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Efficiency enhancement in blue organic light emitting diodes with a composite hole transport layer based on poly(ethylenedioxythiophene): poly(styrenesulfonate) doped with TiO_2 nanoparticles

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ABSTRACT

Blue color organic/polymeric light emitting diodes are very important because they can be used for tri-color display applications, fluorescence imaging, and exciting yellow phosphor for generating white light for general illumination. But the efficiency of blue organic/polymeric light emitting diodes is considerably low due to their large band gap that requires higher energy for effective emission. In this paper we report the enhancement in polyfluorene blue organic light emitting diodes with a polymer nano-composite hole transport layer. Blue light emitting diode based on polyfluorene as an emissive layer and poly(3,4 ethylenedioxythiophene):poly(styrenesulfonate)–titanium dioxide nanocomposite as the hole transport layer were fabricated and studied. Different concentrations of titanium dioxide nanoparticles were doped in poly(3,4 ethylenedioxythiophene):poly(styrenesulfonate) in the hole transport layer and the performance of the devices were studied. Significant enhancement in the blue peak at 430 nm of polyfluorene has been observed with increase in concentration of TiO_2 nanoparticles in the hole transport layer. The turn on voltage of the device has also been found to improve significantly with the incorporation of titanium dioxide nanoparticles in the hole transport layer. The optimized concentration of titanium dioxide in the hole transport layer for most efficient device has been found to 15 wt.%.

1. Introduction

Organic light-emitting diodes (OLEDs) have attracted great attention in research and industry for the last two decades. Major applications of OLEDs are in color display devices and general lighting due to their capability to emit light with high efficiency and the production of homogeneous large area emission on glass as well as flexible substrates. There are mainly two types of light emitting materials in OLEDs, i.e., small molecule based organic compounds and long chain polymers. Small molecule based OLEDs are fabricated using thermal evaporation techniques and other expensive fabrication techniques. On the other hand, polymer light emitting diodes (PLEDs) have gained special importance due to the ease in fabrication using solution processing techniques, such as, spin coating and inkjet printing. A considerable amount of research has been carried out in the synthesis of variety of polymers for light emission applications, out of which polyparaphenylenes (PPVs) and polyfluorenes (PFO) are well known materials. Polyfluorenes are particularly attractive class of blue light emitting polymers which exhibits high luminescence quantum yields [1]. High brightness with fairly high thermal stability is one of their distinguishing features [1]. Polyfluorene consists of pairs of phenyl rings joined together by a methylene bridge which serves to lock the ring pairs into a coplanar arrangement and can be functionalized without distorting the torsional angle between the fluorene units [2]. This feature has made polyfluorene derivatives attractive as emissive materials in displays as well as general purpose lighting. Blue color emitting PLEDs are very important because they can be used for color display applications, fluorescence imaging, exciting yellow phosphor for generating white light and other sensor applications. Therefore, efficient and long life-time blue light emitting PLEDs are very important for these applications.

But the main problem with the polyfluorene family based PLEDs is that they are not stable and inefficient during the operation as a blue color emitting light source [3]. Further, they suffer from an unwanted green emission band (450–550 nm) along with the desired blue emission (~430 nm). Therefore, these devices do not emit pure blue light which is required in color displays for high color gamut, white light generation and fluorescence imaging.

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The origin of the green emission is attributed to either intermolecular excimer formation [3,4] between polyfluorene chains or the presence of fluorenone defects in the polymer backbone [3,5]. Excimers are dimerised units in the excited state that emit at lower energies. This excimer emission affects the color of the emission and the lifetime of the light emitting diodes [3,4]. The effect of excimer emission at lower wavelengths can be suppressed if the blue color emission is enhanced. We have found that efficient blue emission can be achieved from a polyfluorene based OLED using polymer nano-composite hole transport layer (HTL) in the modified device architecture.

Recently, it has been reported that efficiency as well as stability of OLEDs can be enhanced by introducing TiO_2 nanoparticles in HTL [6]. TiO_2 is considered as good photo-catalytic semiconductor due to its large band gap and low hole/electron recombination probability. Some other properties which make it suitable to use in HTL are high charge conductivity, good stability, low cost and nontoxic behavior. Investigations of polymeric composite films using TiO_2 nanoparticles has been reported by Dinh et al. [6] in the fabrication of PLED using MEH-PPV as emissive layer. Asbahi et al. [7] introduced TiO_2 nanoparticles in PFO and demonstrated the enhancement of green color light peaking around 530 nm and suppressing the blue peaks at 450 nm and 428 nm. The efficient green color emitting electro-phosphorent OLEDs have already been fabricated, such as, based on $Ir(ppy)_3$ organo-metallic complexes, in which nearly 100% internal efficiency has been achieved by means of harvesting both singlet and triplet excitons [8]. Therefore, it is the blue color OLED/PLED devices which requires more improvement in EL enhancement, color purity, *I–V* characteristics and life-time. In this paper we demonstrate the enhancement in polyfluorene based blue OLEDs with polymer nano-composite HTL. The effect of modified HTL has been studied, in which poly (3,4 ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was doped with TiO_2 nanoparticles to improve its hole injection properties in a blue emitting PFO device. Different concentrations of TiO_2 nanoparticles were doped in PEDOT:PSS and optimum doping concentration was found to obtain an efficient PFO device with enhanced blue emission at 430 nm and with suppressed green emission at 500 nm, thus leading toward color purity. Experimental results of blue color enhancement, *I–V* characteristics and enhancement in transmission spectra are reported.

2. Experimental details

PEDOT:PSS of low conductivity grade (1 S/cm) dispersed in water and titanium dioxide (TiO_2) were purchased from Sigma Aldrich. Poly(9,9-dioctylfluoenyl-2,7-diyl) (PFO) was purchased from Luminescence Technology Corp., Taiwan. All chemicals were used as purchased. TiO_2 nanoparticles (size ~25 nm) doped PEDOT:PSS was used as HTL. Doping was done in different weight% (0–20 wt.%). Measured amount of TiO_2 nanoparticles in water were sonicated for 6 h and then mixed with PEDOT:PSS polymer by continuous stirring. The prepared mixture of polymer and nanoparticles was kept on stirring for 1 h. Hole transport material was spin coated on the cleaned indium titanium oxide (ITO) coated glass plates and dried in vacuum oven at 120 °C for 1 h. Above this emissive layer of poly(9,9-dioctylfluoenyl-2,7-diyl) (PFO) was spin coated using Apex digital spin coater at 900 rpm for 100 s and annealed at 100 °C for 1 h. LiF/Al were thermally evaporated to make electrode over the emissive layer. Devices 1–5 were made with pure PFO as emissive layer and TiO_2 doped HTL as follows (see Table 1).

Table 1
Doping % of TiO_2 in PEDOT:PSS in the devices.

Device name	Doping % of TiO_2 in PEDOT:PSS (%)
1	0
2	5
3	10
4	15
5	20

By varying the amount of TiO_2 in HTL, the optimum doping concentration was found to be 15% for the most efficient device. Photoluminescence (PL) and electroluminescence (EL) measurements were done using spectroflurometer (Shimadzu) and emission spectrometer (Ocean Optics). *I–V* characteristics were measured using source meter (Keithley-model 2400). Film surface was analyzed using Carl Zeiss scanning electron microscopy and transmission spectra were recorded using UV–Visible spectrophotometer (Shimadzu model 2600).

3. Results and discussion

Fig. 1 shows the SEM images of the PEDOT:PSS with and without TiO_2 nanoparticles deposited on glass. It can be seen from Fig. 1(a) that the film is uniform which consists of PEDOT:PSS layer only. On the other hand, it is clear from Fig. 1(b) that TiO_2 nanoparticles are uniformly dispersed in PEDOT:PSS. In anatase phase of titanium dioxide the atoms align themselves in tetragonal geometry. Valance band of titanium dioxide contains sp^3d hybrid orbitals which are made by the intermixing of 2p orbital of oxygen and 3d orbital of titanium, whereas conduction band is made up of only 3d orbitals of titanium. When electron jumps from valance band to conduction band they enter from hybridized state to purely 3d state leaving positive charge carriers, i.e., holes behind [9]. This process reduces the electron–hole recombination probability in nano-composite layer and hence holes move from HTL to emissive layer of polymer (PFO). This charge carrier property of TiO_2 results in better HTL for PFO device.

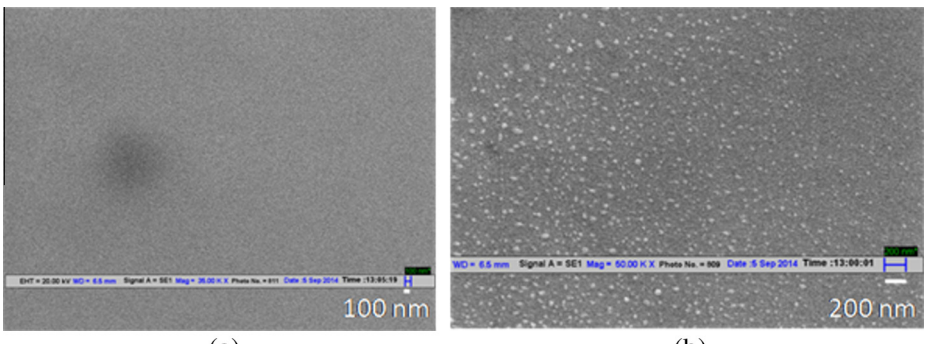

Fig. 1. (a) SEM micrograph of PEDOT:PSS layer and (b) PEDOT:PSS–TiO_2 nanocomposite layer on glass substrate.