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Photoluminescence and I -V Characteristics of Blended Conjugated Polymers/ZnO Nanoparticles

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Abstract: The investigation of photoluminescence and current-voltage (I-V) characteristics of the MEH-PPV/PVK blended polymers doped with ZnO nanoparticles (ZnO NPs). First, PVK polymers were mixed with MEH-PPV in respect to the mass-ratio of 100:15, respectively. And then the MEH-PPV/PVK composites were doped with ZnO NPs with the mass-ratio of 10 wt%, 15 wt% and 20 wt% of total weight blended polymers. Polymer light-emitting diodes (PLEDs), based on a hybrid composite, having structure of ITO/ MEH-PPV/PVK/ZnO/Al were made by spin-coated, and subsequently vacuum-thermally evaporated.

UV-Vis absorption, photoluminescence properties, SEM micrographs of the hybrid composite layer as well as I -V characteristics of the PLED based on the MEH-PPV/ZnO-and PVK/ZnO-heterojunction were investigated. Results obtained show that the turn-on voltage of the polymers/ZnO-based PLED is lower than that of the polymers-based PLED without doped ZnO NPs. This is due to the Auger-assisted energy up-conversion process occurring at the polymers/ZnO-heterojunction that could enhance the luminescence efficiency of the PLED.

Keywords: PLED, photoluminescence efficiency, MEH-PPV, PVK, SEM, spin coating, thermal vacuum evaporation

1. Introduction

It is commonly recognized that the efficiency of polymer light-emitting devices (PLEDs) strongly depends on the efficiency of carrier (holes and electrons) injection and of carrier recombination as well as the balance of hole- and electron-current densities. However, the mobility of holes is generally much higher than that of electrons in most organic conductive materials. This is one of main reasons causing imbalanced carrier injection inside the multi-layered PLEDs based on conducting polymers [1]. Therefore, charge injection balance is an extremely important issue in achieving high efficiency of the PLEDs [2].

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Studying a device structure with a charge-balanced operation, one needs to consider both effects of energy barriers and of e/h mobility on charge injection and charge transport, respectively. Up to now, some papers have been reported on enhancing the electron injection at the interface of cathode/electron transport materials (ETM) by using low work function metals [3-4] or balancing the combination of hole and electron injected from anode and cathode [5-6]. During the device operation, the imbalanced injection of electrons or holes would result in non-irradiative recombination of the charge carrier species at the polymer/cathode or the polymer/anode interfaces.

Another approach to overcome the limitation of electron injection and mobility is to combine conjugated polymers with inorganic semiconductor nanoparticles which have the low energy barrier to the electron injection and high electron mobility. Zinc oxide nanoparticles (ZnO NPs), a wide-band gap semiconductor with high electron mobility and low work function, are promising materials for the LED application [7, 8]. The PLEDs made of a ZnO NPs/MDMO-PPV hybrid polymer composite have shown electroluminescence (EL) intensity greater than that of the PLED made from the pristine MDMO-PPV polymer because of the enhancement of charge injection and transport due to adding ZnO NPs [9]. Moreover, Ajay K. Pandey *et. al.* [10] have revealed that light emitted by the hole/electron-recombination in the conjugated-polymer layer at a turn-on voltage below the polymer's band gap is observed due to an efficient Auger electron-assisted energy up-conversion process occurring at rubrene/perylene diimide-heterojunction.

Besides the PLEDs based on the hybrid polymer, blended polymers were also used for enlarging emission spectrum of PLEDs. The blended polymers of poly(9-vinylcarbazole):poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] abbreviated as PVK/MEH-PPV, excited by laser irradiation at the wavelength of 325 nm, emit the long-wavelength of 300 nm to 600nm due to the Förster resonance energy transfer [11].

In this paper, we have reported bulk-heterojunction light emitting devices based on blended conjugated polymers doped with ZnO NPs to enlarge the emission spectrum from the UV to the visible range. Effects of various amounts of ZnO NPs at polymer/ZnO heterojunction on photoluminescence (PL) properties were investigated. And also the lower turn-on voltage of the PLED made of MEH-PPV/PVK/ZnO in the current-voltage (I –V) characteristics than that of MEH-PPV/PVK (without ZnO NPs doped), based on a hetero-junction between blended polymers/ doped ZnO NPs, is found.

2. Experimental

MEH-PPV, PVK conducting polymers and zinc oxide nanoparticles (ZnO NPs) were purchased from Aldrich Chemical Co. Ltd. Both as p-type conducting polymers dissolved in chloroform solvent, were mixed with a zinc oxide (ZnO) acting as an n-type inorganic semiconductor to produce hybrid polymer composites of MEH-PPV/PVK/ZnO. A device for measuring the current-voltage (I–V), prepared on a glass, had a sandwich structure of ITO/MEH-PPV/PVK/ZnO/Al in which indium tin oxide (ITO) and aluminum (Al) layers were used as an anode and a cathode electrodes, respectively.

Patterned ITO-electrodes corroded from an ITO-layer on a glass-slide were cleaned in EtOH by sonication for 10 min each, and dried in an oven at 60 ^{o}C for 15 min. The ITO-electrode's electric resistance measured is about 60 Ω. Secondly, a compound of PVK and MEH-PPV powder mixed at a mass-ratio of 100 : 15 (in response to 3.3 mg of PVK and 0.5 mg of MEH-PPV) was dissolved in 1ml solvent [11] in which an amount of ZnO NPs equal to a mass-ratio of 10%, 15% and 20% of the polymer compound [12] was added and dispersed in the polymers by sonication in a ultrasonic bath at room temperature (RT). Hybrid composite films were then made by spin-coating the hybrid compound solution on both glass-slides and the ITO-electrodes at RT with a rotation speed of 1000 rpm for the

60 s. For solvent evaporation and polymer-chain stability, the films were latterly cured in a vacuum oven at a temperature of 80 ^{o}C for 2 hours. Finally, we deposited an Al-cathode on the polymers by thermal vacuum evaporation of an Al wire on the hybrid composite film at a pressure of 10 $^{-4}$ Torr, and a deposition time of 30 s to create devices of ITO/MEH-PPV/PVK/ZnO/Al and ITO/MEH-PPV/PVK/Al.

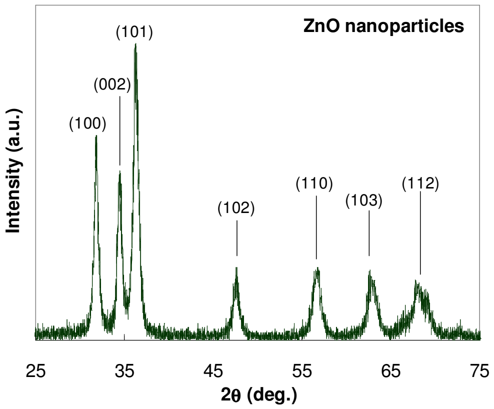


Fig. 1. XRD pattern of ZnO particles.

Structural analysis of ground ZnO NPs was performed by using X-ray Diffractometer (XRD) model D8 Advance (Bruker, Germany) with Cu K_{α} radiation, angle step size of 0.01, and count time of 1.0 s per step. UV-visible absorption spectra of the hybrid composite films were obtained using a model UV-Vis/NIR-JΛSCO 570 (Japan) spectrometer. Surface images of the hybrid composites of MEH-PPV/PVK/ZnO were observed on the scanning electron microscope (SEM), Hitachi, Japan. Photoluminescence (PL) spectra in the rage from 350 nm to 800 nm were collected from a Varian Cary Eclipse (USA) fluorescence spectrophotometer using a xenon lamp (500 W using a He–Cd cw laser) as an excitation source of 325 nm and 442 nm, while I-V characteristics of the device were measured on a PGS-30 potentiometer.

3. Results and discussion

3.1. Structural analysis of ZnO NPs

The X-ray diffraction (XRD) pattern, taken from a ZnO powder before being doped with polymers, is shown in the Fig. 1. The spectrum is composed of seven distinct peaks, in which, the XRD peaks at $2\theta = 31.74^{0}$, 36.26^{0} and 61^{0} corresponding to the (100), (101) and (103) planes of ZnO NPs, respectively. The diffraction peaks suggest that the ZnO NPs are crystalline and have a hexagonal Wurtzite structure [13]. In addition, their average size calculated from the XRD pattern using the Scherer's equation is estimated roughly to be 30 - 40 nm. Doped in the blended polymers, these ZnO NPs were embedded in the conjugated polymers that formed ZnO/MEH-PPV and ZnO/PVK heterojunctions.

3.2. UV-Vis absorption analysis

Figure 2 shows absorption spectra of the hybrid composite film of PVK/MEH-PPV/ZnO with the various mass-ratio of ZnO NPs. It can be seen that there are also two absorption peaks at the range from 330 nm to 650 nm; the small onset at wavelength of 345 nm belongs to PVK absorption while the broad peak at 498 is corresponding to the π–π* transition of conjugated MEH-PPV chains [11]. In addition, both MEH-PPV and PVK absorption decreased with added ZnO concentration was up to 20%, however PVK intensity considerably was reduced while MEH-PPV intensity slightly decreased. This result provides evidence of the incorporation of ZnO NPs into MEH-PPV/PVK blended polymers in which doped ZnO NPs do not lead to degrade the optical quality of the composite films as well as there is no bonding between the blended polymers and ZnO nanoparticles [11-12].

3.3 Photoluminescence spectrum (PL)

Fig. 3a displays photoluminescence (PL) spectra emitted from the MEH-PPV/PVK/ZnO composites in the range of 350 to 800 nm using 325 nm as the excitation source at RT with the different ZnO mass-ratio. The PL spectrum contains a sharp UV emission band centered at 380 nm, 410 nm, and wide green at 560 nm as well as a green-yellow range at around 580 nm. It could be considered that these emission peaks of the composites are considerably affected by the interfaces of PVK/MEH-PPV, ZnO/PVK and ZnO/MEH-PPV heterojunctions. In the first component, Förster energy transfers from the PVK matrix to MEH-PPV one through their interface because the blue emission spectrum of PVK matrix (PVK's peak at 410 nm) excited by laser wavelength of 325 nm overlaps the absorption spectrum of MEH-PPV matrix (its peak at 490 nm). Therefore, green emission intensity of MEH-PPV matrix at wavelength of 560 nm can be enhanced [11].

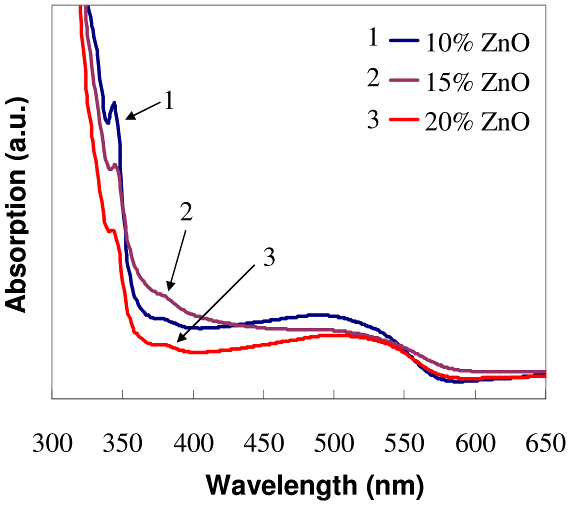
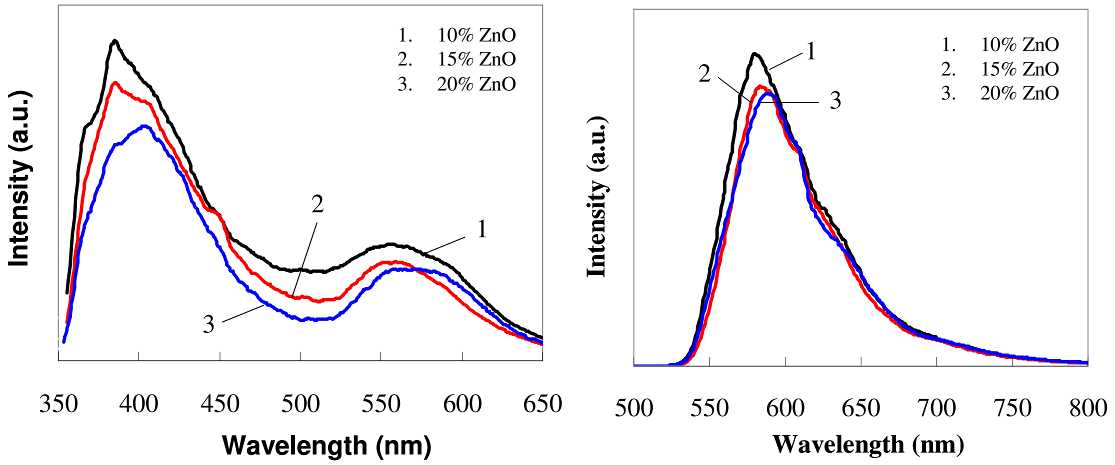


Fig. 2. UV-vis absorption spectra of the blended polymers doped with ZnO NPs.

The present of ZnO NPs, however, affected photoluminescence (PL) emission of blended polymers. A PL spectrum of the ZnO NPs exhibited a peak at 380 nm in the blue region, which corresponds to the band gap energy of ZnO. Moreover, the increase in the ZnO NPs concentration up to the mass-ratio of 20 wt% in the composite film led to form a broad defect-related deep level visible emission, centered in the green-yellow range at around 580 nm. Normally, these two emission bands compete against each other; a strong UV luminescence usually coexists with a rather weak visible emission due to the ZnO NPs growth process.

Photoluminescence emitted from PVK/ZnO and MEH-PPV/ZnO heterojunctions was quenched when compared to that emitted from the pristine polymers. This suggests that the ZnO NPs provided alternative pathways for excited electrons through polymers/ZnO heterojunctions. Therefore, they reduce the possibility of radiative emission of the exciton. In the case of the quenching of MEH-PPV matrix, the alternative pathway is most likely to be a charge transfer process based on the energy alignment of MEH-PPV matrix and ZnO NPs. As we know, the LUMO of MEH-PPV is - 2.8 eV and its HOMO is -5.3 eV while the conduction band (CB) of ZnO NPs is - 4.2 eV and their valence band (VB) is -7.6 eV [12]. During the charge transfer process, when MEH-PPV matrix absorbs photons, electrons are photo-excited into the lowest unoccupied molecular orbital (LUMO) of this polymer and leaving behind holes in the highest occupied molecular orbital (HOMO) that produces electron/hole pairs in MEH-PPV matrix. It is known that the photoluminescence arises from the radiative process that the excited electrons return to the bottom of valance band. In ZnO-blended polymer nanocomposites, however, the excited electrons alternatively inject into the conduction band of the ZnO nanoparticles, because the conduction band edge of ZnO (-4.2 eV) lies below LUMO of MEH-PPV (-2.8 eV). This charge transfer at the interface could reduce the transition probability for the excited electrons from LUMO to HOMO and then reduce the recombination probability of electron and hole. Therefore, it reduces the intensity of MEH-PPV photoluminescence (quenching) [14]. Similarly, when the charge transfer process at the PVK/ZnO NP interfaces occurs (see Fig. 3a) it causes large decrease in the emission peak of PVK matrix at 410 nm. The charge transfer at the interface of hybrid polymers/ZnO heterojunction indicates that the ZnO NPs are effective electron trappers due to their charge mobility and high electron affinity. Accordingly, the observed large decrease in the intensity of photoluminescence emission of PVK matrix indicates that the ZnO nanoparticles in the given nanocomposites are effective electron trappers reducing the number of excited electrons which could be recombined with holes at the HOMO band.



a)

b)

Figure 3. Photoluminescence (PL) of the layer MEH-PPV/PVK/ZnO excited by the excited laser at wavelength of a) 325 nm and b) 442 nm

Figure 3b shows PL spectra of MEH-PPV/PVK/ZnO composites with the different ZnO concentration under the exposure to the laser at wavelength of 442 nm (λ = 442 nm). The excited wavelength of 442 nm does not lead to the generation of electron-hole pairs in the bulk of ZnO NPs and PVK polymer since the photon energy is much smaller than the band gap of two materials.

However, it still promotes an electron to the LUMO band, leaving behind a hole in the HOMO band of MEH-PPV matrix. The electron and the hole can form a bound state called an exciton which later diffuses to the MEH-PPV/ZnO interface, and then dissociates. The charge transfer process (similar to the process mentioned in the previous paragraph) that leads to photoluminescence quenching of MEH-PPV matrix when the ZnO NP concentration increases in the composites. Also, the red-shift of PL emission peaks with the increase in ZnO concentration is due to the longer conjugated polymer chains made by a larger amount of ZnO NPs added to the MEH-PPV/PVK/ZnO hybrid composites. The PL spectrum of the MEH-PPV/PVK/ZnO composite in a range 350 nm to 700 nm with two peaks at 380 nm and 570 nm shows emitted blue-green light that expands the emission band of the hybrid composites from the blue to visible light compared to pristine MEH-PPV and pristine PVK polymers.

3.4. Current-voltage (I-V) characteristics of OLED components

Under forward bias, electrons are efficiently injected from the Al-cathode into the conduction band (CB) of the ZnO NPs due to the negligible injection barrier between ZnO NPs and the Al-cathode. Similarly, injected holes from the ITO-electrode also efficiently transferred across the ITO/MEH-PPV interface due to an injection barrier at a low energy offset of the interface (- 0.5 eV) shown in Fig. 4a. And then, the injected holes quickly diffused in the MEH-PPV area in which their diffusion-range depends on the concentration of ZnO NPs.

Although these electrons and holes could be injected into the ZnO NPs and MEH-PPV from the Al-cathode and the ITO-anode, respectively, they are still confined and accumulated within the ZnO NPs/MEH-PPV hetero-junction. This might be due to the large energy offset of -1.4 eV between the LUMO of MEH-PPV and the CB of ZnO NPs as well as the large energy offset (- 2.2 eV) between the HOMO level of MEH-PPV and the valence band (VB) edge of the ZnO NPs (seen in Fig. 4a), leading to the electrons and holes to hardly transfer through the MEH-PPV/ZnO NPs heterojunction interface.

In this process, the large energy offset of 1.4 eV between the LUMO of MEH-PPV and the conduction band of ZnO NPs leads to electron accumulation at the MEH-PPV/ZnO NP interface. Upon large accumulation of charges at the hetero-junction interface, the electrons at conduction band of ZnO and holes at the HOMO of MEH-PPV form *interfacial charge transfer (CT) excitons*. And then, the resonance energy, released from the non-radiative recombination of these CT excitons, is resonantly transferred to the proximate electrons on the conduction band of ZnO NPs through an *Auger-assisted energy up-conversion* process to produce electrons with sufficiently high energy overcoming the barrier of 1.4 eV. These proximate electrons absorbing energy were injected into the LUMO level of MEH-PPV. In addition, the barrier between the VB of ZnO NP and HOMO of MEH-PPV is enough to accumulate and confine holes to a range of the MEH-PPV/ZnO interface. Finally, injected electrons at the LUMO band of MEH-PPV radiatively recombine with accumulated holes at the HOMO band of MEH-PPV to emit photons with energy, equal to the HOMO-LUMO gap of MEH-PPV [10, 15-16].

Similarly, the interpretation for accumulation of holes/electrons coupled with the Auger electron-assisted energy up-conversion process at the PVK/ZnO NPs hetero-junction interface revealed the radiative recombine between injected electrons at the LUMO and accumulated holes at the HOMO band of PVK, resulting in photon emission at the UV range of the PVK.

Furthermore, current-voltage (I-V) characteristics were measured for two devices mainly-constructed from blended MEH-PPV/PVK with and without ZnO NPs added. It can be seen that the I-V spectrum from the blended polymer/ZnO NPs device is identical to that from the corresponding device without the ZnO NPs. However, the turn-on voltage of the devices having ZnO NPs is significantly lower (approximately 0.8 V shown in Fig 5 left.) than that of the device without ZnO NPs. This sub-bandgap turn-on voltage is attributed to an efficient Auger up-conversion process at the polymer/ZnO hetero-interface that was interpreted above. Furthermore, when larger driving voltage applied, the current of the devices having ZnO NPs highly increased than that of the device without ZnO NPs and it can be easily seen that the slope of the I-V curve at a point of the ZnO/polymer -based device is larger than that of the device without ZnO NPs (see Fig.5). Lower turn-on voltage due to Auger up-conversion process caused by the presence of doped ZnO NPs results in the enhancement of efficiency of light-emitting heterojunction of PLEDs.

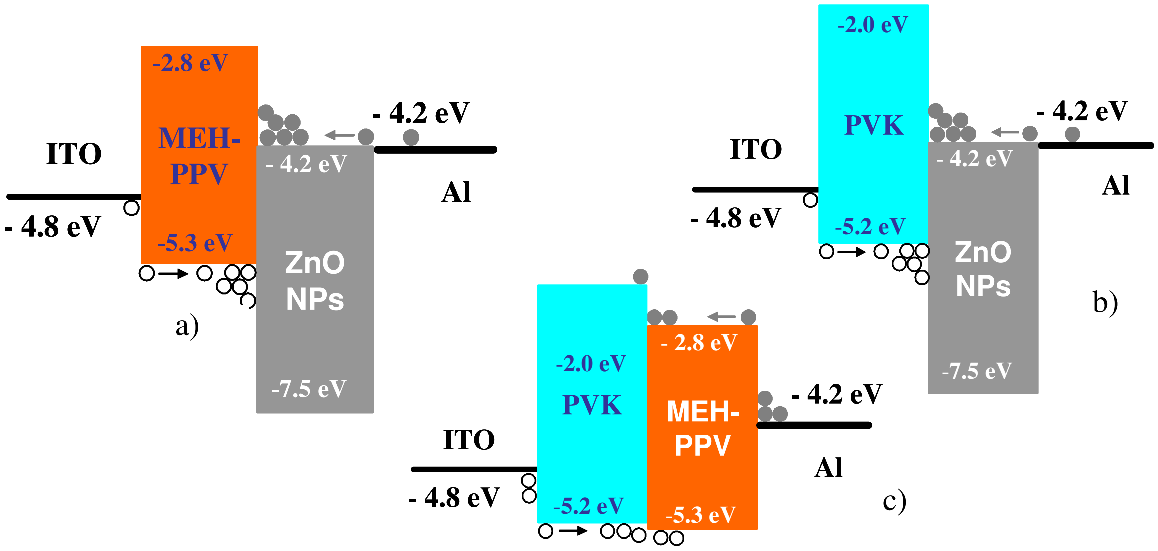


Fig. 4. Schematic energy level diagram of ITO/MEH-PPV/PVK/ZnO/Al device in which each heterojunction of MEH-PPV/ZnO and PVK/ZnO are illustrated.

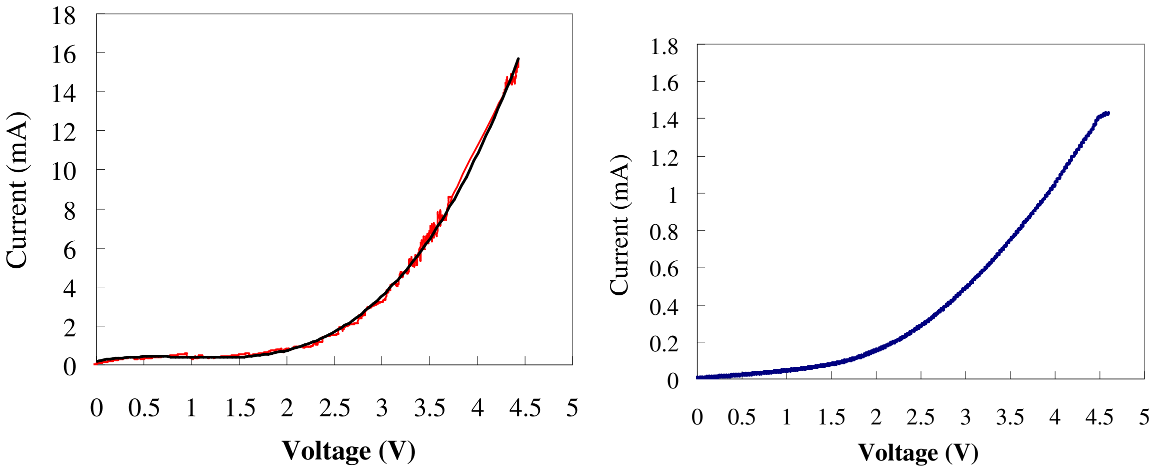


Figure 5. I-V characteristic of the OLEDs based on the structure of left) ITO/MEH-PPV:PVK:20% ZnO/Al and right) ITO/MEH-PPV: PVK/Al.

4. Conclusion

The PLED is based on the structure of ITO/MEH-PPV:PVK:ZnO/Al with MEH-PPV/ZnO PVK/ZnO and MEH-PPV/PVK hetero-junction. The blended MEH-PPV: PVK based on PLED shows the broad photoluminescence emission band extending from the range of 380 nm to 580 nm larger than that of each polymer. And also determining the current-voltage characteristic curves, we found that the turn-on voltage of the polymers/ZnO-based PLED is lower than that of the polymers-based PLED without ZnO NPs. It is believed that the lower turn-on voltage, achieved by the added ZnO NPs than the band-gap voltage of MEH-PPV and PVK polymer is due to an efficient Auger-assisted energy up-conversion process that occurred at the MEH-PPV/ZnO and PVK/ZnO heterojunction. Therefore, the addition of ZnO NPs in the ZnO/polymers-based PLED results in the higher efficiency of luminescence emission compared to the emission of the PLED device based on pristine blended MEH-PPV:PVK polymers.

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