Organic Electronics 34 (2016) 276–283

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Effect of CdSe/ZnS quantum dots on color purity and electrical properties of polyfluorene based hybrid light emitting diode

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ARTICLE INFO

Article history:
Received 27 January 2016
Received in revised form
7 March 2016
Accepted 9 April 2016
Available online 5 May 2016

Keywords:
Organic light emitting diode
Polymer-quantum dot blend
Color purity
Photonic band gap

ABSTRACT

We report enhanced color purity of hybrid organic-inorganic light emitting diode based on polyfluorene-CdSe/ZnS quanum dot (QD) blend as emissive layer. Effect on structural, optical and electrical properties of different doping concentration (0–100 wt.%) of QD in polyfluorene (PFO) was studied. Photoluminescence and electroluminescence spectra confirm the β-formation of PFO by incorporation of CdSe/ZnS QD. Photoluminescence (PL) of blend film was also compared with another method based on one dimensional photonic band gap (1D-PBG) structure that has been used for color purity. In both the cases, that is, QD doped device and 1D-PBG based structures the narrowing of PL spectra was observed. But the fabrication of QD-doped device for color purity is easier than fabricating 1D-PBG structure using multilayer dielectric coating. The present study might find application for QD based color displays, where color purity is an important requirement.

1. Introduction

Organic light emitting diodes (OLED) are most important candidates for display and lighting applications due to their self-luminous properties, scalability, low cost fabrication and mechanical flexibility. OLEDs with different emission color can be fabricated depending on material of the emissive layer [1,2]. Recently, remarkable growth has been noticed in the field of OLEDs to increase its efficiency as well as stability. Improvement in internal and external efficiency has been achieved significantly [3–6]. Internal efficiency near 100% and external efficiency up to 80% have been achieved [7,8]. However, the color purity and stability still remain a challenge. There have been several attempts to improve the color purity in OLEDs, by using micro-cavity OLEDs, tandem structures, nanostructures etc. [9–11], but these techniques such as micro-cavity OLEDs require proper optimization of the thickness of layers and requires multiple layers to fabricate. These problems open the new research field of hybrid organic-inorganic light emitting diodes based on incorporation of inorganic nanomaterials in different layers of OLED. Quantum dots are one of the important inorganic nanomaterials that can be used in OLED's emissive layer due to their outstanding optical properties like narrow spectral peak and brighter emission with full width at half maximum (FWHM < 30 nm). Some of the other properties that makes QDs promising candidate to use in display and lighting devices are their stability, high quantum yield and easy tunability over the visible spectrum [12–16].

Use of quantum dots with polymer results in quantum dot blend which exhibit advantages of both the materials like thin film forming properties of conjugated polymers and excellent optical and electronic properties of nanocrystals. Quantum dots have been used in OLEDs in different ways using different techniques like stamp printing, inkjet printing, electrodeposition, spin coating etc. [17,18] Among these, spin coating is one of the most convenient technique.

In the visible spectrum, blue color (400–450 nm) with high color purity and stability is difficult to produce as compare to other part of visible spectrum. Green and red OLEDs have already been reported with good brightness and color purity but blue color is still struggling with low luminous efficiency [19,20]. Among the conjugated polymers polyfluorenes are very important class of polymers known to have blue emission with a peak in blue region at around 430 nm along with two peaks at 460 nm and 490 nm [21]. In polyfluorenes the main problem is undesirable green peaks near 500 nm due to the occurrence of keto defects while forming films of

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http://dx.doi.org/10.1016/j.orgel.2016.04.015
1566-1199/

the polymer [22,23]. Pure blue light can be obtained from PFO by two methods i.e., by enhancing the blue peak or by suppressing the green emission. To suppress the peaks in green region, a lot of work has been done to enhance blue emission by modifying the polymer chemically using methods like co-polymerization, end capping with electron deficient moieties and substitution etc. [24–26]. But all these methods include complicated chemical synthesis process and required high accuracy of reaction condition for synthesis. Another significant method that can be used is blending of PFO with some hole or electron transport materials [27,28]. This technique is free from complex reactions and less time consuming. In this paper we report the fabrication of thin films of CdSe/ZnS QD and PFO blend which has been used as emissive layer in organic light emitting diode and effect of blend on device performance and color purity is reported. These results have also been compared with another method known as one dimensional photonic band gap (1D-PBG) that can be used for improving the color purity [29]. 1D-PBG is multilayer stalk of alternate refractive index contrast materials. Multiple layers of alternate high and low refractive index material act as photonic band gap for certain wavelength components thus allowing to transmit only narrow band light. Results of spectral narrowing and suppression of green peaks has been demonstrated. The effect on structural and electrical properties of different doping concentration (0–100 wt.%) of QD(CdSe/ZnS) in polyfluorene (PFO) was studied and reported.

2. Materials and methods

Conjugated polymer used in present work was poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO) with molecular weight M_w = 50,000–150,000 purchased from Luminescence Technology Corp., Taiwan. Semiconductor CdSe/ZnS core-shell quantum dots stabilized by octadecyl amine (ODA) in toluene with emission peak at 505–530 nm were provided by M K Impex Corp., Canada. Poly (3,4ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) of low conductivity grade (1 s/cm) dispersed in water and chloroform were purchased from Sigma Aldrich.

PFO-CdSe/ZnS QD blend was prepared by mixing different amount of QD (0–75 wt.%) and PFO in chloroform. Thin films of PFO, PFO-QD blend deposited using Apex digital spin coater. PFO thin film was also fabricated on the backside of PBG (based on periodic layer of silver and magnesium fluoride) coated glass substrate. Photoluminescence (PL) spectra were recorded for all above samples by spectrofluorometer (shimadzu, model-RF-5301Pc).

Hybrid light emitting diodes were fabricated on Indium Tin Oxide (ITO) coated glass plates procured from Vin Karola Instruments. PEDOT:PSS thin films were spin coated at 1300 rpm for 120 s over cleaned ITO plates as hole transport layer and treated at 120 °C for 1 h. Above this PEDOT:PSS layer, emissive layer (EML) of PFO mixed with different amount of CdSe/ZnS QD (0–75 wt.%) were deposited and heated up to 80 °C for 2 h. After this, aluminum was thermally evaporated to function as cathode. Electroluminescence of all the devices were taken using emission spectrometer (Ocean Optics) and source meter (Keithley-model 2400).

3. Results and discussion

3.1. Fourier transform infrared spectroscopy (FT-IR) studies

Pure PFO and PFO-QD blend film to be used as EML were first characterized using FT-IR spectroscopy. In Fig. 1 FT-IR spectra of PFO and PFO-QD blend are presented. The FT-IR Spectra for both the films shows important peaks at 2925 cm^{-1} and 2852 cm^{-1} which is attributed to C–H stretching for alkyl side chain of PFO as reported elsewhere [30]. Along with these two peaks a shoulder at

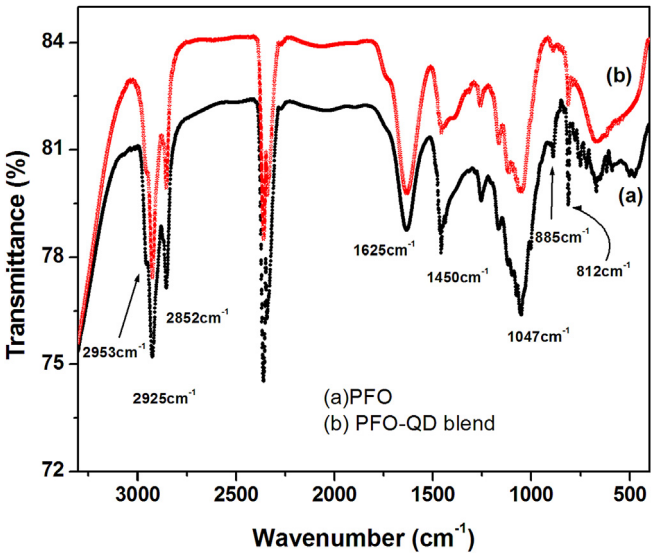

Fig. 1. FT-IR spectra of (a) polyfluorene and (b) polyfluorene – QD blend films.

2953 cm^{-1} appears which represents the C–H stretching for aromatic ring. C=C stretching around 1625 cm^{-1} is enhanced in case of blend due to the formation of β-phase which results in increased conjugation. Whereas intensity of peak at 1450 cm^{-1} for aromatic ring breathing is reduced due to restricted motion of PFO due to planarization in β-phase. Again due to the β-phase generation in plane vibration = C–H (1047 cm^{-1}) enhanced in case of blend and out of the plan alkyl rocking(885 cm^{-1} and 812 cm^{-1}) decreases.

3.2. Atomic force microscopy

AFM analysis was done to study the changes in uniformity of the PFO thin film on adding the CdSe/ZnS QD. For this, AFM images of PFO and PFO-QD shown in Fig. 2(a) and (b), were taken using Scanning Probe Microscope (Bruker's dimension icon AFM with scanasyst). AFM image of PFO polymer thin film shows uniform surface whereas surface of PFO-QD blend is uneven.

3.3. Photoluminescence studies

CdSe/ZnS core shell quantum dots used in this study were characterized by absorption and photoluminescence studies as shown in Fig. 3(a) and (b). Absorption spectra for QDs shown in Fig 3 (a) was recorded using UV–Vis spectrophotometer of Shimadzu (model-UV-2600). Absorption peak for these QDs was found to be at 516 nm approx. PL spectra shows narrow emission (FWHM = 30 nm) peaking at 525 nm, when irradiated with different excitation wavelength of light ranging from 410 nm to 490 nm. When QDs were excited with longer wavelength, the PL intensity decreases due to the obvious reason of lesser energy of excitation.

PL spectra of polyfluorene-CdSe/ZnS core shell quantum dot blend for different wt.% of QD is shown in Fig. 4(a) and (b). Optical excitation of thin film of pristine PFO at 380 nm results in definite vibrionic features with two emission peaks in blue region (436 nm and 463 nm) and a shoulder at longer wavelength of 492 nm (see Fig. 4(a)). To study the energy transfer between polymer and quantum dots, PL spectra of film of blend with different wt.% of QDs were taken under same irradiation wavelength of 380 nm. The spectrum for blend shows slightly red shifted emission with enhanced blue peak at 440 nm whereas undesirable peak at lower wavelength of 467 nm is weakened (Fig. 4(b)). Blend films also