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Effect of the Polymer Emission on the Electroluminescence Characteristics of n-ZnO Nanorods/p-Polymer Hybrid Light Emitting Diode

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Abstract

Hybrid light emitting diodes (LEDs) based on zinc oxide (ZnO) nanorods and polymers (single and blended) are fabricated and characterized. The ZnO nanorods were grown by the chemical bath deposition method at 50 ^{o}C. Three different LEDs, either with blue emitting, orange-red emitting or their blended polymer together with ZnO nanorods were fabricated and studied. The current-voltage characteristics show good diode behavior with ideality factor in the range of 2.1 to 2.27 for all the three devices. The electroluminescence spectrum (EL) of the blended device has an emission range from 450nm to 750nm, due to the intermixing of the blue emission generated by the poly(9,9-dioctylfluorene) denoted as PFO with orange red emission produced by the poly(2-methoxy-5(20-ethyl-hexyloxy)-1,4-phenylenevinylene) 1,4-phenylenevinylene) symbolize as MEH PPV combined with the deep band emission (DBE) of the ZnO nanorods i.e. it covers the whole visible region and manifested as white light. The CIE colour coordinates showed bluish, orange-red and white emission from the PFO, MEH PPV and blended LEDs with ZnO nanorods, respectively. These results indicate that the choice of the polymer with proper concentration is critical to the emitted colour in ZnO nanorods/p-organic polymers LEDs and careful design should considered to obtain intrinsic white light sources.

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1 Introduction

Zinc oxide (ZnO) as a semiconductor is considered as an interesting material for many optoelectronics applications because it has a direct wide band gap of 3.37 eV, a relatively large exciton binding energy of 60 meV combined with other interesting electro optical properties [1]. Moreover ZnO emission band covers the whole visible range due to the existence of a large number of intrinsic and extrinsic deep level defects [2]. This implies that ZnO is a potential material for developing new light sources. On the other hand, ZnO nanostructures have received great attention due to their excellent properties, for example nanowires or nanorods (NRs) may offer extra advantages for optoelectronic device applications due to the increased junction area and improved carrier confinement in one dimension [3]. These NRs are suitable for large scale and low cost production of efficient solar cells and light emitting diodes (LEDs) [4]. Among the various growth methods of ZnO nanorods, the chemical bath deposition (CBD) technique is a low temperature ($\leq 95^{0}$ C) low cost and is a substrate free growth method [5]. Chemically grown ZnO NRs are unintentionally n-type doped and since the reproducibility of stable p-doped ZnO is still out research, the use of a heterojunction is a rational way to utilize ZnO interesting emission properties [6]. Therefore, heterojunction LEDs are of considerable interest i.e. combining another p-type material with n-type ZnO NRs to circumvent the problem of p-type doping [7].

Organic polymer light emitting diodes have potential impact in solid state lighting and flat panel display because of their advantage of low power consumption, low cost and easy manufacturing etc. [8]. As contrary to ZnO n-type polymers are limited and their conductivity is low due to some problems like difficulty in synthesizing, poor solubility and stability in air [9]. Poly (1,4-phenylene vinylene) PPV and its derivatives specially MEH PPV are widely used in the fabrication of organic light emitting diodes (OLEDs) [10]. MEH PPV is a very attractive

conjugated polymer with an orange-red emission and easily dissolved in organic solvents and is useful for various applications [11]. While poly(9,9-dioctylfluorene) PFO is a blue emitting polymer and widely used due to its high photoluminescence efficiency, good hole mobility and variability of the chemical properties [12]. Blended polymer solutions have been used in OLEDs for a long time. By blending the polymers, the photoluminescence efficiency can be increased and the charge transport properties can also be enhanced [13, 14, 15]. Blending polymer is also useful to tune the emitted colour and to control the electrical properties [16, 17]. Combining a p-type polymer with n-type ZnO NRs to form hybrid LEDs is utilizing the advantages of both materials in lighting, and LEDs that can emit in the whole visible spectrum will be possible to achieve [18]. On the other hand this will resolve the problem of the p-doped ZnO. It will also be of interest to fabricate and compare different p-type polymer configurations in ZnO NRs/p-type organic polymers in order to achieve optimized design that provides intrinsic white light of high quality.

Here in this paper, we report on the electroluminescence and colour characteristics of organic-inorganic LEDs made from different p-type polymer configurations with n-type inorganic ZnO NRs grown at low temperature on flexible PEDOT:PSS coated plastic substrate. We fabricated hybrid LEDs using single polymers (i.e. PFO or MEH PPV) with ZnO NRs, and also demonstrated their blended configuration with ZnO NRs based LED. We show that the choice of the polymer is critical to the colour quality and for obtaining intrinsic white light care must be taken regarding the choice of the polymer i.e. the organic part of the hybrid junction. The hybrid LED fabricated from the blended polymer showed intrinsic white electroluminescence emission covering the whole visible spectrum with excellent colour properties.

3

2 Experimental details

Three kinds of LEDs have been fabricated, these were PEDOT:PSS/PFO/ZnO/Al denoted as LED A; PEDOT:PSS/MEH PPV/ZnO/Al denoted as (LED B) and PEDOT:PSS/PFO:MEH PPV/ZnO/Al denoted as (LED C). We used commercially available PEDOT:PSS coated plastic as a substrate due to its flexibility, transparency in the visible region and good electrical properties. The conductivity of PEDOT:PSS coated plastic is 170 siemens/cm and the chemical structure of PEDOT:PSS, PFO and MEH PPV is shown in Figure 1b. All polymers solutions were prepared by dissolving to a concentration of 5mg/ml. The solvent used was chloroform which both polymers are highly soluble in. The PFO and MEH PPV blend was prepared with a molar ratio of 9:1 respectively. The resulting blend solution was homogeneous. After cleaning our substrates with acetone, isopropanol and DI water separately with sonication for 5 minutes the PFO, MEH PPV and PFO:MEH PPV blend were spun coated on the three substrates using 2000 rpm spin speed for 30 sec. This give a thickness of the polymer layer(s) of ~50 nm to 60 nm. This was followed by soft baking for 5 min. at 100 ^{0}C. For the growth of ZnO NRs, spin coating of ZnO seed layer was achieved by following the method described in [19]. This procedure was repeated three times with the same spin speed and time used as above on top of the polymer to provide uniform nucleation sites for the ZnO NRs growth. The chemical bath deposition (CBD) method was used to grow the ZnO NRs. The pre-coated substrates were transferred into a beaker containing an aqueous solution of Zinc Nitrate Hexahydrate ($Zn(NO_3)_2$.$6H_2O$) dissolved in 100 mL of de-ionized (DI) water and Hexamethylenetetramine ($C_6H_{12}N_4$) denoted as (HMT) in 100 mL DI-water to achieve an equimolar concentration of 0.07 M. Then the beaker was loaded into a conventional laboratory
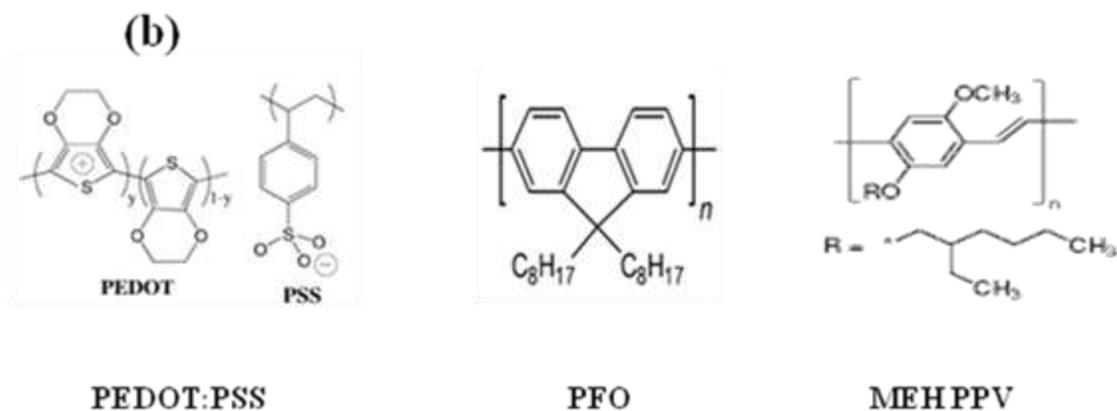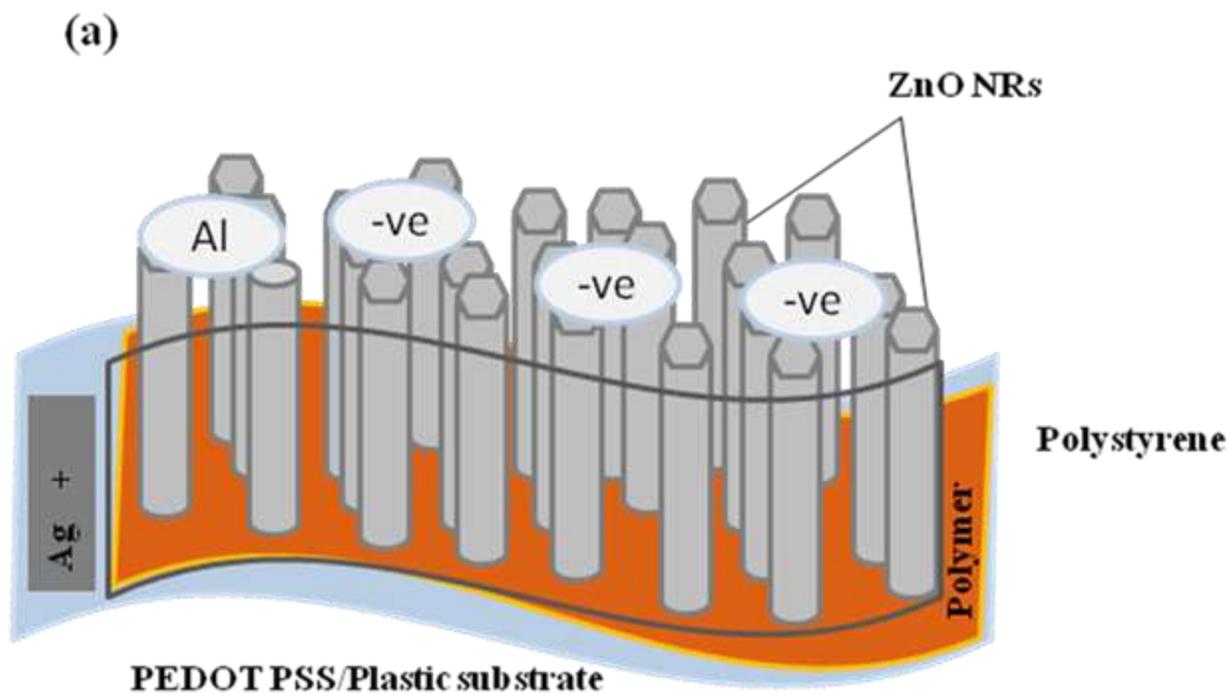
Figure 1:(a) Schematic diagram of the light emitting diode showing the structure of the fabricated LEDs. (b) The chemical structure of PEDOT:PSS, PFO and MEH PPV.

oven at 50 ^{0}C for several hours. Such growth temperature is not expected to affect the polymer layer. The samples were then removed and rinsed in DI- water and left to dry in air. Before

evaporating the top contact an insulating layer is used to fill the gap between the ZnO NRs using polystyrene. The polystyrene solution (50mg/ml) was spun coated at 4000 rpm for 30 sec. and baked for 5 min. Reactive ion etching (RIE) is used to etch the polystyrene on top of the ZnO NRs. The final step of the device was evaporating Aluminum (20 nm) to act as cathode. PEDOT:PSS is used as an anode and silver (Ag) paste on one edge was serve as an electrical contact. For the anode, we simply used silver (Ag) paste on top of the edge part of the PEDOT:PSS coated plastic. All the steps were the same for all the three LEDs. The schematic diagram of the LEDs is shown in Figure 1. All the measurements were performed at room temperature. The films thickness was measured using DEKTAK 3ST surface profiler. Scanning electron microscope (SEM) was used to study the morphology of the grown ZnO NRs. The absorption properties of the solid state films of the polymers were investigated by Perkin Elmer Lambda 900 UV-VIS-NIR Spectrometer. Agilent Parameter Analyzer HP was used to measure the current-voltage characteristics of the LEDs. The room temperature Photoluminescence (PL) spectra were measured with MBD laser source with 266 nm excitation wavelength. The electroluminescence (EL) spectra were examined using Andor-Newton DU-790N CCD.

3 Results and discussion:

SEM images of the ZnO NRs grown on top of the polymers (PFO, MEH PPV and their blend) are shown in Figure 2. Hexagonal shaped ZnO NRs were uniformly covering the polymers layer and there is no morphological difference observed between all the different ZnO NRs on different polymer layers. As shown, the ZnO NRs are well aligned along the perpendicular direction to the substrate with an average diameter of about 90 nm to 200 nm.
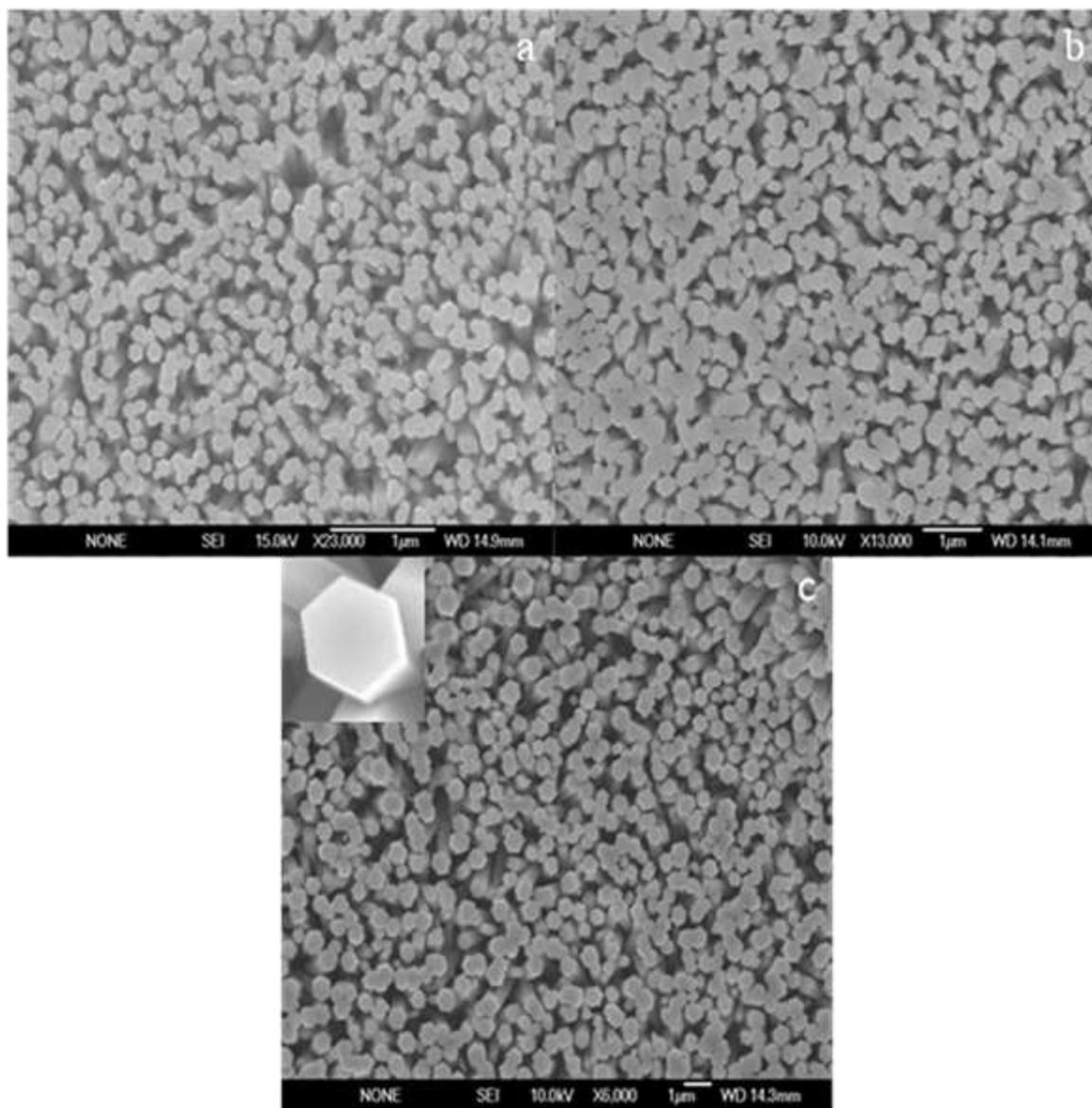
Figure 2: Field emission scanning electron micrographs (SEM) of (a) ZnO nanorods grown at 50 °C on PFO polymer layers on top of PEDOT:PSS/plastic flexible substrate, and in (b) on MEH PPV polymer layer and (c) on blended polymer layer. The inset shows magnified single ZnO nanorod.

Figure 3a shows the current-voltage (I-V) characteristics of all the three LEDs. All the devices show clear rectifying behavior. The conventional diode equation is used to analyze the rectification and the electrical behavior. The semi log plot of the LED C is in the inset of Figure 3a. From the slope and the intercepts of the linear fit of the log plot of the I-
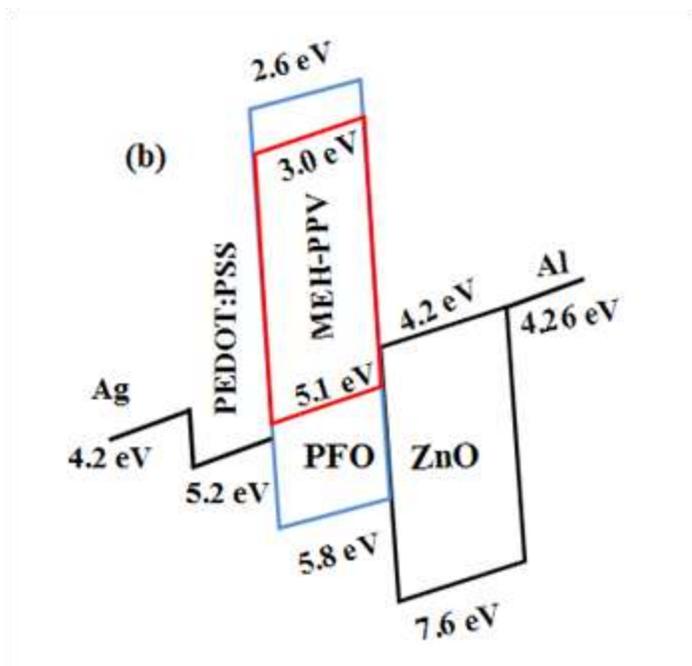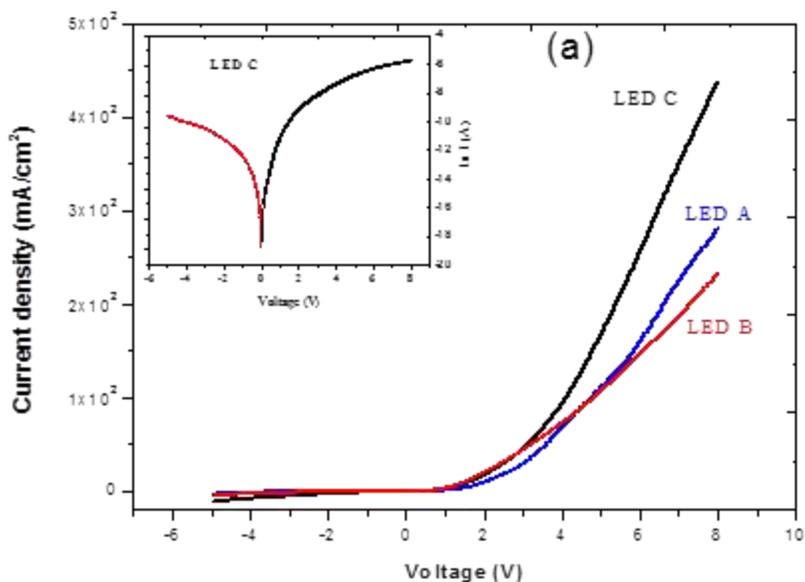
Figure 3: (a) Current-voltage characteristics of the three LEDs demonstrating a good rectification behavior and inset is the semi log plot of the LED C. (b) The energy band diagram of LED C formed using the blended polymers.

V characteristics, we have calculated the values of the ideality factor (n) for all the three LEDs. The ideality factors of LED A, B and C were 2.27, 2.1 and 2.2. This indicates that in principle there is no big difference between the different LEDs regarding the quality of the electrical performance. The value of n is higher than unity and that is attributed to the presence of many surface defects in ZnO and at the interface and due to series resistance [20]. Hence current paths other than the thermoionic emission such as recombination, tunneling etc. exist in such hybrid LEDs. The energy band diagram of LED C is shown in Figure 3b. The band gap of the PFO and the MEH PPV are 3.2 eV and 2.1 eV, as estimated from the HOMO-LUMO energy difference, showing that the MEH PPV has a smaller band gap compared to the PFO [21]. It can be seen from the energy band diagram that there is 1.2 eV and 1.6 eV barriers for electron injection from the ZnO conduction band to the MEH PPV and PFO LUMO (lowest unoccupied molecular orbital), respectively. While the hole injection barrier is 2.5 eV and 1.8 eV from the MEH PPV and PFO HOMO (highest occupied molecular orbital) to ZnO valence band, respectively.

Figure 4 show the optical absorption spectra of the PFO, the MEH-PPV, and their blend. The PFO and the MEH PPV have an absorption peaks at 385 and 510 nm, respectively. The absorption spectrum of the PFO shows a broad band centered at 385 nm due to the π-π* electronic transition whereas the MEH PPV have absorption peak at 510 nm. In the blended film the PFO peak is at 390 nm which is 5 nm red shifted from the PFO film. The absorption is mainly due to the PFO and the MEH PPV is poorly absorbing. Blending with a more MEH PPV has been investigated and it showed almost pure MEH PPV characteristics. This is why we restricted the investigation to 9:1 for the PFO:MEH PPV. This ratio when used in the present ZnO NRs/organic LED design has led to an intrinsic white light with excellent quality. Figure 4b demonstrates the PL spectra of PFO:MEH PPV/ZnO(blended/ZnO) and PFO, while MEH
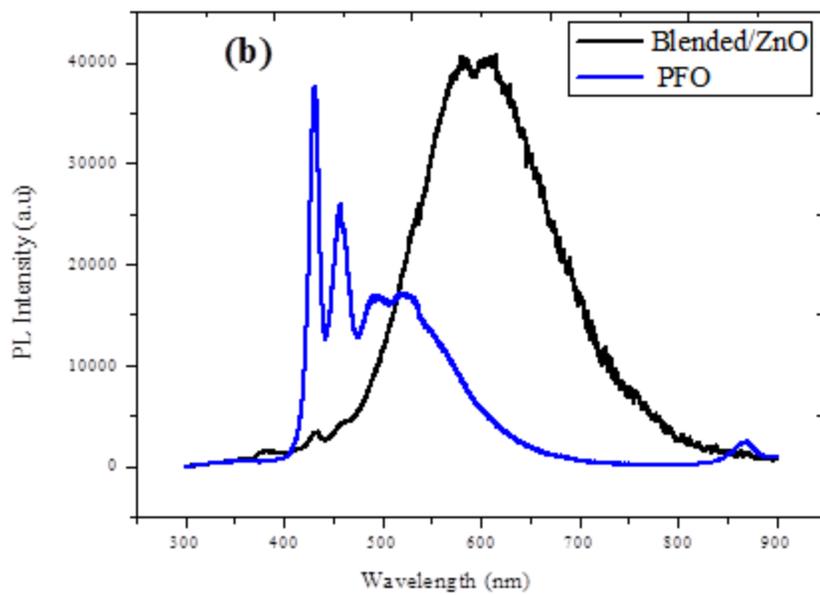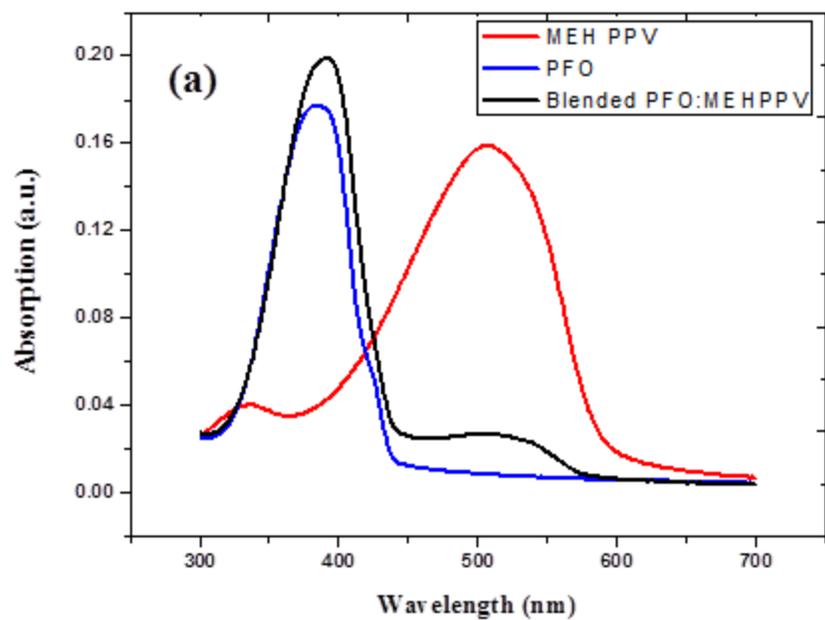
Figure 4: (a) Absorption spectra of the PFO, the MEH PPV and 9:1 blend of the PFO:MEH PPV polymers. (b) Room temperature PL spectrum of PFO and PFO:MEH PPV/ZnO.

PPV spectrum is almost like the EL spectrum (not shown here). The PFO spectrums shows two well-resolved blue peaks with a maxima at 430nm, 457nm and 490nm assigned as 0-0, 0-1 and 0-2 interchain singlet transition [22], together with a featureless broad green band with maximum at 520nm originated due to the defects produced during fabrication processes of the device. One possible reason for the defective green emission in PFs polymer is correlated with fluorenone (o=c) defects also known as on chain defect [23]. On the other hand cross linking of the PFs chains and cleavage of the σ band were investigated as another source for defect emission in PFs [24]. The blended/ZnO NRs PL exhibit the PFO blue peaks at the same position as we discussed above and the ZnO defects related peaks strongly overlapped with MEH PPV (orange-red) peaks, because on the one hand ZnO NRs are densely standing on top of the polymers layer as seen before in figure 2 with their lengths around ~ 2 μm. On the other hand the PL measurements are very sensitive to the sample surface and highly suppressed on the bulk part, therefore most of the PL detected intensity will originate from the top part of the sample (ZnO NRs), as clearly visible in the case of PFO blue peaks in Figure 4b.The featured peaks at ~ 585nm and 615nm can be ascribed to the overlapped emission of MEH PPV with the defect emission of ZnO. The emission peak at 585nm of MEH PPV is assigned to the single chain exciton transition, whereas the peak at ~615nm is due to the intrinsic vibronic structure [25]. The deep band emission DBE of ZnO wide bandgap are always associated with the low temperature growth methods, generally zinc vacancies (V_{zn}),oxygen vacancies (V_o), oxygen interstitials (O_i), zinc interstitials (Zn_i)etc. are the most commonly observed defects giving rise to many electronic transitions in the wide bandgap. The V_o defect has been reported to be responsible for the emission band appears at $\sim$ 530nm while the orange-red emission is due to the transition from Zn_i to O_i [26, 27]. From Figure 4b the ZnO near band emission NBE is hardly visible suggesting that the grown ZnO NRs

in the present study are highly defective, the PL spectrum of the blended/ZnO NRs structure the DBE of ZnO and the electronic transition in MEH PPV collectively produce a broader emission with full width at half maximum FWHM ~ 166nm.

The room temperature electroluminescence (EL) of the three LEDs under forward bias is depicted in Figure 5a. For LED A (PFO/ZnO) it showed an emission peaks at 455 nm, 470 nm, and extended peaks with a two features at 510 nm and 540nm, the first two blue peaks correspond to the PFO as discussed above [28]. The first green peak appeared at 510 nm, this peak has recently been studied by R. Mallavia et al and they have shown that upon electron injection the PF polymers electrochemically degraded leading to the formation of new species and cross-linking of the polymer chains [29]. The band at about 540 nm has two possible sources, the oxygen vacancies V_O in ZnO which is frequently observed in low temperature grown ZnO NRs , or due to the recombination of electrons with interface states in PFO/ZnO [30]. The PFO has also a defect emission reported at ~ 535nm originates from fluorenone defects which are due to thermal oxidation or generating during the device processing [23, 24]. LED B (MEH PPV/ZnO) has an extended emission from 575 nm to 750 nm with a peak at 608nm which corresponds to the MEH PPV due to the PPV backbone that arises from the relaxation of excited Π-electrons to the ground state and the shoulder at 640nm is related to interchain states [31]. At the MEH PPV/ZnO interface the potential barrier for hole injection is 2.5 eV, so few holes can be injected from the MEH PPV side into the ZnO NRs. Hence holes are confined to the MEH PPV layer. The potential barrier for electrons is 1.2 eV and the mobility of electrons in the ZnO is higher than that of holes in the MEH PPV so the recombination primarily occurs in the MEH PPV side. This is the reason why a peaks appeared in the EL spectrum is originating from the MEH PPV. For LED C the EL emission emerged at ~ 450 nm and extended to 750 nm i.e.
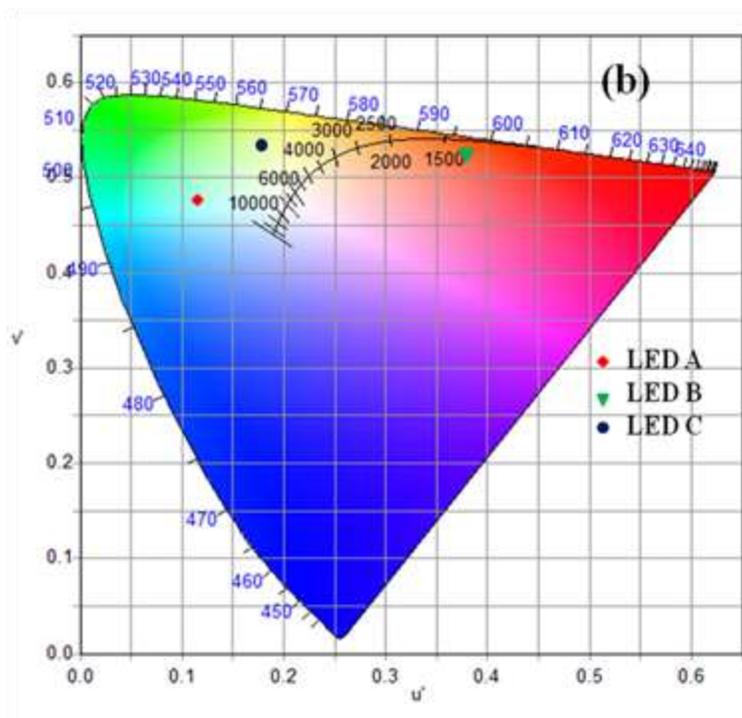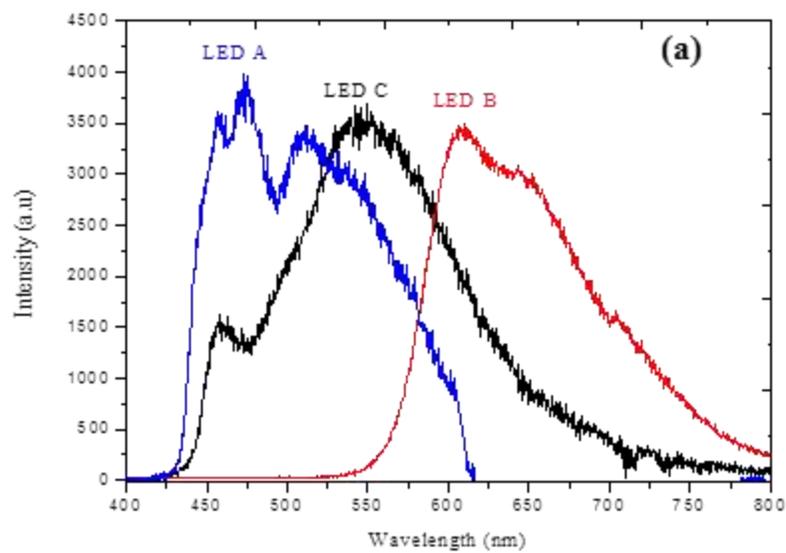
Figure 5: (a) Electroluminescence spectra of the three LEDs, (b) Chromaticity diagram (CIE coordinates) for all the three fabricated LEDs.

covering the entire visible emission. The PFO emission peak is clearly visible at ~ 455 nm, while the green emission from the ZnO DBE along with the orange-red emission from the MEH PPV are completely intermixed yielding a broad visible emission. In the blended polymer layer the smaller bandgap MEH PPV lies inside the PFO which has a larger band gap, in such situation, the excitons, electrons and holes will all move preferentially onto the lower band gap material. This can be exploited by blending small amount of MEH PPV with the larger bandgap polymer, i.e. the PFO in this case. It is seen that even at very low concentration of the MEH PPV in the blend, the energy transfer is predominant and the device gives intense emission from the MEH PPV. The PFO emission is relatively low but is still high enough to influence the colour quality of the device. The emission from both polymers is due to the incomplete energy transfer [32]. We found that a blend ratio of 9:1 regarding the PFO: MEH PPV yields an intrinsic white light with good colour quality (see discussion below).

In Figure 5b the commissions International DE L´Eclairage (CIE) of the different LEDs are plotted. For LED A, a bluish white impression can be seen with colour correlated temperature CCT (11000 ^{0}C) and colour coordinates (x=0.2115, y=0.3724). For LED B the colour coordinates are (0.5897, 0.3630) with CCT of (1335). The LED C shows white impression with colour coordinated (0.3619, 0.4764) and CCT of (4881).

4 Conclusion

In summary, different hybrid ZnO nanorods/polymer (inorganic/organic) heterostructure LEDs were fabricated by using blue, orange-red emitting polymers and also their blend as a p-type anode. These LEDs utilize the advantageous of both the n-ZnO and the p-type polymers. All three LEDs have shown diode behavior and the ideality factors were very close to each other

implying that almost identical electrical properties. Nevertheless the quality of the combined optical emission of the ZnO and the p-type polymer from the three LEDs was quite different. It is shown that the emission from the polymer can change the emitted visible light quality. The blue emission from the PFO, the orange-red emission from the MEH PPV was completely intermixed with the ZnO nanorods defect emission band. This was shown to influence the emitted light and bluish and reddish impressions where observed from the hybrid LEDs integrating the PFO and the MEH PPV polymers, respectively. While blending the PFO and the MEH PPV in a ratio of 9:1 has resulted in an intrinsic white light with good quality. As the ZnO NRs were grown at low temperature and on flexible plastic substrate, these ZnO NRs/p-polymers based LEDs offers low-cost, large-area devices for different lighting applications since the emission can be tuned to form intrinsic white light. In addition other wavelengths are also possible by adjusting the polymer used.

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