Enhanced Light Emitting in CdTe Type (II)-SWNT Composite Diodes

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ABSTRACT-- ***We in this work have studied the effects of single-wall nanotube (SWNT) concentrations with carboxyl acid surface group on the luminance properties of (CdS/ZnS shell/shell Type II) capped CdTe Quantum dots (QDs). Carboxylic acid modified carbon nanotubes (CNTs) were used to interact with water-soluble luminescent mercaptoundecanoic acid-capped Type (II) CdTe QDs. The performance of CdTe type (II) QD light emitting diodes in luminance has been demonstrated by the improvement of doping carboxylic modified carbon nanotubes. This may be due to the chemical interaction bonding between the carboxylic acid modified CNTs and the CdTe type(II) QDs. The effects of size of CNT, doping and crystallization of CNT have been investigated. Here we report the effects of doping on current density, luminance and current efficiency. Suitability of SWNT to improve the performance of LED as against multi-wall nanotude (MWNT) has been discussed.***

Keywords-- Single wall nanotubes (SWNTs), Quantum dots (QDs), Photoluminance, Light emitting diodes (LEDs)

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1. INTRODUCTION

Much attention has been paid during the past two decades to the adoption of quantum confined semiconductor crystallites in solid-state light-emitting diodes (LEDs) [1,2]. Owing to quantum-confinement effects, the optical properties of these nanocrystals quantum dots (QDs) can be tuned in by varying the crystal size [3]. But the small size of the QDs hinders their direct incorporation into electronic devices. However, the efficiency of these devices has so far been limited by difficulties in controlling charge injection into the QD film. One of the schemes is to manage charge transport and generation more effectively in LED structures by blending with a conducting material, such as single-wall nanotubes (SWNTs), which are an important variety of carbon nanotube, and were already modified in order to improve their solubility. The over all trend confirms that the luminance of the undoped device is inferior to that of the doped – blended ones [4].

The main objectives of this work has been to study the possibility of enhancing the properties of light emitting devices like LED. The size of CNT and doping can play a significant role. The use of Type (II) CdTe QDs , effect of doping and varying conditions of CNT have been given special attention. Results have been interpreted in terms of the current efficiency, current density and luminance measured as such.

2. EXPERIMENTAL DETAILS

2.1 Quantum Dot Synthesis and Characterisation

The CdTe quantum dots were prepared by a 'one pot' route [5]. The optical absorption and the photo-luminescent studies were performed on thin film deposited by spin coating over the spectrosil B disks.

2.2 Device Preparation and Characterisation

The device structure consisted of an emissive CdTe(type II) blended with carboxylic functionalized single-wall nanotubes (SWNTs) layer sandwiched between Indium Tin Oxide nanocrystal layer (ITO/PEDOT) and a thermally evaporated calcium cathode capped with aluminium at a base pressure of approximately 10^{-6} mbar. The anode hole injection performance is improved by depositing poly(ethylene dioxythiophene) doped with poly-styrene sulfonic acid (PEDOT:PSS) onto ITO that has been pre-treated with oxygen plasma at 10 W for 5 min.

The CdTe was deposited by either drop casting or spin coating from a solution (waterbased CdTe QDs+SWNTs). multilayered devices with CdTe were also prepared and tested at a vacuum of 10^{-2} mbar.

3. RESULTS

The physical characteristics of light-emitting diodes were studied to explore the effects of single-wall nanotubes (SWNTs) concentration on the luminance properties of CdTe quantum dots. The typical current density-voltage, luminance-voltage and current efficiency-voltage characteristics for the devices were studied.

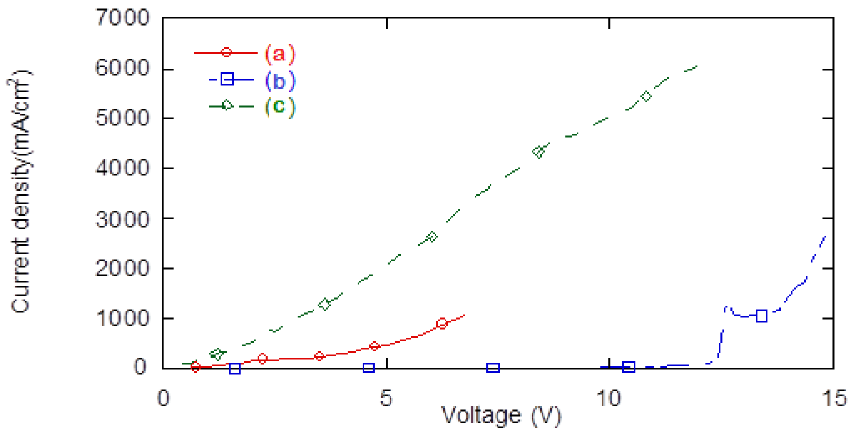

Figure 1 : Current density-voltage plot of,
(a) ITO/CdTe type(II)QD/AL
(b) ITO- PEDOT/CdTe type(II)QD +Ionic liquid/Ca-Al, and
(c) ITO- PEDOT/CdTe type(II)QD+SWNT carboxylic functionalized/Ca-Al

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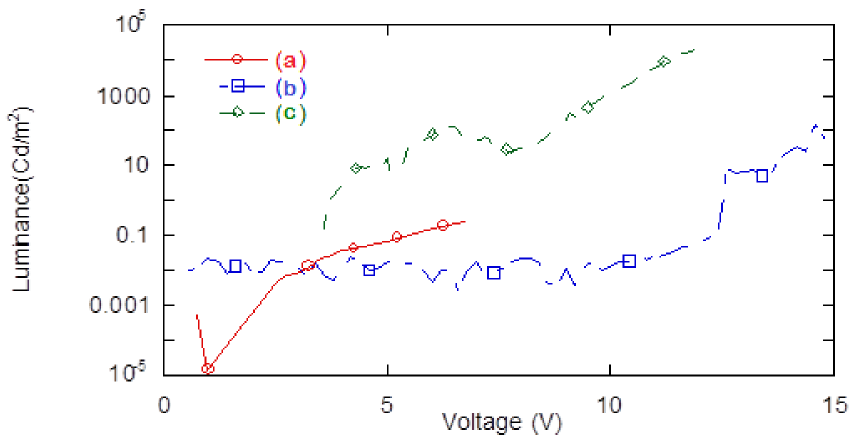

Figure (2) : Luminance-voltage plot of,
(a) ITO/CdTe type(II)QD/Al,
(b) ITO-PEDOT/CdTe type(II)QD +Ionic liquid/Ca-Al, and
(c) ITO/CdTe type(II)QD +SWNT carboxylic functionalized/Ca-Al

Figure 1 shows that doping increases the current density of the diodes. The current increases by few orders of magnitude and a high leakage current is observed at low voltages. Figure 2, shows that upon doping, the luminescence increases with light-emitting diode devices exhibiting maximum luminescence of 65227cd/m at 11.9V at (50% doping CNT-Carboxylic). This indicates that the appropriate amount of CNTs doping can improve the maximum luminescence. But the level of improving the maximum luminescence of CdTe type (II) QD light emitting diodes, is limited by the mixed structure of metallic and/or semiconductivity state of the SWNT, which in turn depends on the diameter, chirality and orientation of the carbon nanotubes [6].

Figure 3 shows the current efficiency (photometric) as a function of the voltage. The CNT doping does not significantly shift the maximum of efficiency to lower voltage, but tend to lower the current efficiency. The much

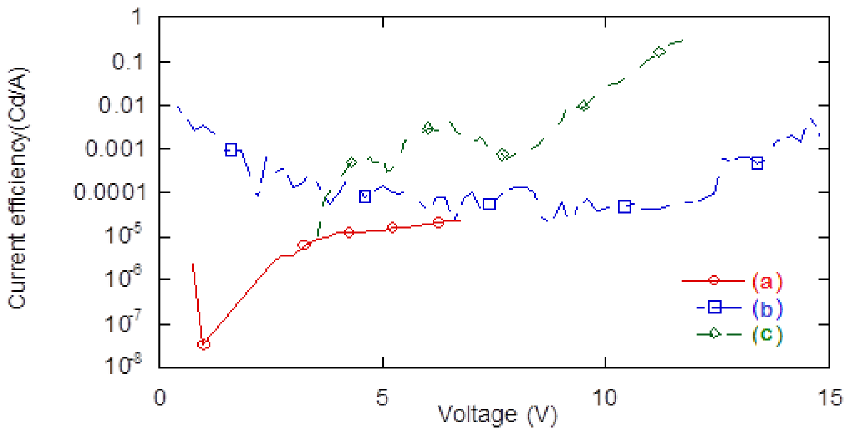

Figure 3 : Current efficiency-voltage plot of,
(a) ITO/CdTe type(II)QD/Al,
(b) ITO-PEDOT/CdTe type(II)QD+Ionic liquid/Ca-Al, and
(c) ITO-PEDOT/CdTe type(II)QD+SWNT carboxylic functionalized/Ca-Al

lower performance with the highest concentration (50 Wt%) as is evident from the high current density at lower bias (Figure 4), the lowest luminescence (Figure 5) and current efficiency (Figure 6) are likely to be attributed to CNT/CdTe aggregation and crystallization. It is clearly evident that the current efficiency increases as the doping level increases up to 25% and that a too high concentration of dopant degrades the device performances.

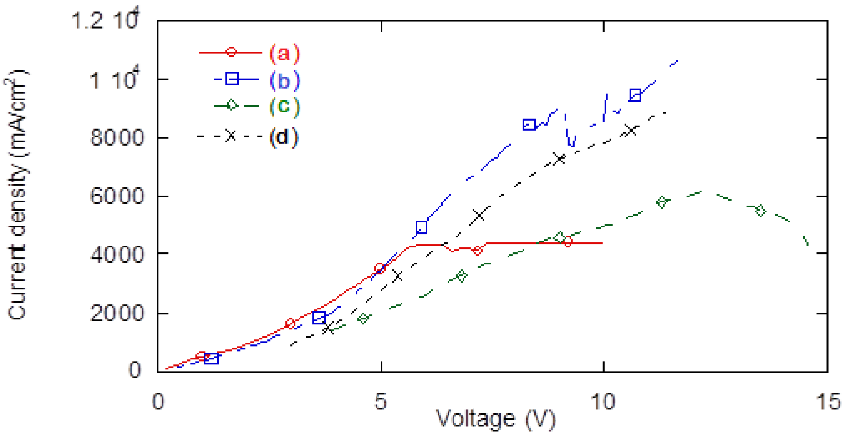

Figure 4 : Current density-voltage plot of ITO-PEDOT/CdTe Type (II)) QD,
(a) +0.025mg/ml SWNT carboxylic functionalized/Ca-Al,
(b) +0.0125mg/ml SWNT carboxylic functionalized/Ca-Al
(c) +0.0062mg/ml SWNT carboxylic functionalized/Ca-Al, and
(d) +0.0031mg/mlSWNT carboxylic functionalized/Ca-Al

This indicates that doping by carbon nanotubes can effectively improve the current efficiency of CdTe-based light-emitting diodes, but not the power efficiency of the devices, possibly because the conductivity of prepared film in the doped devices increases. In a similar work [7] the external quantum efficiency of luminance increased with the CNT concentration before being abruptly quenched, due to the distinct difference between the mobilities of electron and hole in the CNT concentration. The electron mobility increases gradually with the SWNT concentration, while the hole mobility remains almost constant. Above the optimum SWNT concentration, where the electron mobility exceeds the hole mobility, the external quantum efficiency exhibits a drastic drop due to the imbalance in mobilities which causes a decrease in exciton formation.

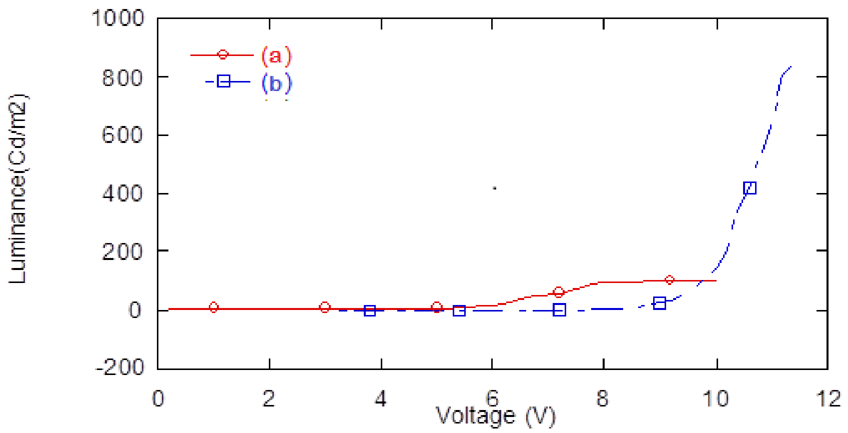

Figure 5 : Luminance-voltage plot of ITO-PEDOT/CdTe Type (II) QD,
(a) +0.025mg/ml SWNT carboxylic functionalized/Ca-Al, and
(b) +0.0031mg/ml SWNT carboxylic functionalized/Ca-Al

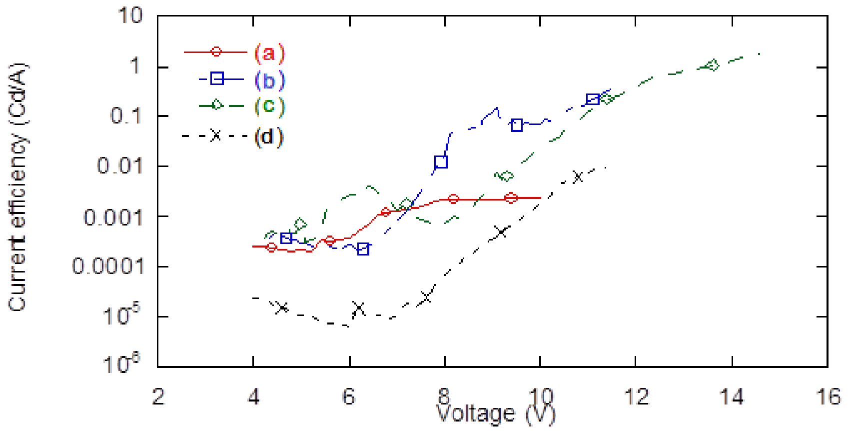

Figure 6 : Current efficiency-voltage plot of ITO-PEDOT/CdTe Type (II) QD,
(a) +0.025mg/ml SWNT carboxylic functionalized/Ca-Al,
(b) +0.0125mg/ml SWNT carboxylic functionalized/Ca-Al,
(c) +0.0062mg/ml SWNT carboxylic functionalized/Ca-Al, and
(d) +0.0031mg/ml SWNT carboxylic functionalized/Ca-Al

4. DISCUSSION

In a recent report [8] the effects of single wall nanotubes (SWNTs) on the electroluminescent performance of organic light-emitting diodes (OLEDs) have been investigated by mixing them in a hole-conducting layer and in a light –emitting layer in OLEDS. It was found that SWNTs play a different role when used as part of a composite in the LEDs.When used in a hole-conducting layer the SWNTs facilitate the charge transport in the transport layer, and, on the other hand, they also act as the exciton quenching centers at the transporting/emitting intetface provided that their concentration is high enough. When used in a light-emitting layer the SWNTs act as an n-type dopant to increase electron transport in a p-type electroluminescent film, and subsequently improve the balancing degree of bipolar injection leading to an enhancement in the electroluminance efficiency. Biswas et al [9] went further in their findings in which a clear type conversion of SWNT from P-type to N-type was caused by a charge transfer from attached QDs to CNTs. The surface condition of SWNT seems to play an important role as it is widely accepted that defect in the carbon nanotubes wall strongly influence the intrinsic properties of CNTs. Defect engineering of CNTs enables chemically functionalized [10] tuning of electronics [11]. SWNT contains defects like pentagon-heptagon rings and shows higher absorption [12] than the multi-wall nanotubes (MWNT).

Another reason for using SWNT instead of MWNT is based on the results presented by S. Hotta et al [13] which indicated that microcyrstalization of the light emitting polymer can occur after the polymer transforms to a more ordered conformation. As a result the excess doping of MWNT to the polymer enhances the crystallization, deteriorates the surface morphology and reduces the efficiency at higher current density. In another study (16) the imbalance of electron and hole mobility was addressed which resulted in a shift of the recombination zone towards an electrode, lowering the device efficiency due to exciton quenching by the metal electrodes. The highest external quantum efficiency was obtained where the electron and hole mobilization awere almost equal. Similar conclusion was reached by W-J Yin et al [14] and this can be traced back to H. S. Woo et al [15].

Study of the effects of multi-wall nanotubes on the photoluminescence properties of CdSe QDs [6] showed that functionalised CNTs terminated by carboxylic had the poorest quenching. However, since CNTS quenched the CdSe QD, the interaction between CNTS and QDs must have happened through an alternative way [17-19]. This alternative non-irradiative path occurs because the electron affinity between the CdSe QDs and the CNTS is sufficiently different that it allows electron transfer from the QDs to the CNTS [18,20]. Ago et al presented the hole-collecting properties of multi-wall carbon nanotube [21]. H. S. Woo et al [15] found that SWNTs in a polymermatrix trap holes injected from the anode act as a hole blocking material. Based on these two studies it may be concluded that in contrast to the SWNTs behaviour, MWNTs showed improvement in performance, due to their metallic or semi-metallic properties . Wang et al [22] obtained higher emission intensity from the OLEDs with MWNT doping, which is different from the results for devices with a similar structure in which SWNT doping was used as the hole-injection layer. The emission intensity was found to have decreased because of the hole traps caused by SWNT doping [5]. The highest luminance is obtained in the device with a concentration of SWNT at (25%) and (12%) respectively.

Devices fabricated with MWNTs are different from those fabricated with SWNTs nanocomposites. This may be due to the different electrical properties of SWNTs which result the hole trapping property in the SWNTs nanocomposites. But the metal or semi-metal properties of MWNTs might improve the hole injection ability of the nanocomposites, similar to the SWNTs behaviour of gold nanoparticles, as they are the efficient hole trap sites, providing hole-blocking characteristics.

Summarizing the results it may be concluded that doping increases the current density of the diodes and upon doping, the luminance increases with light-emitting diode. The appropriate doping amount of CNTs can improve the maximum luminance. CNT doping does not significantly shift the maximum of efficiency to lower the voltage but tend to lower the current efficiency. The CE increases as the doping level increases up to 25% and that a too high concentration of dopant degrades the device performances. This indicates that doping by carbon nanotubes can effectively improve the current efficiency of the CdTe-based light-emitting diodes, but not the power efficiency of the devices. The surface condition of SWNT seems to play an important role as it is widely accepted that defect in the carbon nanotubes wall strongly influence the intrinsic properties of CNTs. SWNT contains defects like pentagon-heptagon rings and shows higher absorption than MWNT. Another reason for using SWNT instead of MWNT is that microcyrstalization of the light emitting polymer can occur after the polymer transforms to a more ordered conformation. As a result the excess doping of MWNT to the polymer enhances the crystallization, deteriorates the surface morphology and reduces the efficiency at higher current density.

5. ACKNOWLEDGEMENTS

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