Research Article

Influence of TiO$_2$ Nanoparticles on Enhancement of Optoelectronic Properties of PFO-Based Light Emitting Diode

Bandar Ali Al-Asbahi, Mohammad Hafizuddin Haji Jumali, Chi Chin Yap, and Muhamad Mat Salleh

1 School of Applied Physics, Faculty of Science and Technology, Universiti Kebangsaan Malaysia (UKM), 43600 Bangi, Selangor, Malaysia
2 Department of Physics, Faculty of Science, Sana’a University, Sana’a, Yemen
3 Institute of Microengineering and Nanoelectronics (IMEN), Universiti Kebangsaan Malaysia (UKM), 43600 Bangi, Selangor, Malaysia

Correspondence should be addressed to Bandar Ali Al-Asbahi; alasbahibandar@gmail.com and Mohammad Hafizuddin Haji Jumali; hafizhj@ukm.my

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Improvement on optoelectronic properties of poly (9,9′-di-n-octylfluorenyl-2,7-diyl)- (PFO-) based light emitting diode upon incorporation of TiO$_2$ nanoparticles (NPs) is demonstrated. The PFO/TiO$_2$ nanocomposites with different weight ratios between 5 and 35 wt.% were prepared using solution blending method before they were spin coated onto Indium Tin Oxide substrate. Then a thin Al layer was deposited onto the nanocomposite layer to act as top electrode. The nanocomposites were tested as emissive layer in organic light emitting diodes (OLEDs). The TiO$_2$ NPs played the most crucial role in facilitating charge transport and electrical injection and thus improved device performance in terms of turn-on voltage, electroluminescence spectra (EL), luminance, and luminance efficiency. The best composition was OLED with 5 wt.% TiO$_2$ NPs content having moderate surface roughness and well distribution of NPs. The device performance was reduced at higher TiO$_2$ NPs content due to higher surface roughness and agglomeration of TiO$_2$ NPs. This work demonstrated the importance of optimum TiO$_2$ NPs content with uniform distribution and controlled surface roughness of the emissive layer for better device performance.

1. Introduction

Organic light emitting diodes (OLEDs) are relatively more efficient compared to inorganic light emitting diodes since they require a relatively small amount of power for the same amount of light produced. Besides that, OLEDs offer several merits such as easy to fabricate, low cost, flexible, and low operating voltage. Typical polymers used in organic light emitting diodes (OLEDs) displays include derivatives of poly (p-phenylene vinylene) (PPV) and polyfluorene (PF). Regrettably, PPV and PF-based light emitting diodes performance are limited by their poor stability as well as low luminance efficiency. The main reason for the low luminance efficiency is low electron mobility, and high energy barrier between the emissive layer and the electrodes resulted in poor electron injection. Incorporation of inorganic semiconductor, which have low energy barrier to electron injection and high electron mobility into polymer, is one way to resolve the transport and electron injection limitations [1–5].

In recent years, polymer/inorganic nanocomposites received much attention from a great number of researchers [6–8]. This is because the composite systems were reported to exhibit better thermal, mechanical, optical, and electrical properties in comparison to the pure polymer. Earlier studies suggested that the suitability and compatibility of any nanocomposite materials for optoelectronic applications can be predicted from detailed study on their fundamental properties in particular conjugated length, energy gap, and energy transfer efficiency [9, 10]. Recently we predicted the suitability of poly (9,9′-di-n-octylfluoren-2,7-diyl) (PFO)/TiO$_2$ nanocomposite as an emissive layer in OLED devices [11].
The PFO has highest occupied molecular orbital (HOMO) of $-5.9\, \text{eV}$ and lowest unoccupied molecular orbital (LUMO) of $-2.9\, \text{eV}$ [12], while the work function values of Indium Tin Oxide (ITO) and Al electrodes are $-4.8\, \text{eV}$ and $-4.3\, \text{eV}$, respectively [13]. Based on these values, the barrier height between the HOMO of PFO and the ITO is much smaller than the barrier height between the LUMO of PFO and the Al electrode (Figure 1). Together with poor electron mobility compared to hole mobility in PFO, huge barrier height between the LUMO of PFO and the Al electrode resulted in the notorious charge imbalance problem in PFO. Insertion of suitable entity into PFO matrix to form a small barrier height for electron injection is thought as the best solution for this problem.

This work investigated the effect of TiO$_2$ NPs contents (valence band and conduction band of $-7.4\, \text{eV}$ and $-4.2\, \text{eV}$, resp. [14]) embedded into PFO on the formation of a smaller barrier height for electron injection at PFO/Al interface. In addition, this work reports the effect of TiO$_2$ NPs content on performance of the PFO-based OLED in terms of turn-on voltage, electroluminescence spectra (EL), luminance, and luminance efficiency. The Commision International de l’Eclairage (CIE) chromaticity diagram was used to map the colors of the OLED devices. Finally, the effect of the film morphology on the device performance was demonstrated.

2. Experimental Procedures

2.1. Materials. The poly (9,9'-di-n-octylfluorenyl-2,7-diyl) (PFO) ($M_w = 58200$) and TiO$_2$ powder (mean size of 25 nm) were purchased from Sigma Aldrich, USA. These materials were stored in the dry box and used without further purification. All materials were dissolved in toluene solvent produced by Fluka. ITO coated glass substrate with a sheet resistance of 50 $\Omega$/sq was purchased from Merck Balzers and used in this study.

2.2. Samples Preparation and OLED Fabrication. As previously reported [11], the solution blending method was employed for the preparation of PFO/TiO$_2$ nanocomposites. TiO$_2$ NPs with different weight ratios (5, 15, 25, and 35 wt.%) were added into fixed concentration of PFO (15 mg/mL). The mixtures were stirred at 600 rpm overnight followed by sonication for 1 h to get homogeneous nanocomposite solutions. Prior to OLED fabrications, the ITO which served as anode was firstly etched and patterned by exposing to the vapor of nitric acid (HNO$_3$) and hydrochloric acid (HCl) in a molar ratio of 3 : 1. Next, the ITO was cleaned sequentially in isopropanol and acetone under ultrasonication for 10 minutes each to clean the surface and remove any impurities.

Using spin coating technique, 100 $\mu$L of PFO/TiO$_2$ nanocomposite solution was deposited onto a substrate with dimensions of 1.2 cm $\times$ 2 cm to form a thin layer. The deposition parameters were fixed at 2000 rpm for 30 sec. Then, it was baked at 120°C for 10 minutes in a vacuum oven to remove the solvent from the film. A thin aluminum layer on the nanocomposite film was deposited using electron beam chamber with deposition rate of 2 Å/min at the chamber pressure of 2.5 $\times 10^{-6}$ Pa.

2.3. Samples Characterization. The current density-voltage (J-V) was obtained using a Keithley 238 measurement system, whereas electroluminescence spectra (EL), luminance, and color measurements were obtained using HR2000 Ocean Optic Spectrometer. The values of turn-on voltage for all devices are defined as the voltage at the device luminance of 0.5 cd/m$^2$. The surface morphology of the films was investigated by Scanning Probe Microscope (SPM) in tapping mode using phosphorus doped Si probe (model Veeco CONT20A-CP, part no. MPP-31123-10).

3. Results and Discussion

3.1. Current Density-Voltage Measurements. The current density-voltage (J-V) characteristics of the pristine PFO and PFO/TiO$_2$ nanocomposites OLED devices are shown in Figure 2. Continuous reduction in turn-on voltage of injection current was observed in the PFO/TiO$_2$ nanocomposite devices as compared to the pure PFO (Table 1). These positive findings can be understood as better injection of charge carrier resulted from lower potential barrier at the nanocomposite-electrode interface [15]. On the other hand, the rising of current density with the TiO$_2$ NPs content may possibly attributed to reduction in both the resistance and activation energy of the PFO/TiO$_2$ layer which facilitated charge transport [1, 12].

![Figure 1: Energy band diagram for Al/PFO/TiO$_2$/ITO OLED device relative to vacuum.](image-url)
Table 1: Optoelectronic characteristics of pristine PFO and PFO/TiO$_2$ nanocomposite light-emitting diodes at various contents of the TiO$_2$ NPs.

<table>
<thead>
<tr>
<th>Emissive layer</th>
<th>Max. luminance (cd/m$^2$)</th>
<th>Luminance efficiency (cd/A)</th>
<th>Turn-on voltage (V)</th>
<th>CIE coordinates</th>
<th>Current density (mA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine PFO</td>
<td>30 at 31 V</td>
<td>0.044</td>
<td>18</td>
<td>0.332 0.486</td>
<td>68.6</td>
</tr>
<tr>
<td>5 wt.% TiO$_2$</td>
<td>252 at 29 V</td>
<td>0.11</td>
<td>16</td>
<td>0.347 0.489</td>
<td>220.0</td>
</tr>
<tr>
<td>15 wt.% TiO$_2$</td>
<td>232 at 25 V</td>
<td>0.06</td>
<td>14</td>
<td>0.373 0.500</td>
<td>373.2</td>
</tr>
<tr>
<td>25 wt.% TiO$_2$</td>
<td>117 at 18 V</td>
<td>0.02</td>
<td>11</td>
<td>0.374 0.509</td>
<td>589.0</td>
</tr>
<tr>
<td>35 wt.% TiO$_2$</td>
<td>7 at 16 V</td>
<td>0.0004</td>
<td>13</td>
<td>0.375 0.477</td>
<td>1783.6</td>
</tr>
</tbody>
</table>

$^a$At maximum luminance, $^b$at luminance of 0.5 cd/m$^2$ as standard.

However, once the TiO$_2$ NPs content increased to 35 wt.%, the J-V curve displayed almost a linear relationship, indicating a change in electrical behavior from semiconductor to resistor behavior. It was found later that this behavior was influenced by its surface profile as evidence from SPM images (Section 3.5).

3.2. Electroluminescence Spectra. The electroluminescence (EL) spectra of pristine PFO and PFO/TiO$_2$ nanocomposite films, under forward bias and at the maximum luminescence, are compared in Figure 3. It can be seen that all devices yielded a broad EL spectra.

The PFO device was observed to emit photons at 428, 450, and 525 nm (Figure 3). The first two blue peaks were consistent with the PFO, which correspond to photoluminescence spectra (PL) [11]. These peaks are attributed to the excitonic emission and its vibronic progression from noninteracting single chains [16]. The third peak is due to the formation of fluorenone defects (keto defects) which are incorporated as C=O in the PFO backbone [17–19]. The photooxidation, electrooxidation, and thermal oxidation are the major reasons for the generation of fluorenone ([(C$_6$H$_4$)$_2$C=O]) defect, which created lower energy emission at 525 nm. Since such defects are mainly generated during fabrication of the device, the low energy emission band (525 nm) is typically more intense in EL than PL.

In the case of PFO/TiO$_2$ nanocomposite devices, the same EL peaks of the PFO were observed, where the emission band (from 525 to 700 nm) was extended with the TiO$_2$ NPs increment. Similar trend was reported earlier in PFO/ZnO LED [2]. It is believed that this extended emission band was due to the presence of different defect sources in the materials such as oxygen vacancies (V$_{O}$), metal ion vacancies (V$_{Ti}$), or recombination of electrons with surface states in metal oxides.

Additionally, all composite devices (up to 25 wt.% TiO$_2$ NPs) exhibited better EL intensity compared to that of pristine PFO. Among these devices, it is clearly observed that the device with 5 wt.% of TiO$_2$ NPs has the highest EL intensity which is attributed to the best balancing between holes and electrons and thus highest electrons-holes recombination [20]. However, device with 35 wt.% TiO$_2$ NPs displayed inferior optoelectronic properties compared to all devices, as will be interpreted in Sections 3.3 and 3.5.

3.3. Luminance (cd/cm$^2$) and Luminance Efficiency (cd/A). There are two crucial factors for an enhancement of both luminance and luminance efficiency upon inclusion of the TiO$_2$ NPs into the PFO. The first is the decrease of LUMO barrier height at electrode interface (Figure 1). The second factor is higher electron mobility in TiO$_2$ NPs (1.7 × 10$^{-4}$ cm$^2$/Vs) [21] compared to that of hole in PFO (1.6 × 10$^{-5}$ cm$^2$/Vs) [17], which lead to recombination of both electron and hole took place in the PFO.

Figure 4 displays the luminance-voltage characteristics of the PFO and PFO/TiO$_2$ OLED devices. It was confirmed that the device luminance was improved with increasing the TiO$_2$ NPs content. As an example, the maximum luminance was enhanced from 30 cd/m$^2$ at current density of 68.6 mA/cm$^2$ in pristine PFO device to 252 cd/m$^2$ at current density of 220 mA/cm$^2$ in the PFO/TiO$_2$ device with 5 wt.% TiO$_2$ NPs. Similar positive trend was observed for luminance efficiency. This means that the incorporation of the TiO$_2$ NPs enhanced
the luminance, luminance efficiency, and current density of the PFO device between 250% and 800%. This dramatic enhancement was attributed to the incorporation of the TiO$_2$ NPs which decreased the LUMO barrier height from 1.4 eV for PFO to 0.1 eV at the PFO/Al interface as shown in Figure 1. In addition, at the PFO/TiO$_2$ interface, the high potential barrier of electron injection (1.4 eV) leads to entrapment of the electrons in the PFO side, before recombination with incoming holes from the ITO (anode) resulted in high luminance. The suggested mechanism of these processes is presented in Figure 5(a). It is worth noting that the hole-electron recombination in the TiO$_2$ side is not allowed, which was evidenced by absence of any peaks in the ultraviolet region as shown in EL spectra (Figure 3).

Dramatic reduction of luminance and EL intensity was recorded once the TiO$_2$ NPs content exceeded 25 wt.%. This could be due to either electrons hopping into the conduction band of the TiO$_2$ or the electrons tunnel through the emissive layer of the PFO without recombining with the holes or combination of both as illustrated in Figure 5(b). This electron hopping and tunneling became severe when there is poor distribution of nanoparticles on the emissive layer.

3.4. Color Measurements. Figure 6 shows the typical CIE coordinates of PFO/TiO$_2$ OLED device when the applied voltage was increased from 18 to 29 V. The consistency between CIE coordinates and the analysis of EL spectra was clearly observed. This figure displays that a shift was demonstrated with a rise in the applied voltage. The CIE coordinates were red-shifted from (0.319, 0.487) to (0.346, 0.505) upon rising applied voltage from 18 to 26 V. After that, it shifted from (0.346, 0.503) to (0.347, 0.489) as the applied voltage increased from 27 to 29 V.

As summarized in Table 1, a slight shift in CIE coordinate was demonstrated with the rise of the TiO$_2$ NPs content at the applied voltage which caused maximum luminance. This means that the produced color was stable, which was consistent with EL spectra (Figure 3). As the applied voltage increased, more electrons could be transported across the PFO/TiO$_2$ high energy barrier into the LUMO of PFO and thus the exciton recombination in the PFO side was increased. On the other hand, the CIE coordinates variation when the applied voltage increased could be attributed to the rise in sensitivity of the electric field during the carrier transport and injection [22]. The increase in the electric field on both boundaries of the emitting layer was caused by the relatively high voltage. Moreover, the red-shift in CIE coordinates as the applied voltage increase is attributed to the extension of the recombination zone as well as keto-type defect formation [22].

3.5. Morphology of PFO/TiO$_2$ Nanocomposite Films. Surface morphology of pristine PFO and PFO/TiO$_2$ films in OLED were observed to play a crucial role in device performance. Figure 7 shows SPM micrographs of PFO and PFO/TiO$_2$ films, which were measured over an area of 2.5 $\times$ 2.5 $\mu$m$^2$. Large protuberance formed on the surface of the PFO/TiO$_2$ nanocomposite films as compared to pristine PFO film. Formation of large protuberance was attributed to the agglomeration of TiO$_2$ NPs due to strong electrostatic force during the deposition process [23]. This observation was in good agreement with the previous report [11].

The root mean square (RMS) roughness exhibited dramatic increment from 1.402 to 77.80 nm as shown in Figure 8. During deposition, the PFO was liquid wetted in the TiO$_2$ NPs in an effect known as capillarity which consequently increased the surface roughness. This induced roughness at
the interface between the Al cathode and the PFO/TiO₂ layer, which assisted electron injection [1].

As shown in Table 1, it can be seen that the device at 5 wt.% TiO₂ NPs exhibited significantly better optoelectronic properties compared to other devices. Despite similar roughness with pristine PFO device, the superior optoelectronic properties of this device suggest the importance of TiO₂ NPs in the nanocomposite system compared to roughness.

As TiO₂ NP contents increased, the devices continued to exhibit reduction in turn-on voltage, a direct consequence of increment in roughness [1]. Unfortunately, this reduction was at the expense of luminance and luminance efficiency. For example, at 15 wt.% TiO₂ NPs content, the luminance and luminance efficiency were dropped by 8% and 45%, respectively, compared to the same parameters for device with 5 wt.% TiO₂ NPs content. As the TiO₂ NPs content increased to 25 wt.% the luminance was halved from the highest value while luminance efficiency was significantly inferior even if compared to pristine PFO. The huge reduction in both properties was contributed by the gigantic increment in surface roughness attributed to the presence of large amount of TiO₂ NPs.

A more dramatic reduction can be observed in device with 35 wt.% TiO₂ NPs content in which the presence of large protuberance, although produce similar roughness with 25 wt.% TiO₂ NPs, resulted in the material to lose its semiconducting behavior as demonstrated in Figure 1. Due to severe agglomeration, this nanocomposite behaved as matrix material which reduced the interface between PFO and TiO₂ NPs and hence significantly reduced charge transport. Similar observation has been reported by Madhave Rao and coworkers in a 2,3-dibutoxy-1,4-poly (phenylene vinylene) (DBPPV)/ZnO nanocomposite at high content of ZnO NRs [1]. Additional evidence of severe agglomeration in the PFO/ TiO₂ nanocomposites system has been demonstrated by FE-SEM images [11].

4. Conclusion

The solution blending method was successfully used to prepare PFO/TiO₂ nanocomposites, which were used as emissive layer in OLED devices. The optoelectronic properties of the devices were strongly influenced by the TiO₂ weight fraction. Based on the current work, the device with 5 wt.% of TiO₂ NPs exhibited the best performance contributed by optimum balance between holes and electrons recombination as well as good surface roughness. In contrast, the device with 35 wt.% displayed the worst performance attributed mainly to extremely high surface roughness and agglomeration. The red-shift of CIE coordinates, which related to maximum luminance, upon addition of TiO₂ NPs illustrating the extension of the recombination zone for holes and electrons in the OLED devices. The current work showed that carefully control TiO₂ NPs content in the starting composition is crucial to achieve optimum balance for excitons recombination.
Figure 7: 2D and 3D SPM images of PFO and PFO/TiO₂ nanocomposites measured over an area of 2.5 × 2.5 μm².
and suitable for the surface roughness for better devices performance.

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References


