Preparation and characterization of nanostructured composite films for organic light emitting diodes

Nguyen Nang Dinh¹, Le Ha Chi¹, Nguyen Thang Long¹, Tran Thi Chung Thy², Tran Quang Trung³ and Hyung-Kook Kim⁴

¹ College of Technology, Vietnam National University, 144 Xuan Thuy Road, Cau Giay District, Hanoi, Vietnam
² Thai Nguyen University of Education, Thai Nguyen City, Vietnam
³ College of Natural Science, Vietnam National University, 227 Nguyen Van Cu Road, 5 District, Ho Chi Minh, Vietnam
⁴ College of Nanoscience and Nanotechnology, Pusan National University, San 30 Jangjeon-dong Geumjeong-gu Busan 609-735, Korea

E-mail: dinhnn@vnu.edu.vn

Abstract. With the aim to improve the photonic efficiency of an organic light emitting diode (OLED) and its display duration, both the hole transport layer (HTL) and the emitting layer (EML) were prepared as nanostructured thin films. For the HTL nanocomposite films were prepared by spin coating solutions of poly(vinylcarbazole) (PVK) and PEDOT-PSS containing TiO₂ nanoparticles onto low resistivity ITO substrates; for the EML, TiO₂-embedded MEH-PPV (MEH-PPV+nc-TiO₂) conjugate polymers were spin-coated onto the HTL. OLEDs prepared from above mentioned films have the structure of multilayers such as Al/MEH-PPV+nc-TiO₂/PVK+nc-TiO₂/ITO and Al/MEH-PPV+nc-TiO₂/PEDOT-PSS+nc-TiO₂/ITO. Characterization of the nanocomposite films showed that both the I-V characteristics and the photoluminescence spectra of the nanocomposite materials were significantly enhanced in comparison to the standard polymers.

Keyword: Nanostructure, thin film, nanocomposite films, OLED.

1. Introduction

Organic light emitting diodes (OLED) have been intensively investigating for the last decade, because they have many potential applications such as optoelectronics, urban lighting, screen for TV and cellular phones, large-arc displays, solar flexible cells, etc [1-4]. However to replace the LED based on inorganic semiconducting materials it is necessary to improve both the time of service and efficiency of the OLEDs. It is known that the efficient device operation requires optimization of three factors: (i) equalization of injection rates of positive (hole) and negative (electron) charge carriers (ii) recombination of the charge carriers to form singlet exciton in emitting layer (EL) and (iii) radiative decay of the excitons. Recently, there have been reported different ways to deal with these problems, for instance, to add a hole transport layer (HTL) between the transparent anode and the emitting layer (EML) [5] and/or an electron transport layer (ETL) sandwiched between the EML and cathode [6]. With these solutions one can enhance electroluminescent efficiency of the OLED, but the long-lasting service sometimes is limited. There is another way to enhance both the efficiency and the service
duration of the devices. It is the use of nanocomposite films instead of pure-polymers served as HTL and EML. The embedded oxides can substantially influence both the electrical, and optical properties of the polymer, for instance MEH-PPV + nc-TiO₂ composite thin films were studied as photoactive material [7]. By adding a hole transport layer (HTL) and an electron transport layer (ETL) to the three-layer device the equalization of injection rates of hole and electron was improved and the higher electroluminescent efficiency of the OLED was obtained. However, a large difference in the structures of an inorganic material (ITO) and an organic poly(vinylcarbazole) (PVK) or polyethylene (3,4-dioxythiophene) (PEDOT) usually causes a poor interface contact between them. By embedding TiO₂ nanoparticles in PEDOT one can expect to enhance both the contact of HTL with ITO and the working function of both the PVK and PEDOT films.

In this work we present the results of the research on the componential layers in OLEDs. I-V characteristics of the devices with the use of nanocomposite films are also presented.

2. Experimental

The ITO-coated glass substrates used for spincoating nanocomposite films were ultrasonically cleaned in distilled water, followed by ethanol and acetone. To deposit the EML composites films onto ITO, MEH-PPV solution was prepared by dissolving MEH-PPV powder in xylene at a ratio of 10 mg of MEH-PPV in 1 ml of xylene. Then, TiO₂ nanoparticles were embedded in these solutions according to the weight ratio of TiO₂/MEH-PPV ranging from 0.05 to 0.20, further referred to as MEHPPV+nc-TiO₂. To obtain homogenously dispersion of TiO₂ in polymer, the solutions were mixed for 8 hours by using ultrasonic stirring. The conditions for spincoating are following: delay time is 120s, rest spin time is 30s, spin speed is 1500 rpm, accelerate is 500 rpm and finally drying time is 2 min. Then the samples were put in a flow of dried gaseous nitrogen for 12 hours. All the samples were put in a fore vacuum box to await the measurements. For preparing an initial solution of PVK and PEDOT, the corresponding pure polymer powders were solved in cloruaform and PSS, respectively. To get both the PVK+ nc-TiO₂ and the PEDOT+nc-TiO₂ films that served as the HTL, the above mentioned procedure for MEHPPV+TiO₂ was used, with however a different content of nc-TiO₂ in PVK and PEDOT (i.e. 35 wt.% and 20 wt.%, respectively). Aluminum coating was used as the cathode was made by vacuum metallization. Thus, the OLEDs with multilayer layers had the structure of ITO/HTL/EML/Al.

The surface morphology of samples was characterized by using a “Hitachi” Field Emission Scanning Electron Microscope (FESEM). Atomic force microscope (AFM) images on a NT-MDT Atomic Force Microscope employed by a tunnel current mode. Nanocrystalline structures were checked by a Philips D-5005 X-ray diffractometer using filtered Cu Kα radiation (λ = 0.15405 nm). Photoluminescence spectra (PL) were carried-out by using a FL3-2 spectrophotometer and current-voltage (I-V) characteristics were measured on an Auto-Lab Potentiostat PGS-30. The UV-VIS absorption spectra were carried out on a Jasco UV-VIS-NIR V570.

3. Results and discussion

Poly(vinylcarbazole) (PVK) blended is a conducting polymer and possesses a bandgap, i.e. the separated energy gap between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of about 3.6 eV [8]. It is transparent and possesses a workfunction higher than that of ITO, so it is often used for the HTL in OLEDs. In this work PVK composite films were prepared also for HTL. Firstly, the PVK+nc-TiO₂ films (the average size of TiO₂ particles is about 35 nm) were characterized by comparing the surface morphology and PL spectra with that of pure PVK. The surface of PVK+nc-TiO₂ nanocomposite films was examined by the SEM technique. Figure 1 shows SEM images of a pure PVK and a composite sample with embedding of 35 wt.% nanocrystalline titanium oxide particles (35 nm in size). The surface of the pure PVK exhibited much smoother than the composite films with large percentages and large TiO₂ particles.
The influence of the heat treatment on the morphology of the films is weak, i.e. no noticeable differences of the surface were observed in samples annealed at 120°C, 150°C and 180°C in the same vacuum. But the most suitable heating temperature for other operations like I-V characteristics or PL spectra was of 150°C. In the observed sample, the distribution of TiO₂ nanoparticles is not uniform, there are big bright points indicating clusters of the nanoparticles with larger size than that of initial nc-TiO₂. This proved that by using the ultrasonic stir the nanoparticles were not completely dispersed. However, the photoluminescence (PL) spectra of the composite exhibited quite different from the one obtained for the pure PVK (figure 2). Under an excitation of a large-energy photonic beam (nitrogen laser of 337.1 nm) the PL intensity of the PVK+nc-TiO₂ increased about 3.5 times in comparison with the PL intensity of the pure PVK under the same excitation source. From Raman spectra, it is known that nc-TiO₂ particles embedded into PVK did not make the molecular structure of PVK change. Thus the PVK+nc-TiO₂ can be seen as a composite material, where nc-TiO₂ particles were surrounded by PVK creating numerous TiO₂/PVK interfaces inside the composite.

The mechanism of the increase of PL intensity for the composite is complicated. It is strongly dependent on the size and concentration of nc-TiO₂ embedded in. In this case the TiO₂ particles had the size of 35 nm and some large clusters were formed, so the effect in enhancement of PL intensity of the composite may be attributed to the presence of interfaces between large oxide particles and

---

**Figure 1.** SEM of PVK (a) and PVK+nc-TiO₂ (30 wt.% of TiO₂) annealed in vacuum at 150°C (b).

**Figure 2.** PL spectra of a pure PVK (bottom) and PVK+nc-TiO₂ (top) under excitation of laser beam with $\lambda = 337.1$ nm.
polymer. Under the excitation electron from the valence band jumped to the conduction band of TiO$_2$, then diffused to the PVK at the interface, because the Fermi level of TiO$_2$ is higher than the LUMO level of PVK. From the LUMO this electron transferred to the lower energy level in the HOMO of PVK emitting a photon. This resulted in the improvement of the photoemission.

Let us see the PEDOT case. It is known that PEDOT is also used for the HTL in OLED, because it has a high transmission in the visible region, good thermal stability and high conductivity [9-10]. To enhance the interface contact between ITO and PEDOT, TiO$_2$ nanoparticles were embedded into PEDOT.

Figure 3 shows the AFM of the pure PEDOT and the composite with the percentage of 20 wt.% TiO$_2$ nanoparticles (5 nm in size). With such a high resolution of the AFM one can see a clear round distribution of nanoparticles in the polymer due to the spin-coating process. For the pure PEDOT, the surface is smooth. The TiO$_2$ nanoparticles made the composite surface rougher in nanoscale and created numerous TiO$_2$/PEDOT boundaries in the composite film.

Figure 3. AFM of a pure PEDOT (a) and a PEDOT composite film with 50 wt. % of nc-TiO$_2$. 

Transmittance spectra of a pure PEDOT and a nanocomposite film plotted in figure 3 shows the AFM of the pure PEDOT and the composite with the percentage of 20 wt.% TiO$_2$ nanoparticles (5 nm in size). With such a high resolution of the AFM one can see a clear round distribution of nanoparticles in the polymer due to the spin-coating process. For the pure PEDOT, the surface is smooth. The TiO$_2$ nanoparticles made the composite surface rougher in nanoscale and created numerous TiO$_2$/PEDOT boundaries in the composite film (figure 3 shows the AFM of the pure PEDOT and the composite with the percentage of 20 wt.% TiO$_2$ nanoparticles (5 nm in size). With such a high resolution of the AFM one can see a clear round distribution of nanoparticles in the polymer due to the spin-coating process. For the pure PEDOT, the surface is smooth. The TiO$_2$ nanoparticles made the composite surface rougher in nanoscale and created numerous TiO$_2$/PEDOT boundaries in the composite film (figure 3). From this figure one can see that the PEDOT+nc-TiO$_2$ was strongly absorbed in the near UV range and weaker in the near IR range. The transmittance decreased with the increase of the embedded TiO$_2$ concentration, above 20 wt.% the transmittance lowered to a value smaller than 60%. The HTL film with such a low transmittance can not be utilized in OLEDs. At the range of the emission light of the MEH-PPV, namely from 540 to 600 nm, the transmittance of the 20 wt.% TiO$_2$ embedded PEDOT reached a value as high as 75%. This transmittance is a bit lower, but still comparable to the transmittance of the ITO anode. So we used this film for the HTL in the multilayer OLEDs. The electrical conductivity of the PEDOT blend is high; it reaches up to 80 S/cm [11]. But the presence of TiO$_2$ nanoparticles in PEDOT may result in the cleavage of the polymer conjugation pathway, consequently the decrease in conductivity of the film. However, a negligible decrease in conductivity does not much affect the performance of a OLED when using the composite as a hole transport layer.
Similar results of PL measurements for the PVK+nc-TiO2, when the MEHPPV+TiO2 nanocomposite excited at a short wavelength, the PL intensity of the MEH-PPV composite increased about 4 times larger than the one of pure MEH-PPV (figure 5). The photoluminescence spectra were measured on a FL3-2 spectrophotometer with a He-Ne laser as an excitation source ($\lambda = 325$ nm). Notice that, with such a short wavelength excitation both the polymer and composite emitted only one broad peak of wavelengths. From this figure, it is seen that photoemission of the composite film exhibits much higher luminescence intensity than that of the pure MEH-PPV. A blue shift of a peak from 580.5 to 550.3 nm was observed similarly to the result in [12] reporting on PL spectra of a hybrid MEH-PPV/nc-MoO3 film. This result is consistent with currently obtained results on the polymeric nanocomposite [13], where the blue shift was explained by the reduction of the chain length of polymer, with embedded TiO2 nanoparticles. The fact that the blue shift was not observed for the PVK composite proved the size of the TiO2 particles embedded in PVK was larger than that in MEH-PPV. Thus, for such a small size of 5 nm, nc-TiO2 particles can be seen as the nanocrystalline grains located in the polymer, and then the increase of PL intensity for this MEH-PPV nanocomposite film can be explained by the large absorption coefficient for TiO2 grains. This similar phenomenon was explained due to the non-radiative Förster resonant energy transfer (FRET) [14] from TiO2 nanocrystals to polymer with excitation of wavelength less than 350 nm.

To have clear understanding of the effect of nanoparticles in composites films used for both the EML and HTL, the OLEDs were made from different layers, such as a single pure EML diode (ITO/MEH-PPV/Al, adopted as SPD0), two diodes with double polymers (ITO/PVK/MEH-PPV/Al and ITO/PEDOT/MEH-PPV/Al, adopted as DPD1 and DPD2,
respectively), a double polymeric composite layers, where the MEH-PPV+TiO₂ composite was used as EML and the PVK- or PEDOT-composite film was used as HTL (ITO/PVK+TiO₂/MEH-PPV+TiO₂/Al and ITO/PEDOT+TiO₂/MEH-PPV+TiO₂/Al or PKCD and PECD, respectively). The I-V characteristics of these devices are shown in figure 6. From this figure one can notice the following:

(i) The turn-on voltage for the diodes lowered from SPD0 to DPD1, DPD2 and PKCD. The smallest value of the turn-on voltage was obtained for the PECD device. This indicates that the equalization of injection rates of holes and electrons was improved due to both the HTL and the ETL added to the OLED.

(ii) The PEDOT film served as the HTL is better than the PVK composite. It favours the hole injection from ITO into the organic composite EML deposited on the HTL, resulting in an enhancement of the I-V characteristic. Thus the turn-on voltage decreased from 4.2 to 2.6 V (for PVK) and to 2.4 V (for PEDOT) (see curves “a, b and c” in figure 6). Nanoparticles in both the EML and HTL films have contributed to significantly lowering the turn-on voltage of the device (see the curve “d and e” of PKCD and PECD diodes).

![Figure 6. I-V characteristics of OLED with different laminated structure:](image)

(a) – Single MEH-PPV, SPD0
(b) – with PVK layer, DPD1
(c) – with PEDOT layer, DPD2
(d) – with both EML and PVK composites
(e) – with both EML and PEDOT composites.

It is known that the effect of both the HTL and ETL on the enhancement of the I-V characteristic was explained, without argumentation due to the equalization of injection rates of holes and electrons. But the question why the nanoparticles can improve the device performance is still open. For instance, in [15] the authors attributed this enhancement to stimulated emission of optically-pumped MEH–PPV films when TiO₂ particles were embedded in. Whereas, in [16] by their obtained results the author indicates that no evidence of line narrowing or changes in the line shape are observed at different voltages implying that the mechanism for improved performance is distinctly different from that found in optically-pumped TiO₂/MEH–PPV films. The authors concluded that optical scattering phenomenon is not causing the increase in performance. Another possible explanation is that the nanoparticle surfaces increase the probability of electron-hole recombination; however, again this would result in a change in the external quantum efficiency, rather than the current density as is observed [16].

From the data of PL spectra for the PVK and MEH-PPV nanocomposites, as well as the transmittance for the PEDOT composite, we have observed the improvement in PL intensity for the first two composites and the stronger absorption for the third one (see figures 2, 3 and 5). Similar phenomena obtained for nanohybrid layers were explained due to the TiO₂/polymer boundaries causing differences in band gap between oxide nanoparticles and the conjugate polymer [17]. Based on these results we take an explanation for the improved performance which supports the suggestion by Carter et al. [16]. It is suggested by the change in device morphology caused by the incorporation of nanoparticles into the solution. During the spinning process in the spin-coating technique, the
nanoparticles can stick by strong electrostatic forces to the HTL and to themselves, and capillary forces can then draw the MEH–PPV solution around the nanoparticles into cavities without opening up pinholes through the device. This will result in a rough surface over which the Al-cathode is evaporated and subsequently a large interface between the cathode and the electroluminescent composite material. Thus at a low voltage, charge-injection into MEH–PPV is expected to be cathode limited; the very steep rise in the I–V curves for the composite diodes suggests that more efficient injection at the cathode is occurring which could be caused by the rougher interface of the nanocomposites. At the higher-voltage, transport in MEH–PPV appears to be space-charge limited. This possibly is also the reason why using the PVK composite as the HTL was less efficient in comparison with using PEDOT composite, where the nanoparticles (35 nm in size) embedded in the first are much larger than the one (5 nm in size) embedded in the second.

The electroluminescence quantum efficiency can be calculated by using a simple expression obtained by Tsutsui and Saito in [18], as follows:

\[
\eta_L = \gamma \eta_r \cdot \phi_f
\]

where \(\gamma\) is a double charge injection factor which is dependent on the processes of carrier injection and is maximal (\(\gamma = 1\)) if a balanced charge injection into the emission layer of the device is achieved, i.e. the number of injected negative charge (electron) equals the number of injected positive charge (hole); \(\eta_r\) quantifies the efficiency of the formation of a singlet exciton from a positive and a negative polaron, and \(\phi_f\) is the photoluminescence quantum efficiency. From the PL spectra and I-V characteristics obtained one can see that \(\gamma\) for the PECD is the largest due to the addition of the best HTL like PEDOT+TiO_2 film. The \(\eta_r\) and \(\phi_f\) of the PECD may be improved due to the embedding of TiO_2 nanoparticles into both the emission and hole transport layers. Thus the electroluminescence quantum efficiency of the multilayer polymeric composite diodes can be qualitatively evaluated from equation (1) and suggested much larger than for the single polymeric layer device. For the accurate estimation of the electroluminescence quantum efficiency of a multilayer OLED we shall focus our forthcoming research work on the electroluminescence properties of such laminated structures.

4. Conclusion

Both the hole transport layer and the emitting layer were prepared as nanostructured thin films by embedding nc-TiO_2 particles into PVK, PEDOT and MEH-PPV. The HTL nanocomposite films were spin-coated onto low resistivity ITO substrates. TiO_2-embedded MEH-PPV conjugate polymers were spin-coated onto the HTL. Two types of the multilayer OLEDs of the laminated structure of Al/MEH-PPV+nc-TiO_2/PVK+nc-TiO_2/ITO and Al/MEH-PPV+nc-TiO_2/PEDOT+nc-TiO_2/ITO were prepared for I-V measurements. Characterization of the nanocomposite films showed that both the photoluminescence and I-V characteristics of the nanocomposite materials were significantly enhanced in comparison with the standard polymers. From these results one can expect a large electroluminescent efficiency of the OLEDs made from these layers.

References
[1] Salafsky J S 1999 Phys. Rev. B 59 10885
[2] Burlakov V M, Kawata K, Assender H E, and Briggs G A D, Ruseckas A and Samuel I D W 2005 Phys. Rev. B 72 075206
[3] Petrella A, Tamborra M, Cozzoli P D, Curri M L, Striccoli M, Cosma P, Farinola G M, Babudri F, Nao F and Agostiano A 2004 Thin Solid Films 451-452 64
[4] Spanggaard H and Kerbs F C 2004 Sol. Energy. Mat. Sol. Cells 83 125
[5] Choulis S A, Choong V E, Mathai M K and So F 2005 Appl. Phys. Lett. 87 113508
[6] Markov D E and Blom P W M 2005 Phys. Rev. B 72 161401(R)
[7] Kawata K, Burlakov V M, Carey M J, Assender H E, Briggs G A D, Ruseckas A and Samuel I D W 2005 Sol. Energy Mat. Sol Cells 87 715
Acknowledgments
This work is supported in part by the Protocol in Scientific Cooperation between Vietnam and South Korea during period of 2009 - 2010.