

Hole transporting layers for organic light emitting diodes

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In this work, we have investigated poly(9-vinylcarbazole) (PVK) and N,N'-Bis(3-methylphenyl)-N,N'-diphenylbenzidine (TPD), and the incorporation of TPD in PVK, as hole transporting layers (HTL) for organic light emitting diodes (OLED's) based on 8-hydroxyquinoline aluminium (Alq₃) as a light-emitting and electron transporting layer. The sandwich structures ITO/HTL/Alq₃/Al have been obtained on commercial polyethylene terephthalate (PET) substrates, coated with indium tin oxide (ITO). Several spin-coating solutions were evaluated for deposition of the polymer layer.

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1. Introduction

In the last decade, organic light emitting diodes (OLEDs) using small molecules [1] or polymers [2], have attracted considerable attention due to their ease of production, low cost, low operating voltages, wide viewing angles, tunability of the color emission, fast response time, compatibility to flexible substrates and ease of forming large areas [3]. Although enormous progress has been made for OLEDs in recent years, there are still several problems that need to be solved. These include improving the brightness and luminous efficiency, lowering the turn-on voltage and increasing the lifetime of the devices.

We have shown [4], that PVK and TPD are promising materials as hole transporting layers (HTL) for OLED. We have found that both decrease the drive voltage and improve the performance of the OLED devices compared to the reference mono-layer structure. In this work we study the incorporation of TPD in the polymer matrix of PVK, aiming at further improvement of the performance of OLEDs.

2. Experimental

Four types of device were investigated: ITO/PVK/Alq₃/Al, ITO/PVK/TPD/Alq₃/Al, ITO/(PVK:TPD)/Alq₃/Al and ITO/TPD/Alq₃/Al as a reference structure (where Alq₃ = 8-hydroxyquinoline aluminium).

Materials: TPD and PVK were purchased from Aldrich. Alq₃ was synthesized in the Department of Organic Chemical Technology, Faculty of Chemistry at the St.Kliment Ohridski University of Sofia by T.

Deligeorgiev [5]. All materials were used without further purification.

Device fabrication: Devices with area 1 cm² were prepared on polyethylene terephthalate (PET) substrates coated with ITO (40 Ω/sq) as the anode material, also purchased from Aldrich. A 5 mm wide ITO strip line was formed by selective etching in hydrochloric acid (HCl) and nitric acid (HNO₃) with a volume ratio HCl:HNO₃:H₂O = 1:1:2 for 1 min at room temperature. Then the patterned ITO substrate was cleaned in acetone, isopropanol and rinsed in deionized water.

The HTL (40 < δ < 90 nm) of PVK and PVK:TPD composite films (10wt% TPD relatively to PVK) were formed by spin-coating from 0.5-3.0% solutions in dichloroethane (filtered through a 0.4 μ glass filter) at 2000 rpm.

The TPD layer (δ=40 nm), the emissive layer (EL) of Alq₃ (δ=100 nm) and the Al cathode (δ=120 nm) were obtained by thermal evaporation in a vacuum better than 10⁻⁴ Pa at rates of 2-5 Å/s.

Measurements: The morphologies of the deposited HTL and EL were studied with a scanning electron microscopy (SEM) (Philips 515).

The current-voltage (I/V) curves were measured with a Unigor 3p programmable power supply multimeter and a Servogor S millivoltmeter.

The luminescence (L) was measured in continuous DC mode and the light output was detected using a calibrated silicon photodiode.

The luminous efficiency (η_L) in candelas per amp [cd/A], calculated by Eq. 1, was used for quantifying the properties of the OLEDs [6].

$$\eta_L = L / I \quad (1)$$

Samples were not hermetically sealed from the atmosphere and were measured under ambient conditions.

3. Results and discussion

Fig. 1 presents the typical nonlinear current/ voltage (I-V) and luminescence/voltage (L-V) characteristics of the ITO/PVK/TPD/Alq₃/Al and ITO/TPD/Alq₃/Al (reference) devices. Three layers of PVK with thickness 28, 30 and 45 nm were obtained by spin coating from solutions of 0.5, 1.0 and 1.5 wt% of PVK. The thickness of the evaporated layers of TPD was 40 nm, determined in our previous paper as most suitable for maximum emission and lowest turn-on voltage [4]. It was found that as the thickness of the PVK layer increased, the current density (Fig. 1a) and the corresponding luminescence decreased (Fig. 1b). Meanwhile, the peak of the luminous efficiency (Fig. 1c) and the turn-on voltage were shifted towards higher voltages compared to the reference device. Obviously, the introduction of PVK as a second layer of the HTL in OLEDs impedes the charge transfer.

Later, we studied the incorporation of TPD in the polymer matrix of PVK as a HTL. Fig. 2 shows L-V and η_L -V curves for PVK:TPD composite layers obtained on the basis of solutions with different concentrations of PVK. It was found that the current density and the luminescence (Fig. 2a) increased with thickness up to 0.75 wt% PVK, due to the improvement in the charge balance. Further increases of the thickness of the HTL reduced the luminescence, probably due to hindrance of the charge transfer. It was established that the composite layer with 0.75 wt% of PVK possessed the best performance: the highest luminance and luminous efficiency (Fig. 2b) and turn-on voltage (Fig. 2a) lower than that of the reference structure.

Fig. 3 shows the optimal obtained L-V and η_L -V curves for ITO/TPD/Alq₃/Al, ITO/PVK/Alq₃/Al, ITO/PVK/TPD/Alq₃/Al, ITO/ (PVK:TPD)/Alq₃/Al devices. The reference device ITO/TPD/Alq₃/Al shows good luminance and luminous efficiency, but due to the well known trend to crystallization of TPD thin films, the lifetime of the device is too short. It could be stressed that the PVK:TPD composite layer structure demonstrates the best characteristics. The incorporation of TPD in PVK improves the current density, luminescence and luminous efficiency and reduces the turn-on voltage compared to the others devices.

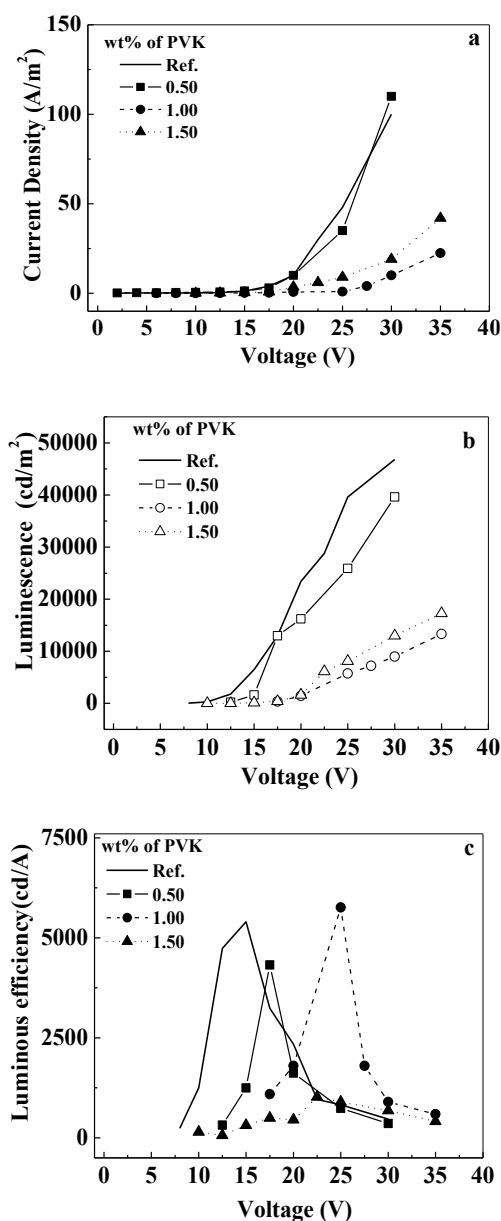


Fig. 1. (a) Current density / Voltage (I/V); (b) Luminescence / Voltage (L/V) and (c) Luminous efficiency / Voltage (η_L /V) curves for ITO/PVK/TPD/Alq₃/Al and reference structure: ITO/TPD/Alq₃/Al - Ref.

The time dependence of the luminance of the same OLED devices at 15 V is presented in Fig. 4. The lifetime of the reference device ITO/TPD/Alq₃/Al is shorter than that of the other structures. Again the most prolonged operating time is demonstrated by the device with a HTL obtained from a PVK:TPD composite layer.

SEM micrographs of ITO/PVK, ITO/PVK/Alq₃, ITO/TPD, ITO/TPD/Alq₃, ITO/PVK/TPD, ITO/PVK/TPD/Alq₃, ITO/PVK:TPD, ITO/PVK:TPD/Alq₃ are presented in Fig. 5.

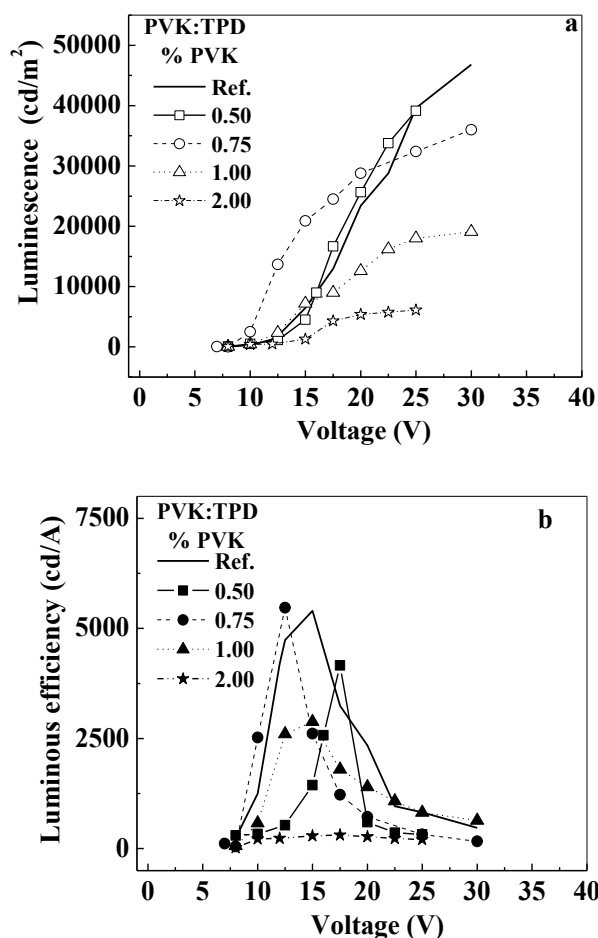


Fig. 2. (a) L/V and (b) η_L/V curves for ITO/PVK:TPD/Alq₃/Al and reference structures. Concentrations of PVK in the solutions are shown. The concentration of TPD in the PVK:TPD composite is 10.00 wt% relative to PVK.

The surface of the PVK solid layer (Fig. 5a) deposited on the PET substrate covered with ITO is smooth and homogeneous without defects and cracks. The surface of the devices after deposition of Alq₃ is nearly the same (Fig. 5b). A SEM micrograph of a TPD thin film sample (Fig. 5c), deposited by vacuum evaporation on ITO, shows a porous and granular surface morphology which is a prerequisite for recrystallization and oxidation. The surface morphology of TPD thin films vacuum deposited on the ITO/PVK (Fig. 5e) is substantially improved, but still many defects are observed. The surface of the composite films of PVK:TPD (Fig. 5g) is very smooth and homogeneous, without defects and cracks, which explains their best performance.

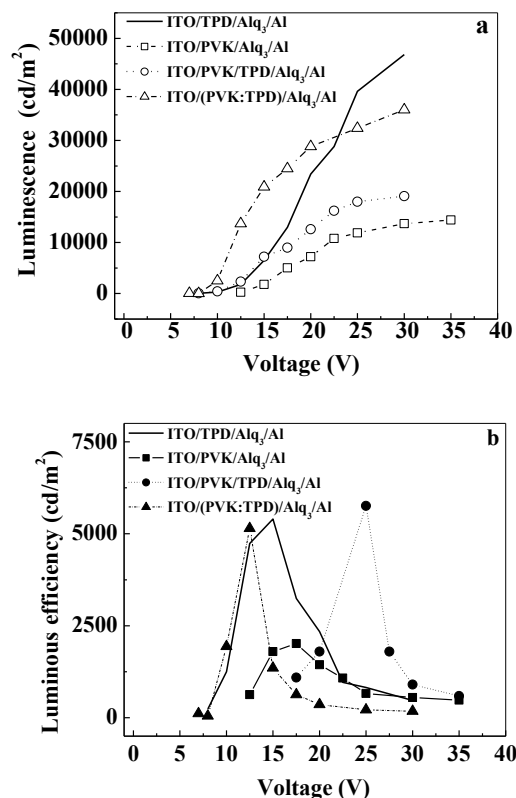


Fig. 3. (a) L/V and (b) η_L/V curves for ITO/TPD/Alq₃/Al, ITO/PVK/Alq₃/Al, ITO/PVK/TPD/Alq₃/Al, ITO/(PVK:TPD)/Alq₃/Al.

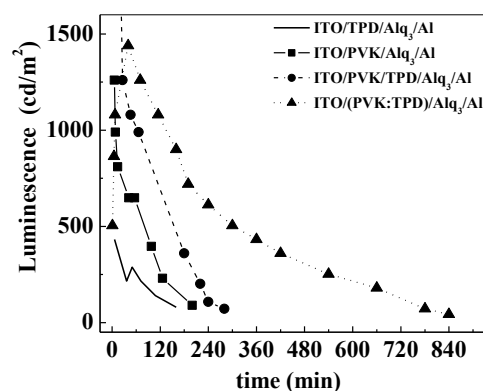


Fig. 4. OLED operating times of ITO/TPD/Alq₃/Al, ITO/PVK/Alq₃/Al, ITO/PVK/TPD/Alq₃/Al and ITO/(PVK:TPD)/Alq₃/Al at 15 V DC voltage.

It should be noted that the results presented in this paper concerned OLED devices developed on flexible PET substrates. Most of the results published by other authors are for devices developed on glass substrates.

It is known that devices on glass substrates have the best luminescence characteristics and are more stable with the time.

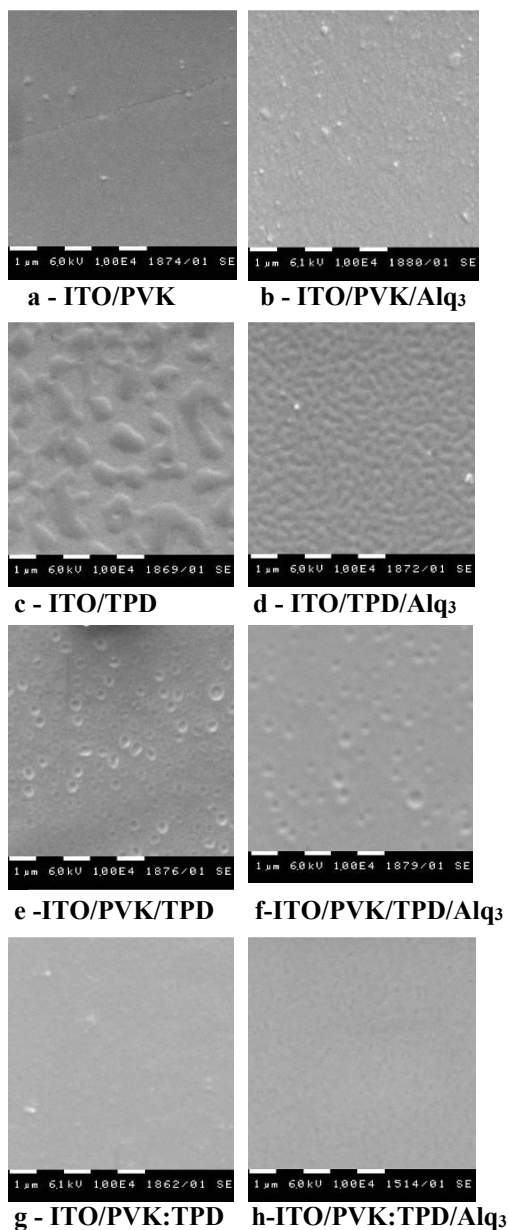


Fig. 5. SEM micrographs of different structures.

Flexible substrates like PET, etc. for OLED are more permeable to moisture and oxidation and that is why it could be expected that the time of operation of such devices would be shorter [7].

The results obtained in this paper with a HTL from composite PVK:TPD films are one successful step towards the development of OLED devices on flexible substrates with very good performance – turn-on voltage 8 V and maximum luminance 30000 cd/m² (at 16 V). These characteristics are consistent with the results of other authors for similar device structures [8].

4. Conclusions

On the basis of the results presented in this paper the following conclusions can be made:

- PVK, TPD and TPD incorporated in PVK were studied as hole transporting layers in ITO/HTL/Alq₃/Al structures.
- Composite PVK:TPD films are most suitable as HTL.
- The OLED characteristics: turn-on voltage 8 V and maximum luminance 30000 cd/m² (at 16 V) were competitive with current standards for fluorescent emitters.
- OLED structures were developed creating the possibility for the study of different electroluminescent substances.

Acknowledgements

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