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Organic-inorganic nanocomposites for hybrid polymeric light-emitting diodes (HPLEDs)

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The presented approaches possess a new paradigm to tune of optical properties of polymers by introducing nanoparticles. Hybrid nanocomposite offers a low-cost solution-processable approach that compromises new opportunities for printed LEDs. On the other hand the HPLED sare the subject of ample concern for next-generation display technology with the prospective to be printed into manifold design areas and/or pixels. The OLEDs and HPLED are concocted by using conjugated polymers (PFO, SY) and a hybrid approach is implemented by introducing the ZnO NPs into polymers to tune the emission color and external quantum efficiency (EQE) of HPLEDs. Moreover, the results proposed, that by introducing nanoparticles into the polymer matrix, the EQE of the HPLEDs could be increased by 65%. We believe that the improved efficiencies of these devices are facilitating the commercialization of these devices.

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Keywords: Plastic light, printed LEDs, HPLEDs, OLEDs, ZnO

1. Introduction

Polymeric electroluminescence is an inspired technological activity aimed to develop high-value products to contribute in optoelectronic industry [1]. Recent light-emitting polymer materials have endowed the concept of “plastic light” with superior characteristics including self-emission, high-speed response, light weight, and compatible with the conventional lighting industry, which truly makes it a disruptive technology within the lighting industry, and offers new opportunities for exploitation. [1,2]. A smart quality of luminescent polymers is printable; thus it holds a great potential for the next generation flexible displays using roll-to-roll processing [3]. Consequently, luminescent polymers are providing economic advantages over other elaborate device fabrication techniques and a rapid development in this material technology, holds promise for the next generation of flat panel displays [4, 5].

The motivation for doing research in polymer-based optoelectronic devices comes from the possibility to tailor the chemical and electrical properties of polymers according to the requirement of application which can be tailored through chemical structure modification or conformation control during processing. The emission colors of polymers can be adjusted; therefore, the luminescence polymers are capable for the white light, multicolor displays, and flexible devices. Different methods are reported for the fabrication of WLED [4]. Single polymer WLEDs can be synthesized by incorporating two or three chromophores into a polymeric chain, but its synthesized is very difficult [6]. The WLED could be developed by multilayered polymer architecture. However, in multilayer architecture, usually it is necessary to fulfill the requirements of extended operational lifetime, which limits the use of multilayer polymer architecture in various applications [7]. The performance of multilayer polymer WLEDs is influenced by processing conditions which effect the opto-electrical characteristics. Owing to the low charge carrier mobility, the polymers have low luminance efficiency, which has driven the research to introduce

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highly efficient nanoparticles into the luminescence polymers to accomplish the advantage of their eccentric assets.

Hybrid nanocomposites are the combination of the superior properties of organic materials (flexibility, lightweight, ease of processing) and inorganic materials (electrical, thermal, and optical properties) that unveil the finest of both worlds [8, 9]. In this context, many approaches have been reported in the literature, but ZnO is indeed a highly promising metal oxide with exceptional properties that make it an excellent candidate for hybrid nanocomposites. ZnO nanoparticles (NPs) are an attractive choice for hybrid opto-electric devices due to chemical stability, environment friendly, low cost, and solution process capability, which can lead to a synergistic effect, where the combination of these two materials results in enhanced optical efficiency of the hybrid PFO-SY-ZnO NPs nanocomposites [3].

In this paper, we used a hybrid PFO-SY-ZnO NPs nanocomposites for the development of cost-effective and amenable to solution-based processable hybrid polymeric light-emitting diodes (HPLEDs). The combining the ZnO NPs and polymers enhanced the luminescence and EQE of the devices as reported. On these premises, it is clear that solution processable HPLEDs would boost the LED technology in the market, and HPLEDs are emerging as a potential competitor to traditional organic light-emitting diodes (OLEDs).

2.Experimental details

2.1. Preparation of nano- particles

The materials used are purchased from Sigma-Aldrich. We mix the 0.05 M concentration of $Zn(CH_3COO)2H_2O$ in methanol with 0.02 M concentration of Potassium hydroxide. To prepare the ZnO NPs the KOH is mixed slowly with $Zn(CH_3COO)2H_2O$ at room temperature then stirrer the solution at 60 °C for 1 60 min. Afterward, the centrifugation (3000 rpm for 30 min) were used to separate ZnO NPs. ZnO NPs can be synthesized by different methods including sol-gel, hydrothermal, or precipitation methods. The ZnO NPs size and shape is manageable by varying the solvent, reactants and processing temperature and it is reported the size of ZnO NPs is in the ranging 81-85 nm by sol gel fabrications method [10]. Jahidul Haque et al. also reported the size of ZnO NPs fabricated by the sol-gel method ranges 15-68 nm [11]. Bulcha et al. reported the ZnO NPs grown by hydrothermal methods are flower-like in shape and 1 nm to 100 nm in size [12]. By precipitation methods the size of the ZnO NPs prepared is reported between 700–1400 nm [13]. The size of reported ZnO NPs is 21 nm to 31 nm and in hexagonal shape.

2.2. Preparation of hybrid nanocomposites

The polymers used in this study PFO and super yellow SY were purchased from Sigma-Aldrich. The luminescent polymers PFO and SY were dissolved in toluene with the ratio 5mg/ml. The hybrid nanocomposites and polymers (Polymer-ZnO NPs) were mixed in 1:1 ratio and ensure uniform dispersion; the solution was stirred for 60 min at 60 °C.

2.3. Fabrication of HPLEDs

Glass substrates coated with ITO were used to fabricate the HPLEDs. The substrates were cleaned with by TL1. The PEDOT:PSS was spin-coated on the substrates at 3000 rpm for 1 min , the thickness of the layer was measured 40 nm with the surface profiler dektak [14]. On one substrate PFO (30nm) was spin-coated at 2300 rpm for 40 seconds on the PEDOT:PSS film to fabricate the OLED [3]. Similarly on the second substrate the SY (35 nm) was spin-coated at 2000 rpm for 30 seconds to make the OLED [15]. Correspondingly on the third substrate the mixture of PFO and SY with ratio 1:8 was spin-coated at 2000 rpm for 30 seconds on the PEDOT:PSS film to make the OLED [16]. To fabricate the HPLED PEDOT:PSS films were spin-coated with polymer-ZnO solution at 2400 rpm for 40 seconds it is 90 nm thick layer which is measured with the surface profiler dektak.

The 100 nm thick Au contact was thermally evaporated on all devices. As shown in Fig. 1, the Schematic diagrams of the HPLEDs illustrate the key components.

2.4. Measurements

The size/shape of the synthesized ZnO NPs were measured by JEOL JEM 1011 TEM. The photoluminescence (PL) spectra were determined by Ossila optical spectrophotometer using excitation wavelength 300 nm. Electroluminescence (EL) and electro-optical analysis were executed with a Newport photodiode (810UV) connected to a Keithley (6517A) and an electrometer photomultiplier detector.

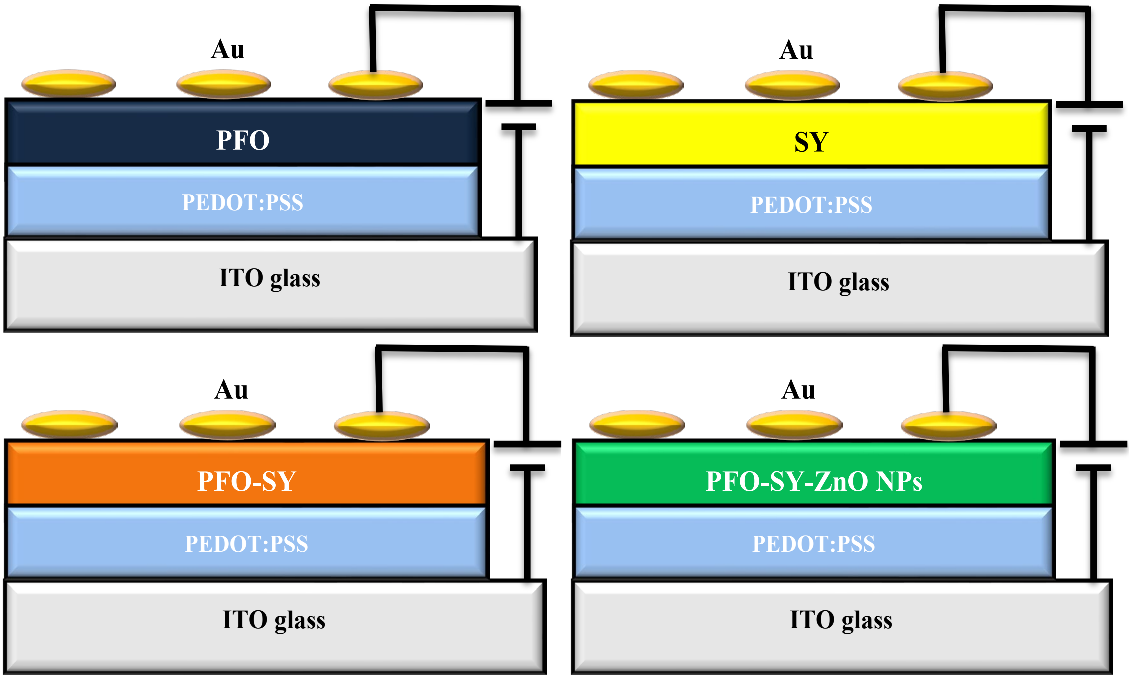

Fig. 1. Design diagrams of the OLEDs and HPLED.

3.Results and discussion

The -OH group on the surface of ZnO interrelate with carboxyl groups in the of polymers making it more compatible and enhance the interaction between hybrids materials. The TEM image of PFO-SY-ZnO nanocomposites provides visual evidence of how the hexagonal nanoparticles are incorporate into the matrix of polymer. The presence of aggregated ZnO NPs in the polymer are shown in the Fig. 2a. The ZnO NPs are clearly embedded within the polymer matrix which is aligns with prior studies [13,17, 18]. The TEM image of the ZnO NPs presented in Fig. 2 (b) confirms their crystalline and hexagonal structure which validate the successful synthesis of ZnO NPs and hybrids nanocomposites.

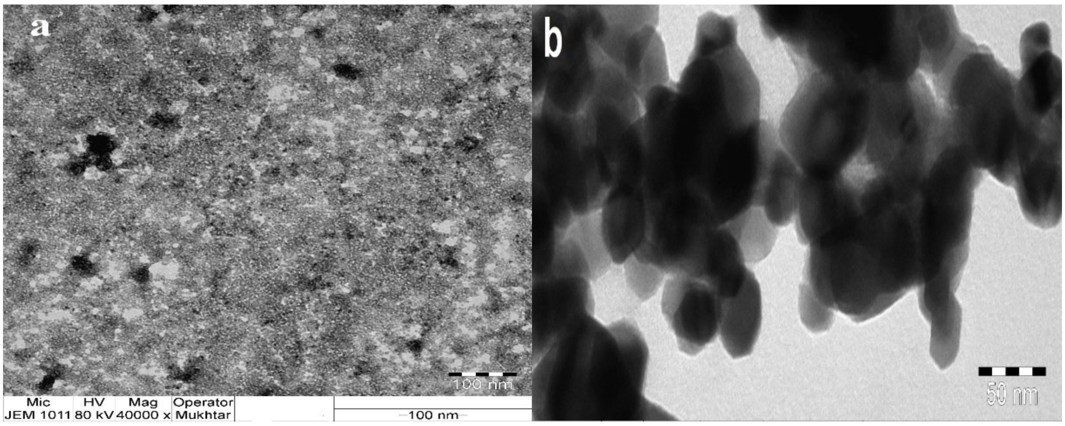

Fig. 2. (a) TEM of the PFO-SY-ZnO nanocomposite. (b) TEM image showing the shape and size of hexagonal ZnO NPs into the polymer matrix.

Figure 3 demonstrates PL spectra of PFO, SY, PFO-SY, ZnO and PFO-SY-ZnO NPs at excitation wavelength 300 nm. The PFO and SY have emission violet and yellow emissions at 430 and 580 nm, respectively. The PFO is an efficient blue emitter emission at 430 nm. The polymer composite of PFO/ SY illustrates emission at 485 nm (Blue) and 530 nm (green) [19]. The PL spectroscopy of ZnO NPs confirmations the UV emission at 380 nm which indicates the presence of ZnO with a direct band gap and secondly a wide band at 500 nm (green) corresponds to radiative recombination [20]. The broad emission band in ZnO is a complex phenomenon resulting from the existence of multiple radioactive defects simultaneously within the ZnO and the broad emission band point depends on the defects concentration in the material [21, 22]

The composite of PFO-SY and ZnO NPs possesses emission bands at 470 nm and 570 nm but the UV emission (380 nm) is missing as shown in Fig. 3. It is reported the photoelectrons from ZnO are traped by polymers therefore PL spectra of ZnO influenced correspondingly [23]. Furthermore, the photoluminescent polymers transfer resonance energy between polymers and inorganic materials thus the PL emissions of studied nano-composites depend on their relative energy levels of both materials [23]. The Bander et al reported the PL quenching in the hybrid system is due to charge transfer from the one material to the other material [24]. Organic polymers have different types of bonds capable of absorbing UV [25]. Therefore, incorporating polymers reduce or shift the ZnO UV emission.

But the addition of ZnO NPs into polymer can have several positive effects, contributing to enhanced device efficiency and performance. Therefore, the introduction of nanoparticles into the polymer indeed leads to significant changes in the PL spectra, which primes to a versatile strategy for engineering the optical properties of composite materials. Our result revealed that the hybrid nanocomposites show peaks of both polymer and ZnO NPs, which countenance that one can control the emission from the polymers by incorporating the ZnO NPs.

The PL spectrum of composite (PFO-SY-ZnO NPs) contains multiple emission peaks; therefore, we use Gaussian functions to distinguish these components. This approach is powerful for identifying and quantifying multiple emission components within complex datasets. Figure 4 clarifies the simulated emissions at 2. 8 eV (444 nm), 2.61 eV (474 nm), 2.21 eV (565 nm) and 2 eV (620 nm). The blue (475 nm) and green (565 nm) peaks are associated to V_O, and O_i defects in ZnO NPs, respectively [26]. The violet (445 nm) and orange (620 nm) emissions correspond to PFO and SY. The combination of polymers emissions violet and orange combined with ZnO NPs emissions outcomes in the white light emission represents a controlled manipulation of optical properties. The composite of ZnO NPs with luminescence polymers holds a great latent to revolutionize the improvement of large-area solution-processable and tunable HPLEDs. This investigation established that incorporating ZnO NPs in polymer mesh might offer a precise control over the luminescence efficiency and emitted colors, which could help to tune the HPLEDs [9, 26]. The luminescence properties of the nanocomposite are influenced by the formation of complexes with ionized Zinc (Zn) atom [26]. There is some evidence of such complex formation and energy transfer, which implies that there are interactions at the molecular or nanoscale level within the hybrid structure that change the optical properties [27, 28].

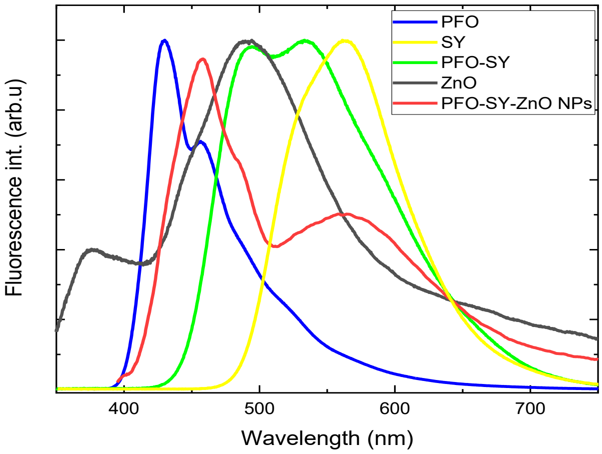

Fig. 3. PL spectroscopy graphs of PFO, SY, ZnO NPs, and PFO-SY-ZnO NPs nanocomposites at excitation wavelength 300 nm.

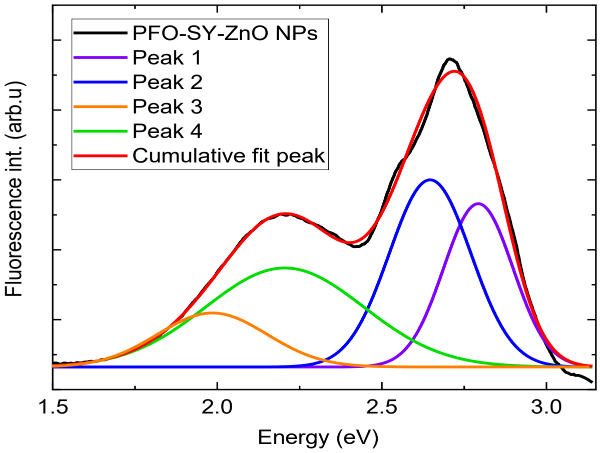

Fig.4. PL spectroscopy graphs of PFO-SY- ZnO NPs nanocomposites with Gaussian function simulations.

Fig. 5 illustrates the EL spectra of LEDs and OLEDs. The PFO OLED shows the standard excitonic emission peaks at 435 and 465 nm [9, 29]. The SY OLED displays the standard excitonic emission light at 565 nm [30].

The EL measurementsofPFO-SY OLED elucidates emission bands at 435 nm from PFO and 560 nm related to SY. The EL diagram of the PFO-SY-ZnO NPs HPLED reveals the emission peaks from PFO, SY, and ZnO NPs. ZnO NPs can facilitate charge recombination within the polymer layer. Upon the accretion of carriers at the polymer/nanoparticle interface, the recombination energy of excitons is transferred to the ZnO NPs these bonds produce electrons with sufficiently high energy to be injected into the polymer's LUMO level [31]. These charge carriers recombine with holes in the HOMO level and emanate photons. The presence of ZnO NPs can lead to an increased formation of excitons within the polymer which are beneficial for efficient light emission in polymers.

Gaussian simulation functionwas employed to analyze the obtained results and differentiate the emission components to clarify their origins. Fig. 6 demonstrates that the emissions componentsat 435 (violet), 465 (blue), 490 nm (cyan), 525 (green), 555 nm (green), and

580 nm (yellow) are in our reported spectra. The violet, blue, and cyan emissions are related to PFO. The green emission band in ZnOis associated with more than one deep level defectsand in the SY the emission at 580 nm is due to exciton emission [8, 32]. Figure 7 reveals the all-emissionlines that are distinguished by Gaussian function. It is observed that the ZnO NPs in the conjugated polymer increase the electron injection at the polymer - cathode interface which enhanced the internal electron-hole equality leading to enhanced luminescence. Furthermore, distribution of NPs in polymer matrix improves the homogeneity of radiation from whole device area. The absorption of UV by ZnO NPs protects the devices from UV degradation which increases the lifetime of organic devices [33]. Polymers are sensitive to oxidation but combining with inorganic ZnO NPs could enhanced the polymer resistance towards oxidation due to remarkably reduction in the keto defects, which correspondingly play an improvement role in light emission [34, 35]. This synergistic effect improves the charge transport, electron-hole recombination, and emission efficiency. The incorporation of n-type ZnO NPs into conjugated polymers is an efficient methodology to improve charge transport and performance of HPLEDs.

The photocurrent–voltage characteristics are crucial to realize the performance of LEDs which provides evidence about the efficiency of the LEDs at different voltages. Figure 8 illustrates the photo-I–V characteristics of the fabricated OLEDs and HPLED measured by photodiode coupled with L-I-V (light-current-voltage) measurements system. Fig. 9 confirmations the EQE for OLEDs and HPLEDs. The EQE for the devices quantifies the efficiency of the device in converting the injected electrons to photons; the calculated EQE values were 0.19%, 0.22%, and 0.55%.Which signifying that the incorporation of ZnO NPs in conjugated polymers can increase the EQE by 65%. The improved efficiencies of these devices are facilitating the development of high-performance HPLEDs for novel applications.

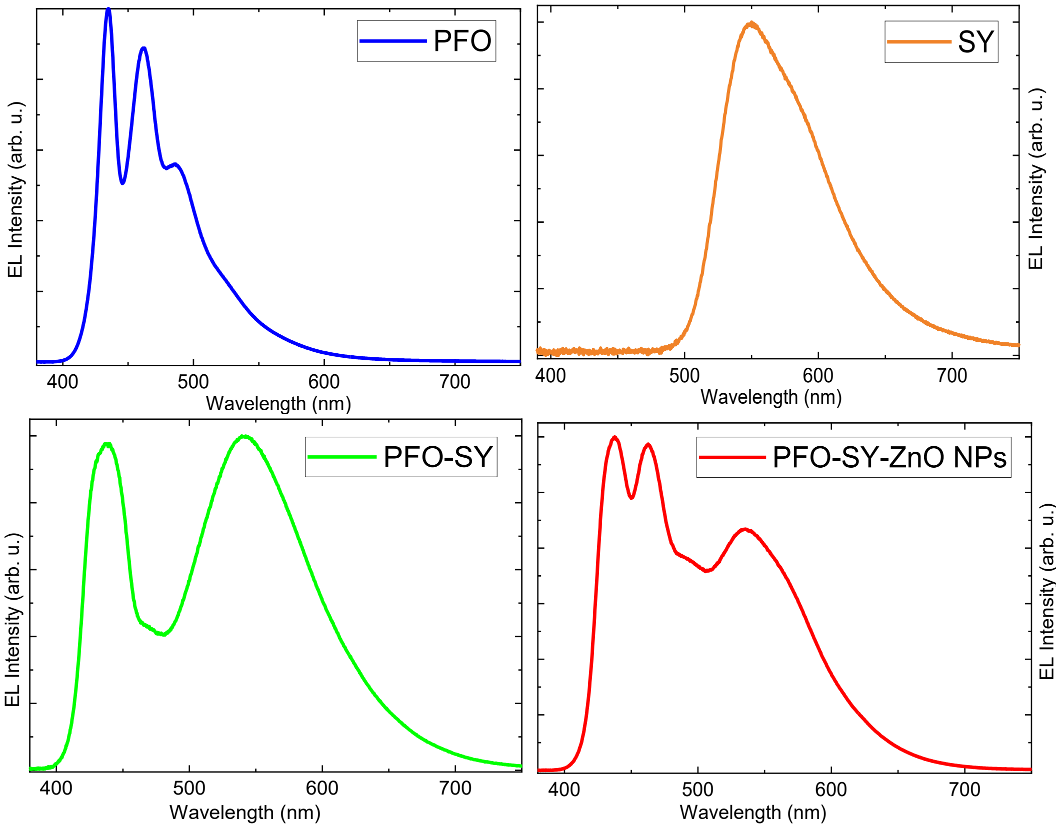

Fig. 5. EL spectroscopy results of PFO, SY, PFO-SY, and PFO-SY-ZnO NPs HPLEDs.

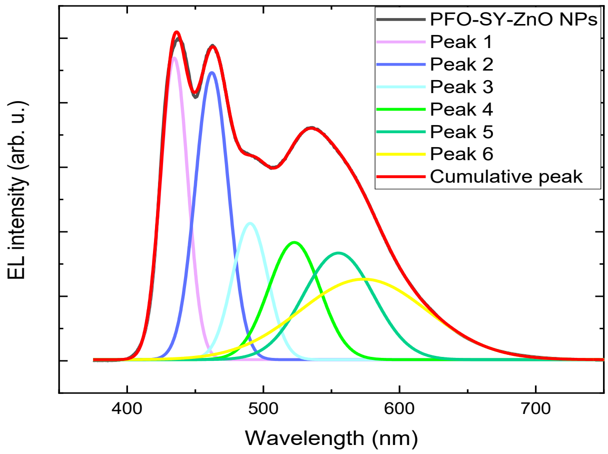

Fig.6. EL spectroscopy of PFO-SY- ZnO NPs PHLED with simulation results.

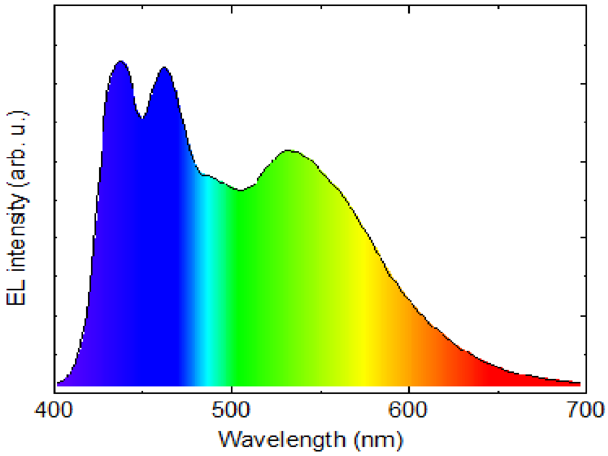

Fig. 7. EL spectroscopy results of PFO-SY-ZnO NPs HPLED showing the full color spectrum.

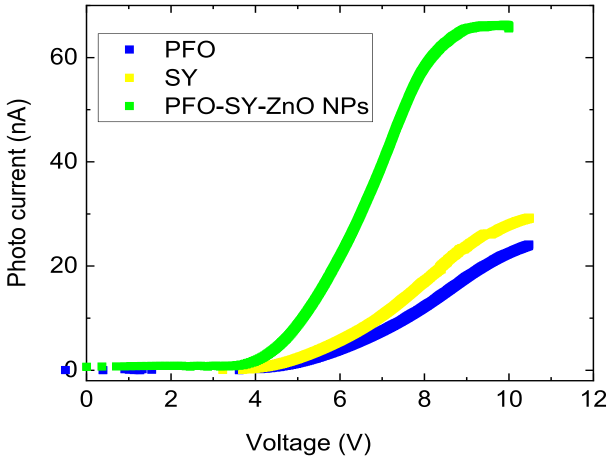

Fig. 8. The photocurrent- voltageresults of the PFO-SY-ZnO NPs HPLED.

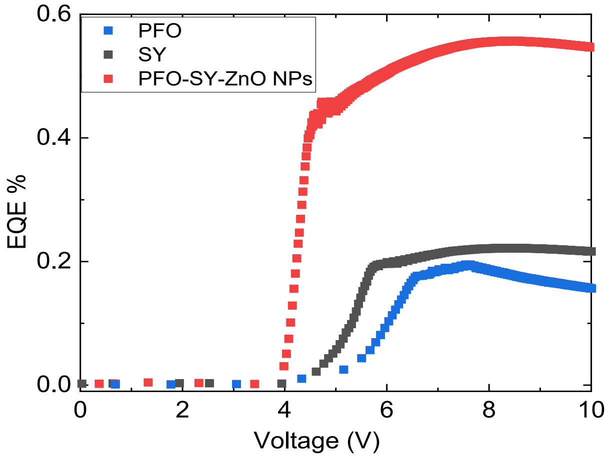

Fig.9. EQE–voltage measurements data for PFO, SY and PFO-SY-ZnO NPs composite HPLEDs.

4.Conclusions

In summary we have demonstrated an approach to tuning the emission colors and EQE of HPLEDs by introduce the ZnO NPs into conjugated polymers (PFO, SY). HPLEDs offers solution processability, enabling large area low-cost printed LEDs. Moreover, the results suggest that the EQE of the HPLEDs can potentially be increased by up to 65% through the mixing of ZnO NPs in the conjugated polymer. Based on these findings, it is evident that the development of solution-processable HPLEDs would significantly kickthe LEDs technology and HPLEDs would be a promising competitor oftraditional OLEDs.

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