Improved performances in light-emitting diodes based on a semiconductor TiO$_2$ nano cluster buffer layer

Phuong Hoai Nam Nguyen and Nang Dinh Nguyen

Faculty of Engineering Physics and Nanotechnology, University of Engineering and Technology, Vietnam National University in Ha Noi, 144 Xuan Thuy Road, Cau Giay District, Hanoi, Vietnam

E-mail: namnph@vnu.edu.vn

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Abstract
Ultra-thin films of TiO$_2$ nano clusters were fabricated and characterized by field-emission scanning electron microscopy (FE-SEM) and transmittance measurements. The x-ray spectra of the TiO$_2$ nano crystals were also studied. The performances of the devices based on the blended conducting polymer are improved by inserting a semiconducting layer of TiO$_2$ nano cluster into the emissive poly[9-vinylcarbazole] (PVK)/poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and Al cathode. The organic light-emitting diodes (OLEDs) show high efficiency and good stability with turn-on voltage lower than 3 V and current density higher than 0.5 mA mm$^{-2}$.

Keywords: nano cluster, conducting polymer, blend polymer, organic light emitting diodes

Classification number: 4.02

1. Introduction
Organic light-emitting diodes (OLEDs) have been applied to flat panel display due to the fact that they are easily manufactured, all solid-state, and have faster switching speed as well as wider viewing angle, etc. Along with developing new technology, OLEDs have the potential to substitute liquid crystal display (LCD) and to become the pacemaker in the display market. High-performance organic light-emitting diodes should have a low operating voltage, high efficiency and relatively good stability. In order to improve the efficiency of devices, various techniques are available as anode or cathode modification, annealing and optical coupling [1–4]. For example, cathode modification has been shown to increase electron injection, so as to improve the electron–hole balance. As a result, the efficiency of the devices can be improved. The electroluminescence efficiencies of organic light-emitting diodes can also be promoted with better charge injection as well as the balance of the opposite charge carriers. It is widely recognized that unbalanced charge carriers due to higher hole mobility in the hole transporting layer and slower electron mobility in the electron transporting layer (ETL) lead to reduced efficiency of OLEDs. It is thus important to balance the injected charges to improve device performance. Recently, much work has been done on device structure especially on the interface of the device [5, 6]. Some organic materials and inorganic insulating materials have been adopted as hole injection buffer layers inserted between the indium tin oxide (ITO) anode and the organic layer, such as copper phthalocyanine (CuPc), polyaniline, SiO$_2$, Al$_2$O$_3$, and so on [7–11]. In this work ultra-thin films of TiO$_2$ nano cluster have been fabricated and characterized. The blend films of poly[9-vinylcarbazole] (PVK) and poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) with optimal weight ratios of PVK/MEH-PPV have been fabricated and used as the emitting layer. The TiO$_2$ nano cluster film was inserted at the interface of this emitting layer. The hole injecting layer is poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT-PSS). It provides an improved efficiency and good stability as compared to the control device. The energy-transfer process from PVK to MEH-PPV was
observed, and thus the emission of MEH-PPV was exclusively observed when the blended polymer film was photoexcited by light whose energy was corresponding to the absorption of PVK. The current–voltage (I–V) characteristics of the devices were also studied.

2. Experimental

In this study some kinds of devices have been fabricated and the devices’ properties were compared with each other. The TiO$_2$ nano cluster film was introduced between the emission layer and the cathode. The device configuration of ITO/PEDOT-PSS/PVK + MEH-PPV/TiO$_2$/Al is shown in figure 1.

The TiO$_2$ nanoparticles were available as an aqueous solution of a 10 wt% suspension of TiO$_2$ in H$_2$O (purchased from Sigma-Aldrich). The TiO$_2$ nano cluster films were prepared by spin-coating at 3000 rpm to investigate the effect of the electrodes buffer layers on the performance of the devices. The conducting polymers PVK and MEH-PPV were purchased from Aldrich Chemical Co. and used as received. Indium tin oxide (ITO) and Al were used as the anode and the cathode, respectively. The shear resistance of the ITO was 25 $\Omega$ cm$^{-1}$. Before use, the ITO substrate and glass were routinely cleaned by ultrasonication in a mixture of acetone and alcohol, alcohol and deionized water [12]. The blended polymers were obtained by mixing PVK with MEH-PPV (PVK:MEH-PPV = 100:15) [13] and then the blends were spin-coated onto the substrates and dried in vacuum at 80$^\circ$C for 2 h. The thickness of the polymer layers were controlled both by spin speed and by the concentration of polymers in solvent. The film thickness was measured by using a $\alpha$ step DEKTAK and found to be around 120 nm. The surface morphology of the TiO$_2$ nano cluster films were investigated by using a Hitachi field emission scanning electron microscopy (FE-SEM) S-4800. The transmittance spectra of the thin films were obtained from a Jasco UV–Vis–NIR V570 spectrometer. The photoluminescence (PL) spectra of the blend conducting polymer films were carried-out by using a FL3-2 spectrophotometer. The current–voltage (J–V) characteristics of the devices were measured on an Auto-Lab Potentiostat PGS-30. All the photophysical measurements were performed at room temperature in air.

3. Results and discussion

Figure 2 is the FE-SEM image of the surface of the TiO$_2$ nano cluster film. It can be seen that the concentration of the TiO$_2$ nanoparticles with 20–30 nm in diameter could be determined to be 3–5 nanoparticle clusters per $\mu$m$^2$.

From the x-ray spectrum of the nanoparticle cluster TiO$_2$ film (figure 3(a)), the crystal structure of the TiO$_2$ can be determined as rutile with a specific peak [14]. The transmittance spectrum of the TiO$_2$ film (figure 3(b)) shows a minimum value at wavenumber of 280 nm, implying that TiO$_2$ nanoparticle can absorb ultraviolet light.
Figure 4. Photoluminescence spectra of the conducting polymer films excited at 325 nm.

Figure 4 compares the PL spectra of bulk films of PVK and PVK + MEH-PPV. The PL emission from PVK film excited at 325 nm overlaps with the absorption peaks of MEH-PPV, and, thus an efficient Förster energy transfer can be anticipated [13].

Figure 5 shows the current density–voltage ($J$–$V$) characteristics of the single layer device (A) and the multilayer devices using the PEDOT-PSS and nano cluster TiO$_2$ films as the anode buffer layer (B and C). The multilayer device (C) was fabricated consisting of a transparent indium–tin-oxide (ITO) electrode, the nano cluster TiO$_2$ film, the blend conducting polymer film and an aluminum (Al) electrode: ITO/TiO$_2$ nano cluster/PVK + MEH-PPV/Al. The thickness of the nano cluster TiO$_2$ film was estimated to be around 20–30 nm.

From figure 5 we see that the $J$–$V$ performances of the devices are strongly dependent on the presence of the nano cluster TiO$_2$ film between the anode and the emitting layer. It can be seen that the current density of the multilayer devices (B and C) are much higher compared with those of the single layer device (A) at the same operating voltage. Also, the threshold field of the multilayer devices is decreased to lower than 3 V. The single layer device performed very poorly. This result suggests that the tunneling of charge carriers between ITO and PVK + MEH-PPV can highly enhance the injection of holes due to the large potential drop across a thin insulating layer; hence, the turn-on voltage is reduced and overall current density is increased. But it shows that the bias voltage to obtain the same current density is obviously increased for the OLEDs with nano cluster TiO$_2$ buffer layer compared with the device with PEDOT-PSS buffer layer. This is probably because the PEDOT-PSS thin layer enhances most of the holes injected from the anode to the emitting layer (PVK + MEH-PPV) due to its holes transporting property. Figure 6 shows the $J$–$V$ characteristics of the device using the nano cluster TiO$_2$ film as anode buffer layer (A) and the multilayer device (B) combined nano cluster TiO$_2$ film as cathode buffer layer and PEDOT-PSS as anode buffer layer, respectively.

Figure 6 reveals that the device which combined nano cluster TiO$_2$ film as cathode buffer layer and PEDOT-PSS as anode buffer layer, respectively, shows the best performance with a turn-on voltage about 2.5 V and maximum current density at 0.7 mA mm$^{-2}$ (device B). The improvements of the performance of the device can be considered in order to explain the behavior of the nanoparticle-cluster-modified devices. The hole mobility in ordinary PPV is two orders of magnitude higher than the electron mobility [15], resulting in a recombination zone that is very close to the aluminum cathode. In addition, the barrier for hole injection is lower than the barrier for electron injection. Hence, the $J$–$V$ characteristics of the device are mainly determined by the holes [16]. The nanoparticle clusters, arbitrarily distributed between the PVK + MEH-PPV and the aluminum layer, create a randomly nanopatterned cathode interface. This gives rise to locally enhanced fields again resulting in a higher electron injection rate, in turn leading to a better charge balance. The enhanced internal quantum efficiency entails finally an increased luminescence. This interpretation is supported by the lower turn-on voltage and the high enhancement factor at low current densities.

4. Conclusion

We have fabricated OLEDs with nano clusters TiO$_2$ film between the emission layer and the cathode. The performance of the device is improved in decreasing turn-on voltage (to 2.5 V) and increasing current density (to 0.7 mA mm$^{-2}$), leading to increase in the efficiency and lifetime of the device. The nanoparticle clusters increase the electron injection at the nanoparticle cluster–cathode interface therefore enhancing the internal quantum efficiency. This effect is particularly beneficial for solution processed devices, since these
nanoparticles are low cost and easy to handle and might be an alternative to additional polymer layers for controlling charge injection and balance.

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