# PREPARATION AND CHARACTERIZATION OF NANOSTRUCTURED THIN FILMS APPLICABLE IN POLYMER LIGHT EMITTING DEVICES

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**Abstract**

This work deals with a composite material based on polymer/inorganic nanoparticles applicable in organic electronics as an active layer. Prepared composite, containing conjugated polymer MEH-PPV as a matrix and ZnO nanoparticles (NPs) as filler, was characterized using spectroscopic and microscopic methods and it was used for preparation of polymer light emitting diodes.

Creation of polymer/inorganic nanocomposite by incorporation of ZnO NPs in polymer matrix leads to better injection of negative charge carriers from cathode into active layer material and thus the achieved electroluminescence of prepared device has much higher intensity (in several orders) in comparison to devices with active layer from neat polymer. Moreover, excellent distribution and dispersion of NPs in polymer improve the homogeneity of radiation from whole device area.

In our contribution, we introduce method how to easily improve performance of polymer light emitting diodes by preparation of nanocomposite based on ZnO nanoparticles incorporated into the conjugated polymer.

**Keywords:** Nanoparticles, composite, MEH-PPV

## 1. INTRODUCTION

Recently, organic light-emitting diodes (OLEDs) have been extensively studied for potential applications such as transparent and flexible display, lighting systems in advertisement and/or in emergency lighting. OLEDs have unique characteristics such as low power consumption, wide viewing angles, excellent colour scale, high contrast ratio, high response, and flexibility [1]. The basic OLED structure consists of a bilayer structure, in which the hole-transport layer and the emission layer were placed between two charge injection contact electrodes, one of which must be transparent [2]. In conventional OLEDs, the work function of the cathode must be appropriately low to facilitate the efficiency of electron injection at the cathode/organic interface, and the work function of the anode must be high enough to ensure the efficiency of hole injection at the anode/organic interface [3]. Understanding of processes occurring at the interfaces between electrodes and the overlying organic layers is a crucial to obtain high device performance.

The electrode/organic interfaces can be modified and properties of final device can be enhanced by introducing buffer layers, electron injection layers, electron transporting layer, hole blocking layer and hole injection layer, hole transporting layers, electron blocking layer in proper sequence between electrodes and active layer. Multilayer architecture of OLEDs has many advantages compared to monolayer devices. Multilayer OLEDs are intrinsically more stable than monolayer devices due to a better balance of charge-carriers and concentration of the charged species away from the electrodes. On the other hand, heterojunction of multilayer OLEDs is susceptible to degradation process due to crystallisation of one or more layers in the device.

Conjugated polymers are a good choice as materials for active layers because they provide in principle both good charge transport and relatively high quantum efficiency for the electro-luminescence. Such devices can be called polymer light emitting diodes (PLEDs). However, in case of use of a conjugated polymer as the active layer, lower stability due to thermal degradation, lower lifetime and high opening bias can arise [4-6].

One approach how to obtain more stable and high performance devices, incorporation inorganic nanoparticles into conjugated polymer matrix can appear. [7]. Recent investigations of perspective materials for PLEDs have revealed that incorporation of n-type inorganic nanoparticles into conjugated polymers is efficient to improve charge transport and performance [8]. In particular, composites based on n-type zinc oxide (ZnO) nanoparticles and p-type conjugated polymers are very interesting for UV LEDs and PLEDs applications. Moreover, ZnO has strong absorption in the UV region and therefore can protect the devices from UV degradation and thus increase the lifetime of organic devices [9].

In this work, we prepared a polymer/inorganic nanocomposites of poly[2-methoxy-5-(2-ethyl-hexyloxy)-1,4phenylene-vinylene] (MEH-PPV) and ZnO nanoparticles with different weight ratios for use as active layer in PLED devices. Such active materials were used for construction of device, which were subsequently tested.

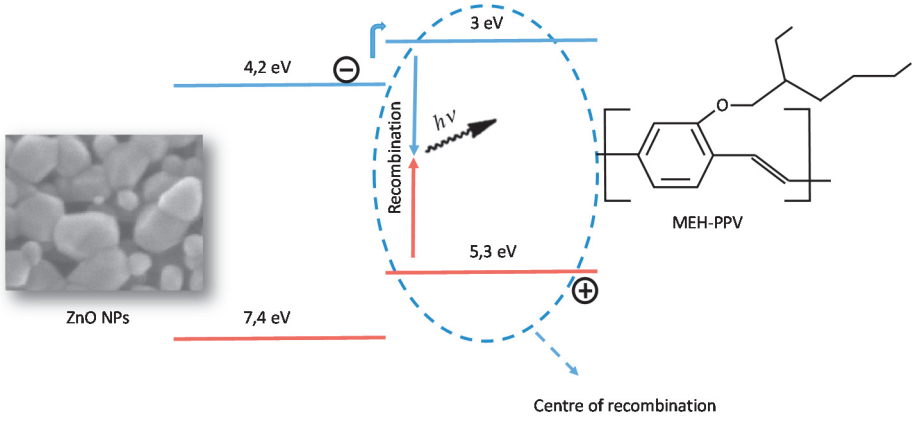


**Figure 1** Diagram showing the effect of nanoparticles

## 2. EXPERIMENTAL

### 2.1. Material

The poly[2-methoxy-5-(2-ethyl-hexyloxy)-1,4phenylene-vinylene] (MEH-PPV) (with $M_n$ = 40,000-70,000) and ZnO nanoparticles (mean size of 50 nm) were purchased from Sigma-Aldrich. The PEDOT: PSS [poly(3, 4-ethylenedioxythiophene) polystyrene sulfonate] (Clevios™ AI 4083) was obtained from Heraeus.

### 2.2. Samples preparation and PLED fabrication

Thin films were deposited on the ITO patterned glass substrate by the spin coating method using spin coater Laurell WS-650-MZ-23NPP. HTL (hole - transporting layer) was prepared from PEDOT:PSS which was filtered prior to use through a 0.45 μm PVDF filter. Different addition of ZnO NPs (7.5; 10; 12.5; 15 % to neat polymer) was added into the polymer solution with concentration of MEH-PPV 10 mg/mL. The mixtures were sonicated for 30 min followed by stirring overnight to get homogeneous nanocomposite solutions. Aluminium cathode was sputtered by Quorum Technologies Q300TT sputter-coater. In **Figure 2**, PLED fabrication process is depicted.

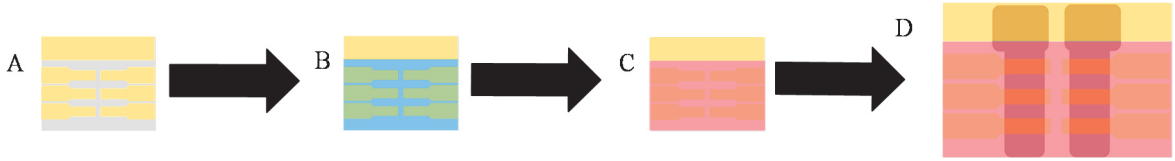


**Figure 2** Scheme of device fabrication, A - quartz glass substrate with patterned ITO, B - Deposition of hole - transporting layer of PEDOT: PSS, C - Deposition of active layer MEH-PPV or MEH-PPV/ZnO NPs, D - Sputtering of Al cathode

### 2.3. PLED characterization

Electroluminescence spectra were measured on UV/VIS spectrometer Avantes Avaspec with integration sphere with 50 mm diameter. Current/voltage characteristic were obtain by multimeter HP 34401A and power supply system HP 6038A and using C/V Charakteristika 2.1 home-developed software. All measurements were performed at room temperature in ambient air.

## 3. RESULTS AND DISCUSSION

### 3.1. Current/voltage characteristic measurement

Current/voltage (J-V) characteristic of the devices with neat MEH-PPV and MEH-PPV/ZnO nanocomposites as active layer are shown in **Figure 3**. Significant reduction of opening bias voltage was observed in the MEH-PPV/ZnO nanocomposite devices as compared to the pure MEH-PPV. With increasing ZnO content in nanocomposite, opening bias voltage rapidly decreases. The most filled nanocomposite with the ZnO content 20 wt. % has more than three times lower opening bias compared to neat MEH-PPV. These results can reveal that the ZnO nanoparticles can play a key role during electron transport to active layer, where the ratio between positive and negative charge is equal and thus the opening bias is approaching to value of optical band gap of emitted light from recombination centres on MEH-PPV.

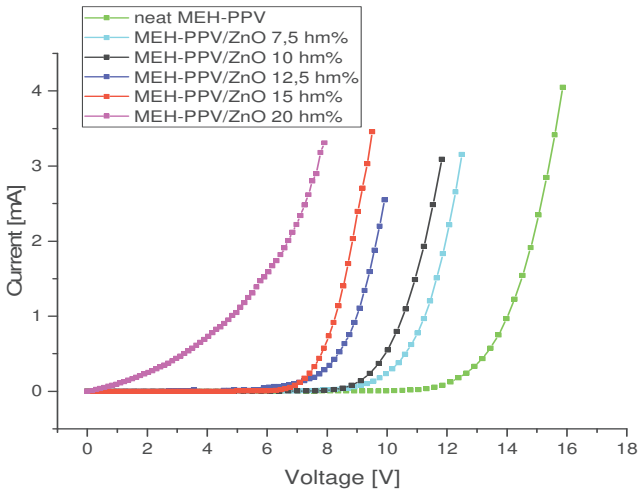


**Figure 3** Current/voltage characteristic of prepared devices

### 3.2. Electroluminescence spectra measurement

Dependence of electroluminescence spectra of fresh devices and devices after 2 hours of lighting operation at 10 V are shown in **Figure 4**. Regarding this, it must be stressed out, that all devices have been made in the air atmosphere being influenced by oxygen and moisture contamination.

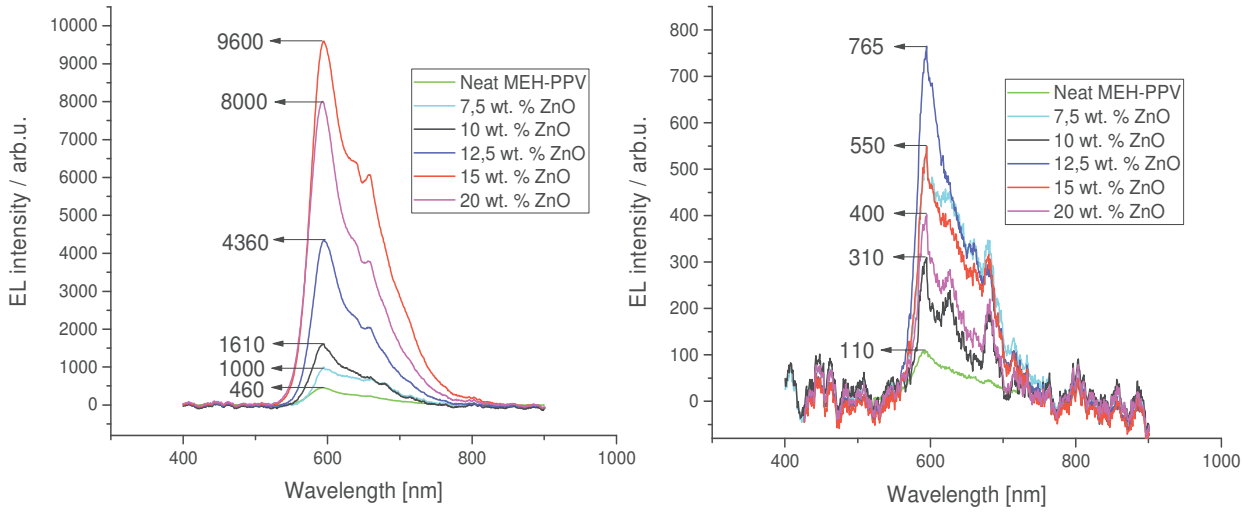


**Figure 4** Electroluminescence spectra of prepared PLED devices, **A** - fresh devices; **B** - after 2 hours of lighting

It is obvious from the results that a considerable improvement in performance of polymer light emitting devices with active layer from nanocomposite compare was achieved in comparison to devices with active layer from neat MEH-PPV. The higher ZnO NPS concentration in the active layer, the higher EL intensity is observed. This is true up to the filler concentration of 15 wt. % however slight reduction of EL intensity was obtained in case the ZnO NPs content achieved 20 wt. %. EL intensity measured on fresh devices with active layer from nanocomposite is higher almost in 1.5 orders in comparison to fresh devices with active layer from neat MEH-PPV. Hereafter, EL intensity after two hours performance of nanocomposite devices is still higher; nevertheless, the difference between nanocomposite device and neat MEH-PPV device is smaller. This could be due to either electrons hopping into the conduction band of the ZnO or the electron tunnel through the emissive layer of the MEH-PPV without recombining with the holes or combination of both. Electron hopping and tunneling become severe when there is a poor distribution of nanoparticles on the emissive layer [10]. Another explanation of the decrease of electroluminescence intensity with filling over 15 wt. % could be that the high content of electrons in active layer calls into existence a disproportion between current transported by electrons and holes. Excess amount of non-recombined electrons can “flow” further through the active layer and can be lost as a leakage current [11].

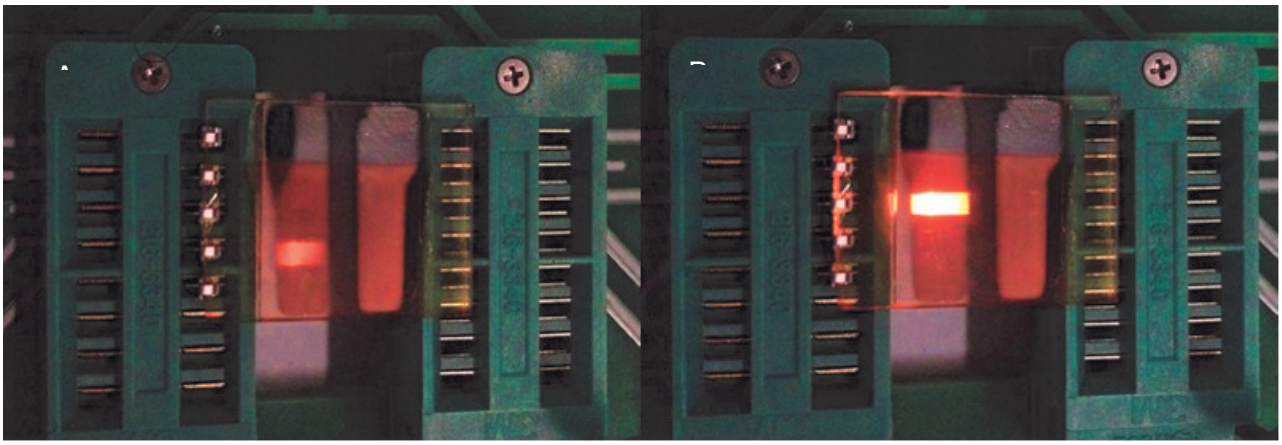

**Figure 5** Prepared PLED devices: A - neat MEH-PPV as an active layer, B - MEH-PPV/ZnO 12.5 wt. % as an active layer, operated at 10 V

## 4. CONCLUSION

To conclude, we have successfully prepared nanocomposite material applicable as an active layer in polymer electronics and we have used these nanocomposites for fabrication of polymer light emitting diodes. The PLED device with active layer from neat MEH-PPV was chosen as a reference to which devices made with active layer from nanocomposite MEH-PPV/ZnO were compared. The results show a substantial improvement in intensity of electroluminescence. We have demonstrated a 2000% increase in the initial EL intensity of these devices. The ZnO nanoparticles incorporated into the polymer matrix increase the electron injection at the polymer - cathode interface therefore enhancing the internal electron-hole equality. Simultaneously due to a high value of LUMO band, ZnO NPs block positively charged holes (**Figure 1**). These both effects are particularly beneficial for solution processed devices, since these nanoparticles are low cost and easy to handle and their direct incorporation to the active layer might be an alternative to additional layers for controlling charge injection and charge carriers balance.

## ACKNOWLEDGEMENTS

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