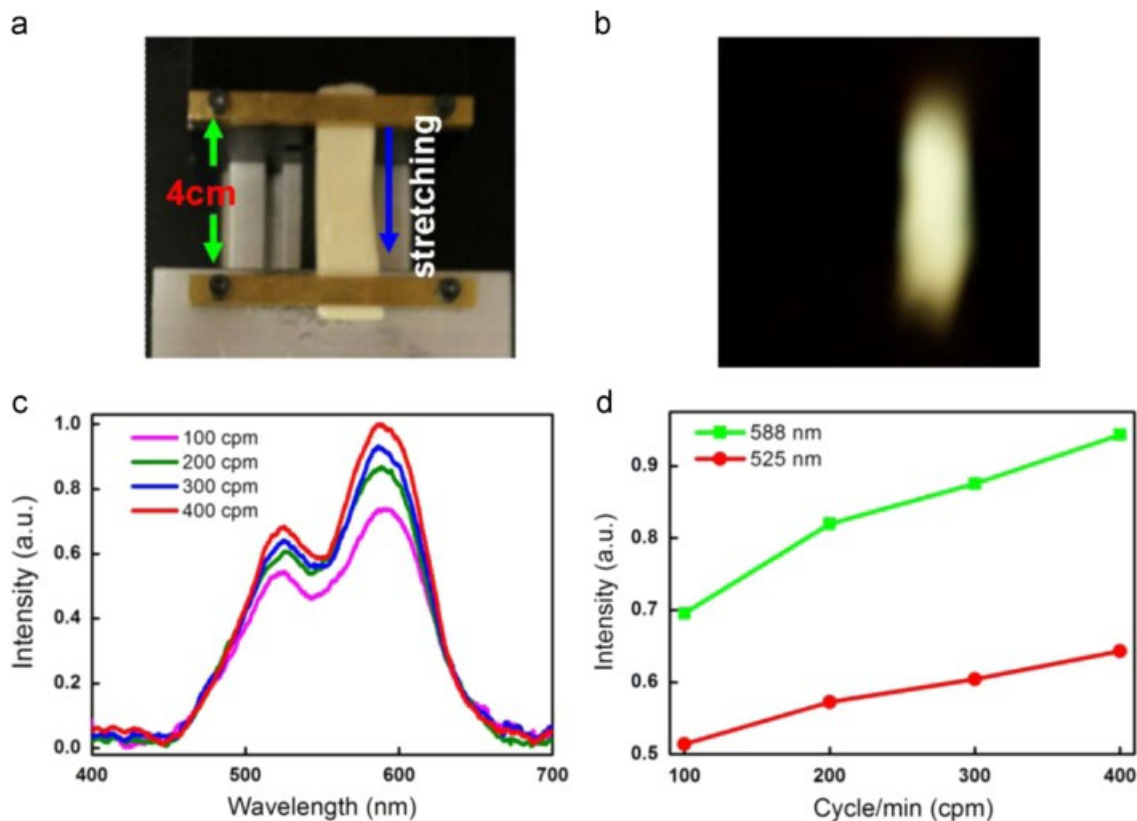

Figure 3 **Photographic image and ML spectra of the white light composite phosphor under S-R stress. (a) Sample mounted on the S-R system. (b) White light-emission from the sample. (c) Luminescence spectra of the sample for the S-R rate between 100 and 400 cpm. (d) The luminescence intensity peaked at 525 nm and 588 nm as a function of S-R rate.**

reported a wind-driven ML device that can emit warm, neutral, and cool white colors by using the mixture of two blue and orange phosphors mixed to polymer [7]. They utilized the high velocity of wind energy belonging to the hurricane or typhoon to produce white light. Comparatively, in our experiment, only single-phase phosphor is mixed to PDMS, and white-light has been demonstrated in the composite phosphor harvesting the mechanical energy, which has the advantages of easy carrying out and low cost.

As the white light can be used for both backlight in display system and general lighting, it is fruitful to compare the color properties of EL and ML from the flexible ZnS:Al, Cu,Mn + PDMS composite as shown in Table 1. Here the

flexible EL device was operated at an external voltage of 100 Vand 1 kHz, and the ML was measured at the S-R rate of 400 cpm. Different luminescence spectra of EL and ML shown in Figures 2b and 3c should be responsible for the measured data listed in Table 1. According to the table, both CIE coordinates and CCTof ML are not exactly same as those of EL. The major cause of the difference is likely that the stretching stress during ML measurement is insufficient to activate the blue emission because of the softness of PDMS as above mentioned. Compared to ML, EL device has different luminescence process and works at higher frequency, which benefits to the blue light emission. At any rate, both ML and EL of the synthesized composite phosphor could be considered as large-area white light sources, differing from commonly used white LED point source where a diffuser is usually needed in application.

Similarly, we mixed another green phosphor of Al and Cu ions co-doped ZnS into PDMS. After well prepared, the green phosphor composite was mounted on the S-R system. Bright green light was seen by the naked eyes during the S-R process as shown in Figure 4a. The green light peaked at 516 nm as shown in Figure 4b is due to the D-A recombination of Al_{Zn}-Cu_{Zn}. The inset of Figure 4b shows the ML intensity of the composite as a function of S-R rate. It seems that the

Table 1 Comparison of white light emissions between EL and ML.

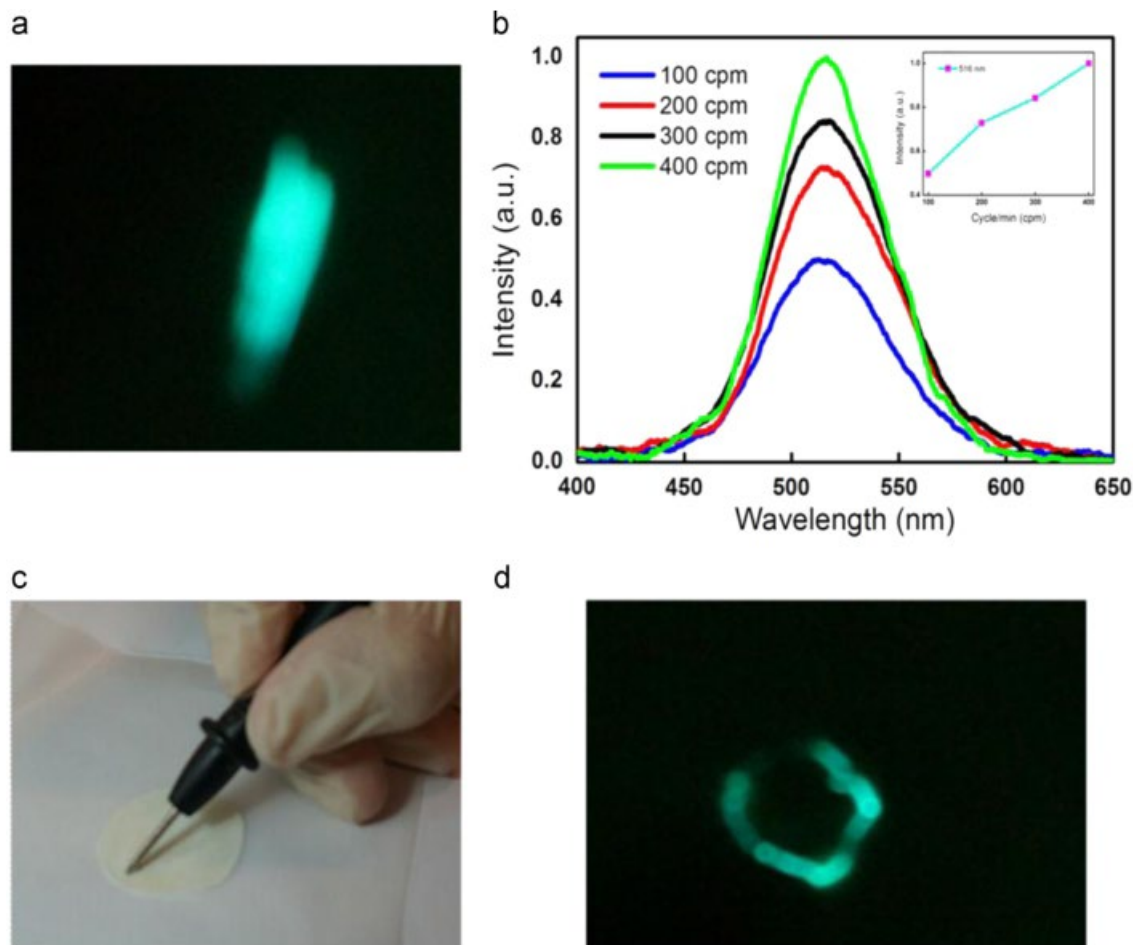| Luminescence type	CIE (x, y)	CCT (K)	Luminance (cd/m2)
EL	(0.3386, 0.3167)	5165	47
ML	(0.3397, 0.3466)	5196	21

Figure 4 **Photographic image and luminescence spectra of the green flexible phosphor composite under mechanical strain. (a) Green light-emission of the sample under stretch strain. (b) Luminescence spectra. The inset shows the luminescence intensity peaked at 516 nm as a function of S-R rate. (c) Photograph of sample under mechanical writing. (d) Green light emission under mechanical writing.**

luminescence intensity is increased linearly with the S-R rate, which is consistent with the result as shown in Figure 3d.

Very recently, triboelectric effect has been explored to generate electricity through the conversion of ambient mechanical energy [29]. Therefore, it is interesting to investigate whether the mechanical friction can be used for generating light. Firstly, the above composite phosphor was spin-coated on a paper. Then the tip scribed across the paper gently (Figure 4c), and therefore the photographic image was taken by a camera with an exposure time of 2.5 s. A bright green light emitted from the contact area of the film was observed by the naked eyes as shown in Figure 4d.

Piezoelectric biaxial strain induced luminescence

PMN-PT is an excellent piezoelectric single crystal with large piezoelectric coefficient of d_{33} $\sim$2000 pC/N and electromechanical coupling factor of k_{33} $\sim$0.9. PMN-PT is capable of producing a large strain. According to our previous studies [30,31], X-ray diffraction measurement can provide an evidence and evaluate the strain provided by PMN-PT. The diffraction peak of PMN-PT can present a shift to lower angles when increasing the applied voltage. Based on the Bragg's law and Poisson ratio of PMN-PT, the out-of-plane and in-plane strains have been calculated in our published works. For instance, the PMN-PT substrate-induced strain was measured to be -0.04% per 100 V [30].

Actually, the strain provided by PMN-PT can be delivered to a variety of functional thin films, quantum wells and 2D materials [13,30–33]. It should be pointed out that the strain provided by the piezoelectric effect is biaxial, which is homogeneous in x and y directions of the sample. Such a piezoelectric strain is different from the above mentioned uniaxial strain produced by stretching or friction. Biaxial strain has previously been reported to induce remarkable changes in band structure and therefore greatly enhance luminescence compared to uniaxial one [32,33]. Herein, it should be helpful to compare the luminescence behaviors of the composite phosphor under different types of strains, namely uniaxial and biaxial strains. Furthermore, we may design and fabricate on-wafer piezoelectric luminescence device by taking the advantage of the PMN-PT piezoelectric actuator. With this mind, a piezoelectric luminescence device composed of the above flexible composite phosphor has been demonstrated in this part. As shown in the Figure 5a, the PMN-PT single-crystal was sandwiched between Au electrodes, subsequently a layer of doped-ZnS + PDMS composite was spin-coated on the top electrode. A dc voltage of 500 V was prior applied to the device in order to positively polarize the PMN-PT substrate. Owing to the converse piezoelectric effect of PMN-PT substrate, the lattice deformation caused by electric field can impose in-plane strain to the doped-ZnS + PDMS composite. As semi-conductor ZnS with a wurtzite structure exhibits a non-central symmetric structure, the substrate-imposed strain
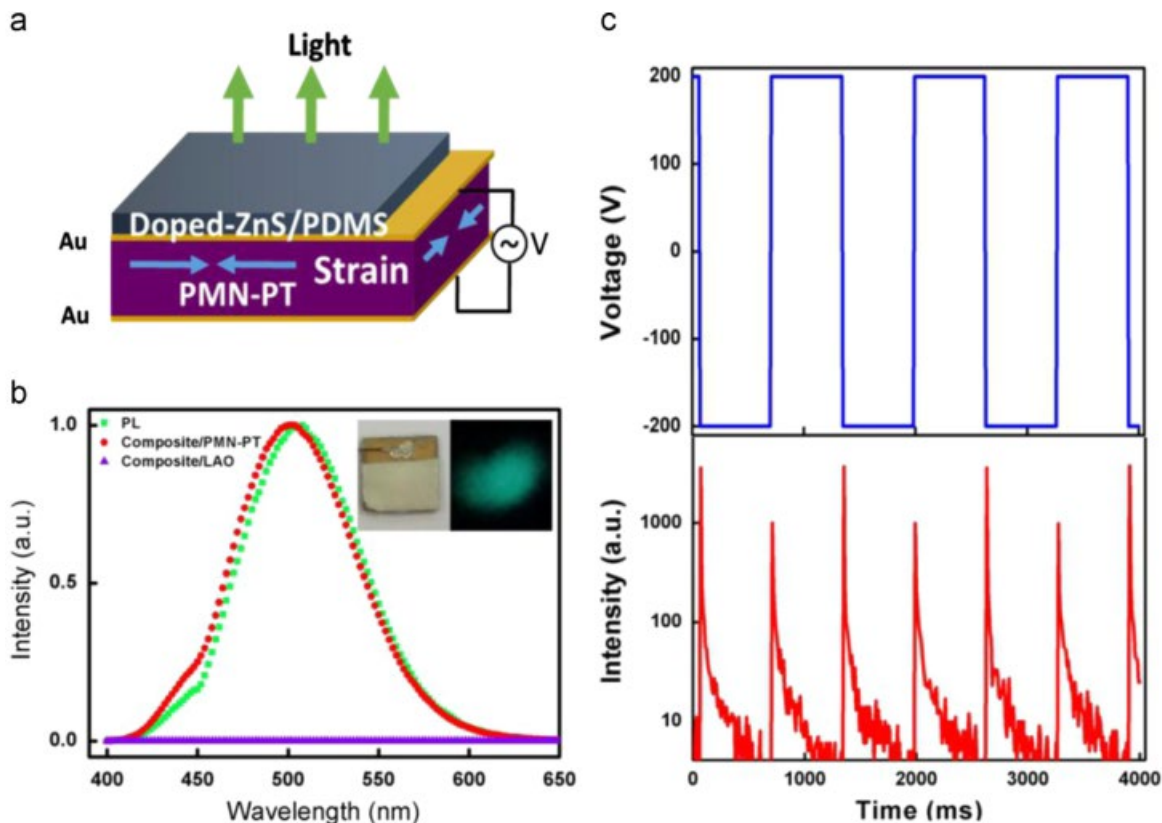

Figure 5 **Device structure and luminescence spectra of the piezo-phototronic luminescence device. (a) Device structure. (b) Luminescence spectra of PL and ML from the sample. The inset shows the tested sample and light-emission under an applied voltage of 400 V$_{pp}$ and 400 Hz. (c) Luminescence intensity peaked at 508 nm as a function of time when a square-wave voltage is applied.**

can induce a piezoelectric potential and subsequently stimulate luminescence [13]. Figure 5b illustrates the luminescence spectrum of the ZnS:Al,Cu + PDMS composite when an ac voltage of 400 V_{pp} at 400 Hz was applied on PMN-PT. Photographs of the actual tested sample of the hybrid structure device and light emission are also included in the insets. During the retention of the ac voltage, the strain applied on the above hybrid structure is changed periodically. As a consequence, ZnS:Al,Cu + PDMS triggered by the biaxial strain arising from PMN-PT emits light, as shown in Figure 5b. For comparison, a non-piezoelectric insulator LaAlO₃ (LAO) was employed to substitute PMN–PT in this system. As expected, no obvious luminescence was observed, further supporting the operation principle of biaxial strain-induced luminescence. The PL spectrum of ZnS:Al,Cu composite phosphor used in this hybrid device is also shown for comparison. The two similar spectra suggest the same dominant emission peaked at 508 nm, which is stemmed from the D-A recombination of Al_{Zn}-Cu_{Zn}.

Figure 5c presents the transient luminescence of the hybrid structure device when applying a square voltage on PMN-PT. Pulsed emissions can be observed in the device stimulated by a square voltage. The peak intensity of luminescence appears when the bias is switched on or off,

indicating the strain-induced luminescence is essentially a dynamic process when a time-varying voltage is applied. Moreover, luminescence intensity peaks are corresponded to both the rising and falling edges of the square voltage. This observation differs from our previous studies on the PLD grown oriented ZnS: Mn_{2+} thin film structure [13]. The mechanism may be related to the polycrystalline ZnS powder with random orientation in this experiment. After attaining a maximum value, the luminescence intensity decreases exponentially with time. Such a change in the emission intensity can be described as [34]:

$$I = I_0 \exp[-\chi(t - t_0)] \qquad (1)$$

where I_0 is the luminescence intensity at $t = t_0$, $\chi = 1/\tau$, and τ is the lifetime of carrier.

Figure 6a shows the luminescence spectra of the device triggered under the bias voltage varying from 100 to 500 V. Note that the luminescence intensity of ZnS:Al,Cu+PDMS composite enhances when increasing the applied voltage as shown in Figure 6b. Similar trend was also found for the measuring frequency dependence of luminescence intensity when the frequency is increased from 200 to 1000 Hz (Figure 6c and d). In the measurements, the increase in luminescence intensity did not show any sign of saturation with the increase in voltage
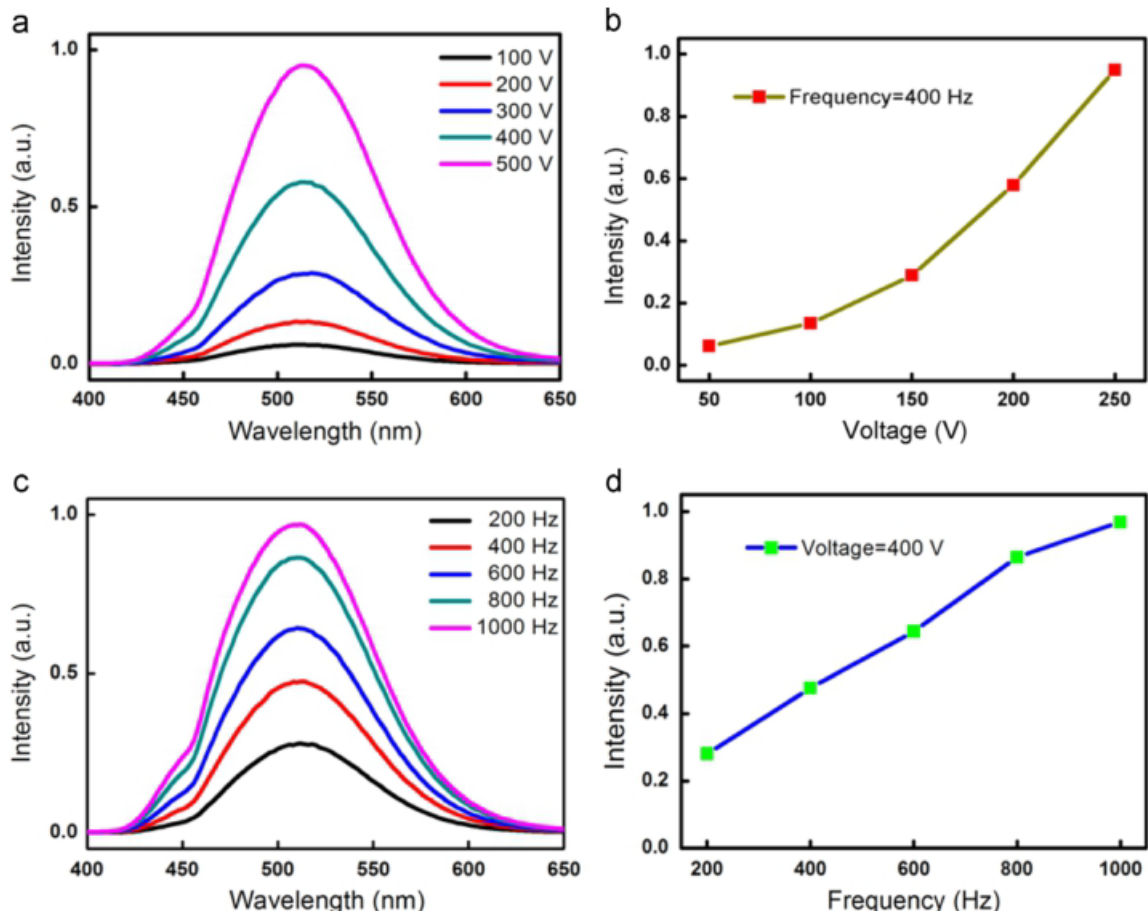

Figure 6 **Luminescence spectra of the piezo-phototronic luminescence device under varying voltage and frequency.** (a) Luminescence spectra of sample under different voltages at 400 Hz. (b) Luminescence intensity peaked at 508 nm response as a function of voltage at 400 Hz. (c) Luminescence spectra of sample under different frequency at 400 V_{pp}. (d) Luminescence intensity peaked at 508 nm response as a function of frequency at 400 V_{pp}.

and frequency within the measurement range. This phenomenon is similar to the earlier reports on the ML intensity from ZnS:Mn and ZnS:Cu under pressure, which was explained by the self-recovery of the detrapped charge carriers [28]. Compared to the above described luminescence under uniaxial strain in earlier section, the light-emission from piezo-phototronic luminescence device here can be precisely controlled based on converse piezoelectric effect, which can operate at high frequency.

Conclusions

In conclusion, flexible composite phosphors have been made by mixing metal ion-doped ZnS in transparent PDMS. Under uniaxial stretch stress, white light emission with CIE coordinates of (0.3397, 0.3466) and CCT of 5196 K is obviously seen by the naked eyes in the flexible composite composed of single-phase ZnS:Al,Cu,Mn. When increasing S-R rate, the intensities of main emission peaks are enhanced, and therefore the overall white light becomes brighter. Interestingly, the developed composite phosphor can sense or harvest broad mechanical energy, including stretch, vibration pressure, and mechanical friction. Therefore, various kinds of light-emission devices, including EL device (Au/metal ion-doped ZnS+PDMS composite/graphene/PET) and piezo-phototronic luminescence device (metal ion-doped ZnS+PDMS composite/Au/PMN-PT/Au) have been designed and fabricated. The flexible EL device yields white light with the luminance of about 47 cd/m2 when triggering an ac voltage of 100 V and the frequency of 1 kHz. The observed luminescence of piezo-phototronic luminescence device is originated from piezoelectric potential induced by PMN-PT substrate, and the luminescence intensity is strongly dependent on not only the rate of biaxial strain change, but also the magnitude and frequency of the voltage applying upon the PMN-PT wafer. The works suggest our developed flexible composite phosphors and devices have the potential for the applications in the fields of novel white light source, energy harvesting, anti-counterfeiting, and self-powered illumination system.

Acknowledgments

References

[1] E.F. Schubert, J.K. Kim, Science 308 (2005) 1274–1278.
[2] C.J. Humphreys, MRS Bull. 33 (2008) 459–470.
[3] J.C. Zhang, C.N. Xu, S. Kamimura, Y. Terasawa, H. Yamada, X.S. Wang, Opt. Express 21 (2013) 12976–12986.
[4] N. Terasaki, H. Yamada, C.N. Xu, Catal. Today 201 (2013) 203–208.
[5] H.W. Zhang, H. Yamada, N. Terasaki, C.N. Xu, Appl. Phys. Lett. 91 (2007) 081905.
[6] S.M. Jeong, S. Song, S.K. Lee, N.Y. Ha, Adv. Mater 25 (2013) 6194–6200.
[7] S.M. Jeong, S. Song, K. Joo, J. Kim, S.H. Hwang, J. Jeong, H. Kim, Energ. Environ. Sci. 7 (2014) (3338-3346).
[8] Z.L. Wang, Nano Today 5 (2010) 540–552.
[9] C.F. Pan, L. Dong, G. Zhu, S.M. Niu, R.M. Yu, Q. Yang, Y. Liu, Z.L. Wang, Nat. Photon. 7 (2013) 752–758.
[10] X.D. Wang, Am. Ceram. Soc. Bull. 92 (2013) 18–23.
[11] Y.F. Hu, Y. Zhang, L. Lin, Y. Ding, G. Zhu, Z.L. Wang, Nano Lett. 12 (2012) 3851–3856.
[12] Q. Yang, Y. Liu, C.F. Pan, J. Chen, X.N. Wen, Z.L. Wang, Nano Lett. 13 (2013) 607–613.
[13] Y. Zhang, G.Y. Gao, H.L.W. Chan, J.Y. Dai, Y. Wang, J.H. Hao, Adv. Mater 24 (2012) 1729–1735.
[14] K.I. Park, C.K. Jeong, J. Ryu, G.T. Hwang, K.J. Lee, Adv. Energ. Mater 3 (2013) 1539–1544.
[15] L Lin, Y.F. Hu, C. Xu, Y. Zhang, R. Zhang, X.N. Wen, Z.L. Wang, Nano Energ. 2 (2013) 75–81.
[16] P. Blake, P.D. Brimicombe, R.R. Nair, T.J. Booth, D. Jiang, F. Schedin, L.A. Ponomarenko, S.V. Morozov, H.F. Gleeson, E. W. Hill, A.K. Geim, K.S. Novoselov, Nano Lett. 8 (2008) 1704–1708.
[17] Z.S. Wu, G.M. Zhou, L.C. Yin, W.C. Ren, F. Li, H.M. Cheng, Nano Energ. 1 (2012) 107–131.
[18] X.S. Wang, C.N. Xu, H. Yamada, K. Nishikubo, X.G. Zheng, Adv. Mater. 17 (2005) 1254–1258.
[19] R.N. Bhargava, J. Lumin. 70 (1996) 85–94.
[20] K. Manzoor, S.R. Vadera, N. Kumar, T.R.N. Kutty, Appl. Phys. Lett. 84 (2004) 284–286.
[21] Y. Liu, C.N. Xu, Appl. Phys. Lett. 84 (2004) 5016–5018.
[22] Z. Lou, J. Hao, Appl. Phys. A 80 (2005) 151–154.
[23] S. Okamoto, E. Nakazawa, Y. Tsuchiya, Jpn. J. Appl. Phys 29 (1990) 1987-1990.
[24] H.M. Zhu, C.C. Lin, W.Q. Luo, S.T. Shu, Z.G. Liu, Y.S. Liu, J.T. Kong, E. Ma, Y.G. Cao, R.S. Liu and X.Y. Chen, Nat. Commun., http://dx.doi.org/10.1038/ncomms5312.
[25] Y.H. Liu, W.D. Zhuang, Y.S. Hu, W.G. Gao, J.H. Hao, J. Alloy Compd 504 (2010) 488–492.
[26] Y.H. Liu, J.H. Hao, W.D. Zhuang, Y.S. Hu, J. Phys. D: Appl. Phys 42 (2009) 245102.
[27] J.Y. Tsao, M.H. Crawford, M.E. Coltrin, A.J. Fischer, D.D. Koleske, G.S. Subramania, G.T. Wang, J.J. Wierer, R.F. Karlicek Jr., Adv. Optical Mater 2 (2014) 809–836.
[28] B.P. Chandra, V.K. Chandra, P. Jha, Appl. Phys. Lett. 104 (2014) 031102.
[29] F.R. Fan, Z.Q. Tian, Z.L. Wang, Nano Energ. 1 (2012) 328–334.
[30] W.J. Jie, Y.Y. Hui, Y. Zhang, S.P. Lau, J.H. Hao, Appl. Phys. Lett. 102 (2013) 223112.
[31] G.X. Bai, Y. Zhang, J.H. Hao, Sci. Rep 4 (2014) 5724–5729.
[32] O.G. Schmidt, K. Eberl, Phys. Rev. Lett. 80 (1998) 3396–3399.
[33] Y.Y. Hui, X.F. Liu, W.J. Jie, N.Y. Chan, J.H. Hao, Y.T. Hsu, L. J. Li, W.L. Gao, S.P. Lau, ACS Nano 7 (2013) 7126–7131.
[34] B.P. Chandra, R.N. Baghel, A.K. Luka, T.R. Sanodiya, R. K. Kuraria, S.R. Kuraria, J. Lumin. 129 (2009) 760–766.