Zinc oxide nanorods/polymer hybrid heterojunctions for white light emitting diodes

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Zinc Oxide Nanorods/Polymer Hybrid Heterojunctions for White Light Emitting Diodes

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Abstract

Zinc oxide (ZnO) with its deep level defect emission covering the whole visible spectrum holds promise for the development of intrinsic white lighting sources with no need of using phosphors for light conversion. ZnO nanorods grown on flexible plastic as substrate using a low temperature approach (down to 50 ^{o}C) were combined with different organic semiconductors to form hybrid junction. White electroluminescence (EL) was observed from these hybrid junctions. The configuration used for the hybrid white light emitting diodes (LEDs) consists of two-layers of polymers on the flexible plastic with ZnO nanorods (NRs) on the top. The inorganic/organic hybrid heterojunction has been fabricated by spin coating the p-type polymer Poly (3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) for hole injection with an ionization potential of 5.1 eV and Poly(9, 9-dioctylfluorene) (PFO) is used as blue emitting material with a bandgap of 3.3 eV. ZnO nanorods (NRs) are grown on top of the organic layers. Two other configurations were also fabricated; these are using a single MEH PPV (red emitting polymer) instead of the PFO and the third configuration was obtained from a blend of the PFO and the MEH PPV. The white LEDs were characterized by scanning electron microscope (SEM), x-ray diffraction (XRD), current-voltage (I–V) characteristics, room temperature photoluminescence (PL) and electroluminescence (EL). The EL spectrum reveals a broad emission band covering the range from 420 to 800 nm, and the emissions causing this white luminescence were identified.

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Introduction

Zinc oxide (ZnO) has a direct wide bandgap of 3.37 eV and a relatively large exciton biding energy of 60 meV. Although ZnO is well known to researchers since the 30s, it has now become very attractive for researchers world wide [1, 2]. The sudden huge increase of the interest in this material is due to many reasons. The self organized growth property of ZnO, enables the growth of its nanostructures on any substrate, being amorphous or crystalline in nature and hence pn heterojunctions of device quality can be achieved using external p-type materials [3]. This is in addition to the possibility of low temperature aqueous chemical growth ($< 100\ ^{o}C$) of these nanostructures [4] and the interesting effect of lowering the growth temperature using this regime of growth. Moreover, ZnO is bio-safe and biocompatible [5]. In addition, ZnO possesses a large number of deep level defects emissions covering the whole visible region, as ZnO emits violet, blue, green, yellow, orange and red lines [6]. These advantageous have led to the sudden increase of interest on ZnO as a material of potential for many applications in recent years. Due to the large bandgap, UV lasers and white light emitting diodes (LEDs) and detectors are possible to achieve using heterojunctions of ZnO nanostructures with other materials. The possibility to obtain different emission colors from ZnO will be of potential for the development of white light emitting diodes with no need for light conversion material like in e.g. GaN LEDs. This is in addition to the possibility to improve existing LEDs, e.g. combing ZnO and GaN will lead to avoid the use of phosphors for light conversion.

Here we demonstrate and characterize white LEDs based on the combination of ZnO nanorods and organic semiconducting polymers. Although pure organic LEDs (OLEDs) emitting white light have been demonstrated, the present LED offers some advantageous over pure OLEDs. Among them is the fact that we avoid using n-type polymers which suffer from ´instability. In addition the use of ZnO nanorods will enable the fabrication of large area LEDs with single contact. This is due to the many discrete pn junction formed by single ZnO nanorods. This implies that using a single contact to the ZnO nanorods through a top conducting transparent layer a large area white LED can be achieved. This would not be possible to achieve using pure OLEDs.

Recently ZnO have been demonstrated as a material of potential for many applications e.g. photonics, bio- and chemical sensors etc. [1, 5]. The combination of ZnO in the nanostructure form with organic semiconducting or conducting layers for photonic applications has been reported since 2004 [7]. In this paper we present our recent findings on the growth of ZnO nanorods NRs using the chemical growth approach. We discuss and analyze the effect of lowering the temperature on the structural and optical properties of the NRs. White light electroluminescence from two different heterojunctions composed of ZnO NRs with organic polymers will be presented and discussed.

Experimental

Zinc oxide NRs presented here were grown by the aqueous chemical growth at low temperatures (96 ^{o}C and down to 50 ^{o}C). The procedure is a two step process. The first step is the use of a ZnO nano-particle seed layer to act as the nucleation site. Although the growth of ZnO nanostructures benefit from the self organization growth property of this material, the use of the seed layer is essential for obtaining uniform and well aligned NRs. Hence care must be taken in preparing the seed layer solution and during the coating of the substrate with this solution. Usually the seed layer deposition is followed by post deposition temperature annealing in the temperature range of (250-350 ^{o}C). We have not employed any temperature annealing of the seed layer after coating, but concentrated our effort to prepare homogenous seed layer solution since it has a major effect on the uniformity of the growth of the nanostructures. In the present devices the seed layer was deposited 3-5 times to insure uniform distribution of the ZnO nano-particles over the whole substrate area. All the chemicals used were commercially purchased from Sigma-Aldrich and were used with no further purification. The aqueous solutions were prepared using clean room deionized water. The zinc oxide nano-particle seed layer solution was prepared using mixing Zinc Acetate Dehydrate (C4H6O4Zn.2(H2O) in methanol aiming at 0.01M concentration. Then this solution was heated up to 60 oC. A drop-wise solution of KOH in methanol (0.03M) was added under vigorous stirring and the whole solution was kept at 60 oC for 2 hours. Such solution is expected to contain ZnO nanoparticles with particle size in the range 3-5 nm [8]. The nanoparticles solution was then spun coated on the cleaned substrates many times at spin

speed of 2000 rpm for 40s. Another aqueous solution was prepared by dissolving Zinc Nitrate Hexahydrate (Zn(NO3)2.6H2O) in 100mL deionized water to achieve (0.15M) targeted concentration, and Hexamethylenetetramine (HMT, C6H12N4) in 100 mL DI-water to obtain (0.1M) solution. The two solutions were transferred to a 250 mL beaker under stirring for 5 minutes, pre-coated substrates with then immediately submerged horizontally inside the beaker containing the precursor solution. Then the reaction containers were directly inserted in a regular laboratory oven kept at a fixed temperature. We have used temperatures ranging between 96 ^{o}C and 50 ^{o}C for several hours. After the chosen reaction time elapsed, the substrates were thoroughly soaked in deionized water under ultrasonic agitation to remove any residual salts and then were dried at room temperature. Different substrates were used as mentioned above. Here we choose to show results obtained using flexible plastic (coated with PEDOT:PSS as examples of the use amorphous substrates, respectively. After growth different techniques were used to characterize the structural and optical properties of the grown ZnO NRs. This was achieved by using scanning electron microscopy (SEM), and x-ray diffraction (XRD). In addition, the electro-optical properties were also investigated using photoluminescence (PL) and electroluminescence (EL). Finally the color quality was extracted to obtain the color rendering index of the emitted light from ZnO NR/p-polymer hybrid junction LEDs fabricated using different polymers to investigate the effect of the polymer emission of the LED performance. The SEM morphology analysis was performed using JEOL JSM-6301F equipment. While the x-ray diffraction (XRD) was measured with Cu Kα line at wavelength 1.54Å. Room temperature PL measurements were performed using a Coherent MBD266 laser operating at λ= 266 nm. The EL behavior of the fabricated devices was examined with Keithley 2400 source meter, while the EL spectra were assembled via Andor Shamrock 303iB spectrometer supported with Andor-Newton DU-790N CCD.

Results and discussion

Figure 1a-b show a typical SEM of ZnO NRs grown by the above described aqueous chemical growth at 50 ^{o}C on flexible plastic coated by a bi-layer of top Ag thin film of a thickness of about 125 nm, and a bottom layer of PEDOT:PSS polymer layer of about 50 nm thickness. As can be seen the grown ZnO NRs were grown with good

vertical alignment and excellent spatial distribution. The thickness of these nanorods is about 100 nm and the length is about 2.5 μm. All the grown ZnO NRs on different substrates showed almost similar properties apart from a difference in the thickness and the length when the growth temperature is varied. Figure 2 shows the XRD pattern obtained from the sample shown in Figure 1. As clearly seen the ZnO (002) peak is dominating the diffraction, an indication of the vertical growth of the ZnO NRs along the vertical c-axis. All the peaks are labeled as indicated in the figure. The unlabeled peak belong the flexible plastic substrate. As mentioned above the seed layer preparation and deposition together with the growth temperature are in fact important parameters in defining the quality and dimensions of the grown ZnO NRs. ZnO NRs grown by the aqueous chemical growth usually achieved at 95 ^{o}C is always discussed as having poor optical quality leading to many deep level radiative defects commonly appearing in the optical and electro-optical emitted spectra. The optical quality mentioned here is manifested as a broad deep level emission (DLE) appearing the visible range due to the combination of different native point defects. The origin of this DLE band has been under debate for many years. Moreover, to reduce the native defects and obtain better optical properties of ZnO NRs grown at 95 ^{o}C, usually the NRs are annealed [9]. Here we will discuss and show a route for obtaining ZnO nano-crystal with good optical quality. Nevertheless, the discussion below will reveal that lowering the temperature more than 95 ^{o}C will in fact not degrade the crystalline quality of the grown ZnO NRs. Another crystal quality ZnO NRs with less radiative point defects accompanied by morphological changes will be obtained when the growth temperature is reduced. As mentioned above the samples presented here were grown at different temperatures including 95 ^{o}C, 75 ^{o}C and 50 ^{o}C. We have observed that as the growth temperature is increased the length of the ZnO NRs is increased and in addition the grown NRs are becoming thinner in diameter. The scenario proposed involves two cases. For the highest growth temperature i.e. (>90 ^{o}C) the seed layer particle size of the critical radius of nucleation decreases compared to the cases of growth at lower temperatures, while the nucleation rate increases as a consequence of increasing the zinc solubility as the temperature increases. In other words, at higher temperatures there is a competition between the nucleation on the substrate surface and the axial growth of the NRs. This implies that for the same growth

parameters, the same solution concentration, and growth duration, this competition will lead to shorter and thicker NRs as the temperature is increased. At the same time the density is maximized when the temperature is increased. On the other hand as the temperature of growth is decreased i.e. growth at 50 ^{o}C, the critical radius of nucleation remains constant over the growth duration and as a consequences longer ZnO NRs are obtained. This suggested scenario is in fact consistent with our observation on the morphology of the ZnO NRs grown at different temperatures. It is important to mention that regardless of the substrate surface used and the lattice mismatch to ZnO crystal. These results indicate that the controllability over ZnO NRs can be achieved by optimizing the growth parameters independent of the substrate used. In fact this is an important finding as it allows the growth of ZnO NRs on almost any substrate. This also confirms the self organized growth property of this material. Another important consequence of lowering the growth temperature is the concentration of the deep level native defects. As mentioned above, it was believed that NRs grown at lower temperature possesses a large amount of deep level defects compared to samples grown at higher temperatures. The ZnO NRs were grown at 95 ^{o}C as described above. Figure 3 shows the room temperature PL spectra of the PFO (without ZnO NRs) and for the ZnO NRs/PFO/PEDOT:PSS (ZnO-hybrid LEDs). As can be seen from the figure the room temperature PL spectrum of the PFO (without ZnO NRs) reveals two violet emissions at 428 nm and 450 nm, and a weak broad blue-green emission centered at 480 nm. The room temperature PL spectra of the ZnO-hybrid LED consisted of ultraviolet (UV) emission centered at around 380 nm, PFO violet/blue emissions and two deep level emission (DLE) bands from ZnO NRs. These are the green band centered at 509 nm and the red band centered at 655 nm. The origin of the DLE has been controversial for decades. This is probably one reason for the debate, since different samples have different defect configuration due to the different growth method used for each case and also the different growth conditions. The probable radiative intrinsic deep level defects in ZnO are oxygen vacancy (V_O), zinc vacancy (V_{Zn}), oxygen interstitial (O_i), zinc interstitial (Zn_i), oxygen anti-site (O_{Zn})), and zinc anti-site (Zn_O) [2].

Figure 4 shows the room temperature PL spectra of different ZnO NRs grown at 95 ^{o}C, 75 ^{o}C and at 50 ^{o}C. In general the main feature of all three PL spectra is the

appearance of two emissions. One sharp UV emission due to ZnO near band edge (NBE) emission and the second is the broad deep level emission band centered in the green region and covering almost the whole visible range. The ZnO NRs grown at 95 ^{o}C shows a weak NBE with the highest FWHM (14 nm) compared to the other two samples. While the samples grown at 75 ^{o}C has a FWHM of 12.8 nm for the UV emission and possesses a UV emission with higher intensity compared to the previous sample. Finally the ZnO NRs grown at 50 ^{o}C possesses a UV peak with a FWHM of only 8.8 nm and the intensity of the UV emission is even higher than the other two ZnO NR samples. The trend of the FWHM and intensity of the UV emission as the growth temperature is decreased is in fact consistent with the trend of the intensity of the DLE band. The DLE band intensity decreases as the growth temperature is increased. The ratio of the NBE/DLE is taken as a measure of the optical quality, with a large value indicating an improved crystalline quality [2]. From Figure 4 it is clear that this ratio is decreasing as the growth temperature is increased. In fact the intensity of the NBE for the ZnO NRs grown at 50 ^{o}C is enhanced by three times as compared to the sample grown at 95 ^{o}C. This implies that the optical quality of the grown ZnO NRs is improved as the growth temperature is decreased.

Some of the samples grown here were further processed to fabricate LEDs. The details of the fabrication process can be found in [10]. In the present paper we show results from ZnO NRs/p-polymer and ZnO NRs/p-GaN. For the ZnO NRs-p-polymer hybrid junctions we used different combination regarding the polymer side of the hybrid junction. Since the polymer emission is important as it can influence the emitted wavelength, it will be important to fabricate LEDs using ZnO NRs combined with different polymer. We have fabricated three different LEDs on these structures and these three LEDs where fabricated using PFO (blue emitting polymer), MEH PPV (red emitting polymer) and their blend. Figure 5 show the EL spectra of the three LEDs under forward bias. As can be seen the three different LEDs yielded a broad spectrum but there is a large shift in the center of the emitted spectrum. LED A (ZnO NRs/PFO) has an emission peaks at 455 nm, 470 nm and 510 nm. The first two blue peaks corresponds to the PFO and they are due to the excitonic emission and its vibronic progression from non-interacting single chains [11], and the third peak which extended from 510 nm to 610

nm has been attributed to various defects sources that is either point defects such as oxygen vacancies V_O, zinc vacancies V_{Zn}, or due to recombination of electrons with surface states in ZnO [12]. LED B (MEH PPV/ZnO) has an extended emission from 575 nm to 750 nm with a peak centered at 605 nm which corresponds to the MEH PPV due to the PPV backbone that arises from the relaxation of excited Π-electrons to the ground state [13]. 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 sharp peak appeared in the EL spectrum and it is originating from the MEH PPV. For LED C (formed by the blended PFO and MEH PPV) the EL emission emerged at ~ 450 nm and extended to 750 nm i.e. 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. We found that a blend ratio of 9:1 regarding the PFO: MEH PPV yields an intrinsic white light with good colour quality.

In order to distinguish the white-light EL spectra components and the contribution of the PFO emission we used a Gaussian function to simulate the experimental data as shown in Figure 6 (a). The simulated EL spectrum shows six different emissions at 449 nm, 471 nm, 501 nm, 531 nm, 583 and 634 nm which are associated with violet, blue, green, yellow and red, respectively. The emissions at 531 nm (green), 583 nm (yellow) and 634 nm (red) are associated with intrinsic deep level defects in ZnO. The green band is the most investigated and most debated band in ZnO. The green emission has been

explained to be originating from more than one deep level defect; V_O and V_{Zn} with different optical characteristics were found to contribute to the broad green luminescence band [14]. The yellow emission was proposed due to the transition from conduction band to O_i and red emission due to transition from Zn_i to O_i [14]. However no consensus has been reached regarding the origin of the different observed colors, partly due to the different defect configuration in different samples [15]. We have many states in the ZnO band gap due to native defects in ZnO. The energy states of various native defects had been calculated or experimentally measured in the band gap of ZnO. The emissions at 449 nm 471 nm and 501 nm are due to exciton emission of PFO. The minute contribution in green emission from PFO is due to the formation of excimer [16]. These PFO related violet and blue emissions combined with ZnO defect related green and red emissions results in the white-light emission. The Figure 6 (b) reveals the room temperature EL spectra with all emission covering the whole visible spectrum.

To investigate the emitted color quality of the presented hybrid inorganic-organic LEDs color chromaticity coordinates were plotted. Figure 7 displays the chromaticity coordinates of the three different hybrid LEDs. For the first LED, i.e. LED A fabricated using ZnO NRs/PFO, a bluish white impression is achieved with correlated color temperature of 11000 ^{o}C and having color coordinates of (x=0.2115, y=0.3724). In the case of LED B the coordinates were x=0.5461 and y=0.3724. Finally for LED C fabricated by using the blended polymer (PFO and MEH PVV), the color coordinates were 0.3619 and 0.47964, i.e. a white impression is achieved in this case.

At present we are designing different ZnO nanorods based LEDs for efficiency measurement. Although no output power data are yet available for ZnO nanorods based LEDs, the published internal quantum efficiency (IQE) results obtained from ZnO nanorods are promising [17, 18]. ZnO nanorods grown by a similar low temperature process showed IQE of 28% when measured by a He–Cd laser under excitation power density of 22 W/cm^2 at a wavelength of 325 nm [17]. While a higher value of 52% for the IQE of the near band edge emission was report for ZnO nanorods grown by the metal organic chemical vapour deposition (MOCVD) [18]. While performing our measurements in dark, a clear white impression was clearly visible with the naked eye from the presented LEDs.

Conclusion

In this paper we have shown that lowering the growth temperature when using the aqueous chemical growth aqueous can lead to better crystalline quality contrary to what was believed before. Three times improvement of the intensity of the UV emission is observed when comparing ZnO NRs grown at 50 ^{o}C to those grown at the commonly used growth temperature of 95 ^{o}C. Moreover, lowering the growth temperature will also be accompanied by morphological changes on the ZnO NRs. These changes are due to the fact that the higher the growth temperature the higher the nucleation radius of the seed particle(s) and hence this morphological changes are manifested in longer and thinner ZnO NRs as the temperature is reduced further. Moreover, this low temperature growth (at 50 ^{o}C) is demonstrated on crystalline as well as amorphous substrates (flexible plastic) and it turns out that the crystalline quality is not affected by the substrate. Light emitting diodes fabricated from ZnO NRs on both categories of substrates are demonstrated. On the amorphous flexible plastic substrates, hybrid devices using p-type organic semiconducting polymer emitting in the visible region are fabricated and characterized. The effect of the polymer emission on the LEDs performance was investigated for blue emitting polymer, red emitting polymer or a blend of both hybrids junctions. The results indicate that the polymer emission can shift the center of the broad band effectively. The best white impression was obtained when using blended polymers with a low concentration of the lower bandgap polymer. The presented results of the hybrid organic-inorganic structure on flexible substrates (plastic) provides a potential for the development of intrinsic white light sources compatible with existing armature.

Acknowledgement:

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Figure captions

Figure 1: SEM micrographs of ZnO nanorods grown at 50 $^\circ$C following ACG procedures on (a) Ag thin film coated flexible plastic and (b) on PEDOT:PSS coated flexible plastic foil.

Figure 2: XRD of the ZnO nanorods grown at 50 ^{0}C on Ag coated flexible plastic substrate.

Figure 3: Room temperature photoluminescence (PL) spectrum of the ZnO NRs/PFO hybrid structure and the PL spectrum of the PFO on PEDOT:PSS plastic.

Figure 4: Room temperature photoluminescence (PL) spectra of ZnO nanorods grown at 50^{0}C, 75^{0}C and 95 ^{0}C on Ag coated plastic.

Figure 5: Electroluminescence (EL) spectra of the three different LEDs fabricated using ZnO NRs/p-polymer hybrid junctions, the spectrum labeled by A is for the case of using the PFO, while B indicates the case of using the blend of PFO and MEH PPV, and finally C indicates the case of using the MEH PPV polymer.

Figure 6: (a) Room temperature EL spectrum with Gaussian fitting (b) The EL spectrum showing the whole visible range as distinguished by the Gaussian fitting.

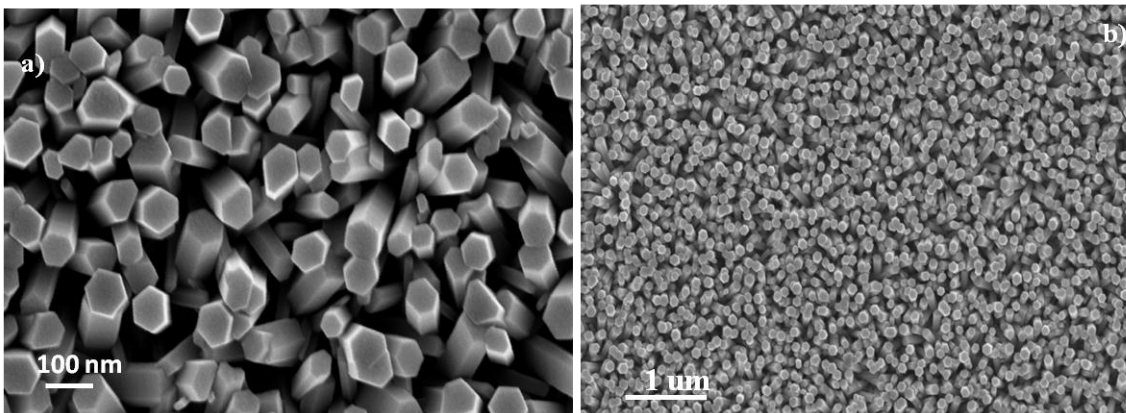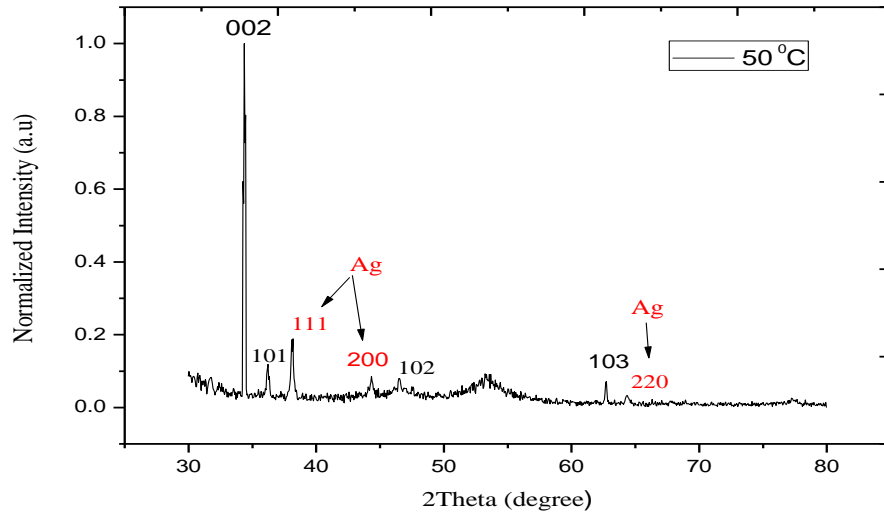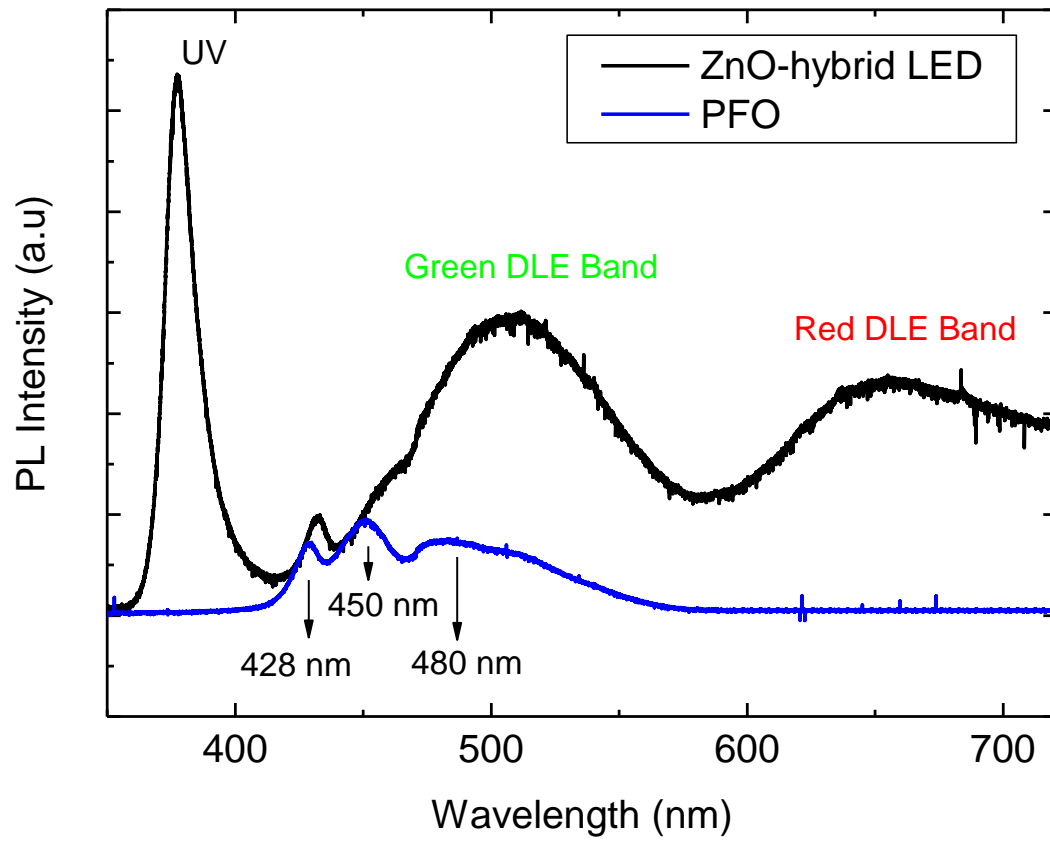**Figure 7:** Chromaticity diagram (CIE coordinates) of the three hybrid LEDs.
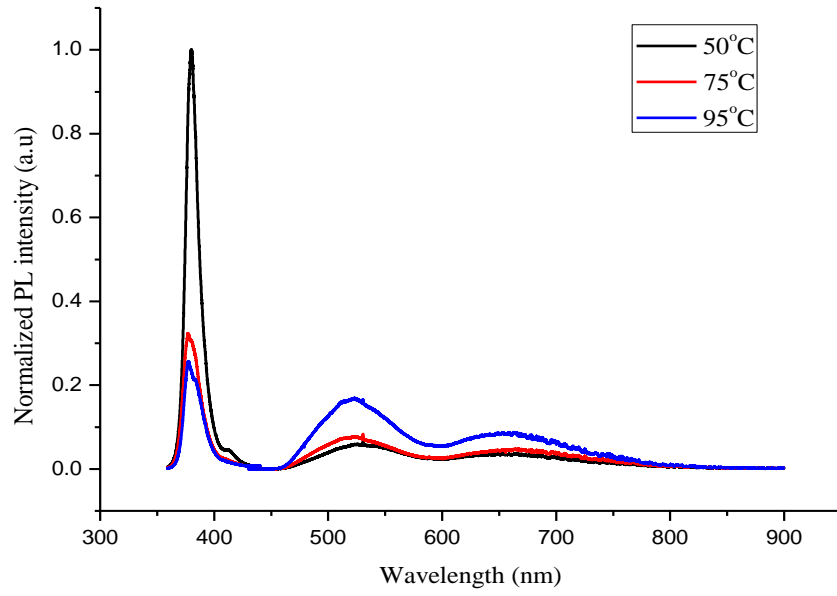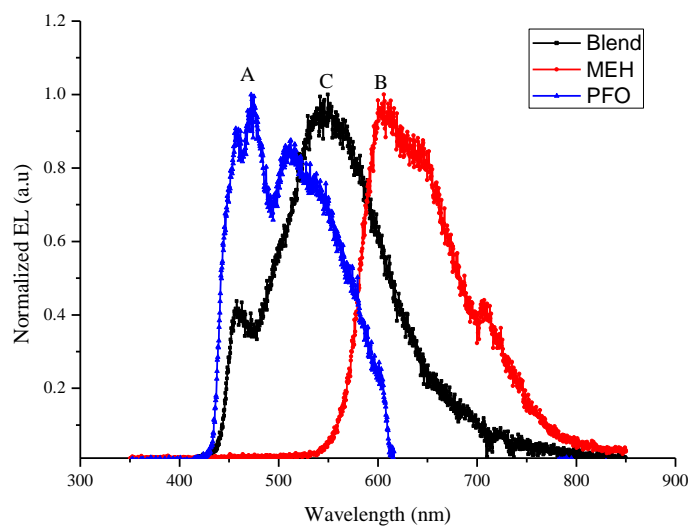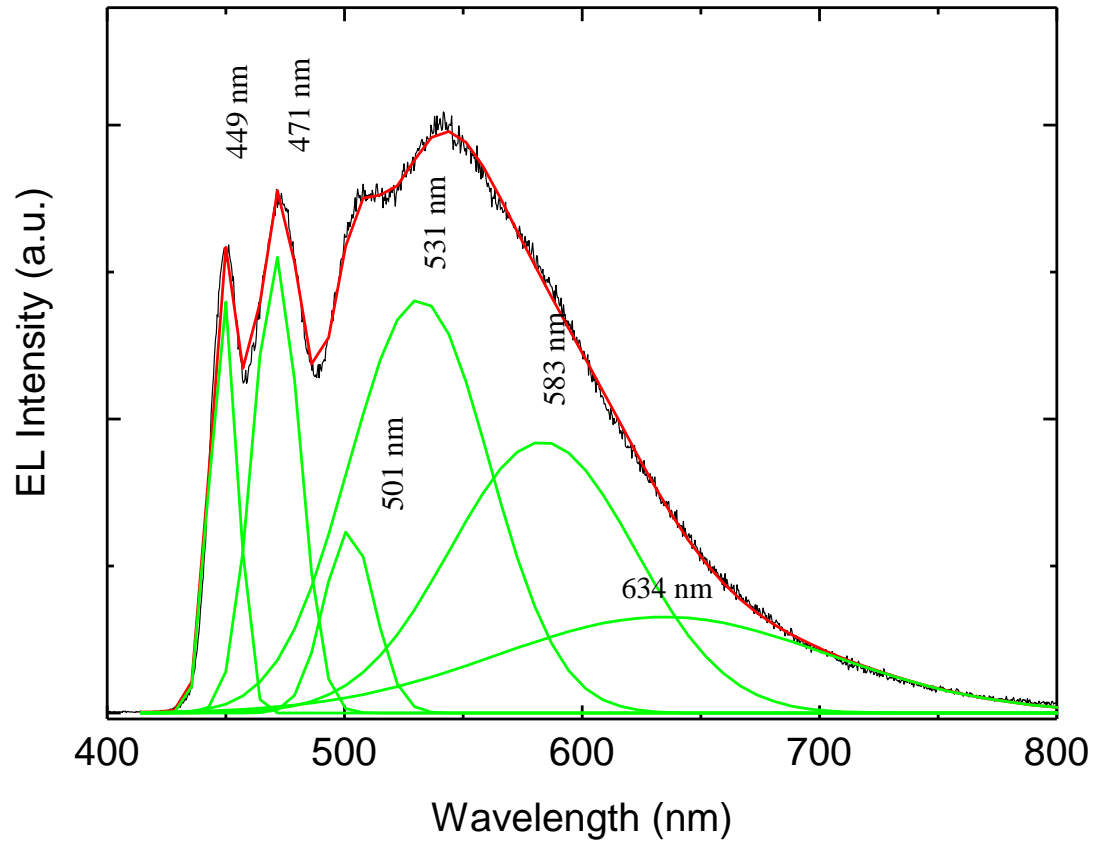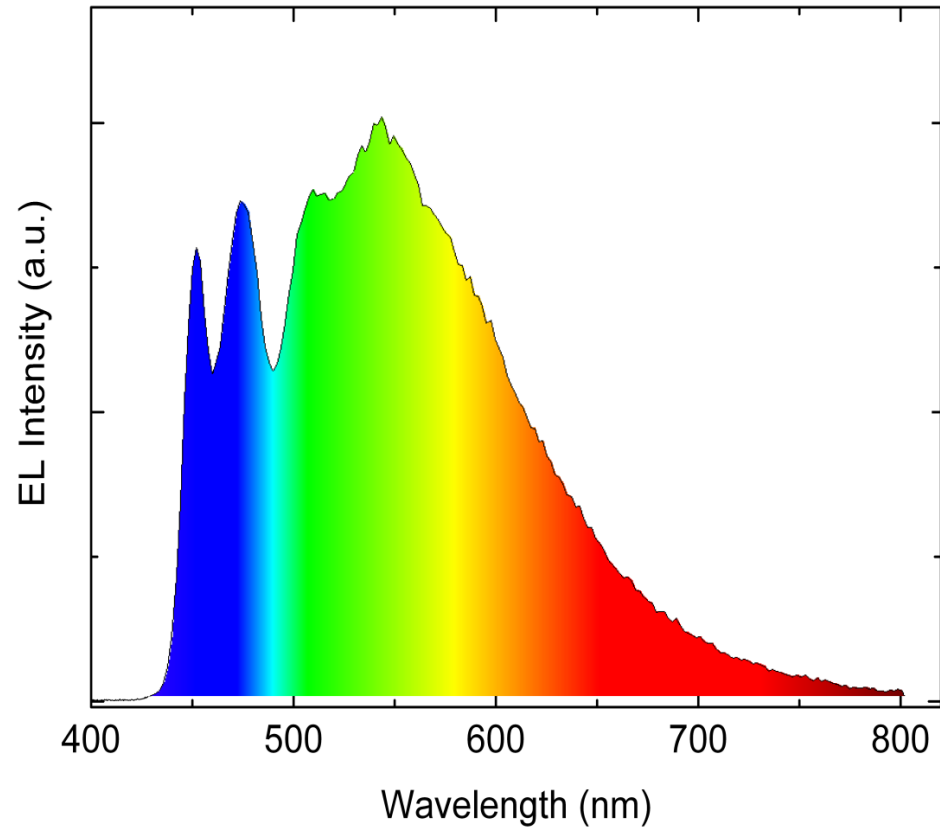
Figure 1:

Figure 2:

Figure 3:

Figure 4:

Figure 5:

Figure 6a:

Figure 6b:

Figure 7: