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Improved performance of inverted quantum dots light emitting devices by introducing double hole transport layers

Congbiao Jiang, Huiming Liu, Baiquan Liu, Zhiming Zhong, Jianhua Zou*, Jian Wang, Lei Wang**, Junbiao Peng, Yong Cao

Institute of Polymer Optoelectronic Materials and Devices, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou, 510640, China

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ABSTRACT

Here we reported very bright and highly efficient deep-red quantum dot light-emitting devices (QD-LEDs) with inverted structure by introducing double hole transport layers (HTLs) consisting of 4,4′,4″-tri (N-carbazolyl)-triphenyl-amine (TCTA) and N,N′-bis (naphthalen-1-yl)-N,N′-bis (phenyl)-benzidine (NPB). The turn-on voltage of the optimized device was as low as 1.9 V, the maximum current efficiency and luminance were 8.68 cd/A and 15,000 cd/m^2, respectively. However, for the best performance of QD-LED with single hole transport layer, the turn-on voltage reached up to 3.6 V, the peak current efficiency was only 3.84 cd/A and the maximum luminance was 7700 cd/m^2. The enhancement of the performance is attributed to the stepwise HTL structure, which can decrease the hole-injection barrier from HTL to QD emitting layer and reduce the turn-on voltage of QD-LEDs. Besides, the lower highest occupied molecular orbital of TCTA can suppress the accumulation of electrons at the interface of QDs/HTL and separate the carrier accumulation zone from the exciton formation interface, which can balance the carriers transportation and enhance performance of QD-LEDs.

1. Introduction

Quantum dot light emitting devices (QD-LEDs) have advantages of good color purity and photostability, narrow emission bands, broad wavelength tunability over the entire visible spectrum due to its size dependence [1]. All these attractive characteristics make quantum dots being a promising candidate for the emissive material in LEDs, which has been intensively studied and developed for next generation display and solid-state lighting [2,3]. QD-LEDs were invented about two decades ago and there was great progress in enhancing device performances, close to that of organic LEDs [4,5]. The external quantum efficiency (EQE) has been increased from less than 0.01% to over 20% [4,6]. At the present, the EQE for RGB QD-LEDs all can reach up to 20.5% [4] 14.5% [5], 10.7% [7] respectively. Recently, Qian's group [5] has reported a full series of blue, green and red QD-LEDs, all with high EQE over 10% and long lifetime, which suggests that QD-LEDs can be widely used for commercialization. In order to improve the performance of QD-LEDs, a lot of work has been done [4–6,8,9,7,10–27]. The first QD-LEDs was reported with the structure comprised CdSe core-only QD emitting layer and polymer electron transport layer (ETL) sandwiched between two electrodes. Because of lower carrier mobility of organic semiconductor, QD-LEDs did not perform well and operating voltage was as higher as 4 V [6]. As we know, photophysical behaviors of colloidal quantum dot materials have been shown to strongly depend on their shell structure and composition [5,19,28,29]. For core–shell quantum dots, the shell has lower confinement of electron wave function than for the corresponding hole [4,28,29]. In order to improve the ability of electrons injection and reduce the cost, wet process of inorganic ZnO nanoparticles has been found and widely used as the electron transport materials in QD-LEDs due to its high electronic mobility and lower conductive band. In fact, highly efficient QD-LEDs have been fabricated with ZnO nanoparticle as ETL [4,5,9,20,28–32].

It is well-known that each layer of conventional devices is deposited by spin-coating while the fabrication process of devices maybe exist corrosion of solvents within solution-process. And after ZnO depositing by spin-coating, devices need to be baked at over 120 °C to remove residual solvents and relatively high heat-

* Corresponding author.
** Corresponding author.
E-mail addresses: zou1007@gmail.com (J. Zou), mslwang@scut.edu.cn (L. Wang).

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temperature can destroy the organic layers like HTL [10]. Therefore, another device structure is designed, namely inverted device structure, where ITO is utilized as transparent cathode and ZnO nanoparticles are deposited on ITO by spin-coating as ETL. After that light emission layer (quantum dots), HTLs and anode are deposited layer by layer. Compared with conventional device structures, inverted device structures have many advantages. Firstly, QD-LEDs with inverted device structures just have ETL (ZnO nanoparticle) and QD emission layer deposited by solution-processed, avoiding solvents to destroy underlying layers. Secondly, many small molecules with high carrier mobility can be deposited as HTLs by thermal evaporation technique. Moreover, multilayer HTLs can be deposited by thermal evaporation technique without any damage to underlying layer, which can improve the performance of QD-LEDs. Recently high-performance of inverted hybrid structure red QD-LEDs with an EQE of 18% was reported [21]. Considering that efficient electron injection and interface engineering have been achieved for ZnO nanoparticle as ETL, one alternative approach to enhance device performance is optimizing HTL to simultaneously achieve efficient hole injection and exciton confinement in QD emission layer. To date, it is well known that a large carriers injection barrier exists between HTL and QD emission layer due to shallow HOMO of organic transport materials. Hence, in order to enhance carriers injection and transportation from HTL to QD emission layer, the higher LUMO to block electrons and lower HOMO to decrease the hole injection barrier for hole transport materials is necessary.

In this work, to further investigate the effects of HTLs in QD-LEDs and obtain highly efficient devices, we firstly introduce CBP as hole transport material in red QD-LEDs and the best performance of devices shows a turn-on voltage at 3.6 V and peak current efficiency at 3.84 cd/A. Then double HTLs of TCTA/NPB is utilized in the same red QD-LEDs. The maximum current efficiency and luminance of deep-red QD-LEDs with double HTLs are 8.68 cd/A and 15,000 cd/m^2, respectively. The enhancement is attributed to the deep HOMO energy level of TCTA, which can realize efficient hole injection into quantum dot layers and reduce the barrier of hole-injection to achieve low turn-on voltage. Besides, TCTA layer can suppress the accumulation of electrons at the interface of QDs/HTL and separate the carrier accumulation zone from the exciton formation interface. In addition, bilayer HTLs can balance the carriers transportation to achieve high current efficiency.

2. Experiment details

As depicted in Fig. 1, the configuration of devices is ITO/ZnO (35 nm)/CdSe–CdS–CdZnS QDs (35 nm)/HTL (60 nm)/MoO_3 (8 nm)/Al (200 nm).

Here ITO coated glass with a sheet resistance of 15–20 Ω per square is used as the substrate (from China Southern Glass Holding Corp.). The substrate is pre-patterned by photolithography to give an effective device size of 15 mm^2. Prior to device fabrication, the substrates were thoroughly cleaned in sequence in ultrasonic bath of acetone, isopropanol, detergent, deionized water, isopropanol, and dried in a vacuum baking oven. Then ITO substrates were treated with 20 min oxygen plasma, ZnO NPs (30 mg/ml, in ethanol) layer was deposited on the ITO glass by spin coating at 4000 rpm for 40 s and baked at 120 °C for 10 min in a nitrogen glove box, then cooling down to the room temperature. ZnO NPs was synthesized per procedures in previously reported literature [9,26]. Zinc acetate dehydrate ($Zn(Ac)_2\cdot 2H_2O$) was used as a starting material. A precursor solution was prepared as follow: 1.23 g of $Zn(Ac)_2\cdot 2H_2O$ is dissolved in 55 ml of methanol at room temperature and 0.48 g of potassium hydroxide (KOH) was dissolved in 25 ml of methanol at 60 °C. Then two individual solutions were mixed and stirred at 60 °C for 2 h under nitrogen ambient. ZnO NPs as white precipitate appeared, which needed to be further purified by centrifugation and washing with ethanol. Finally, ZnO NPs was dispersed in ethanol solvent with concentration of 30 mg/ml and 150 ul ethanol amine added as stabilizer. Here ZnO NPs acts as electron transport material. After that CdSe–CdS–CdZnS QDs

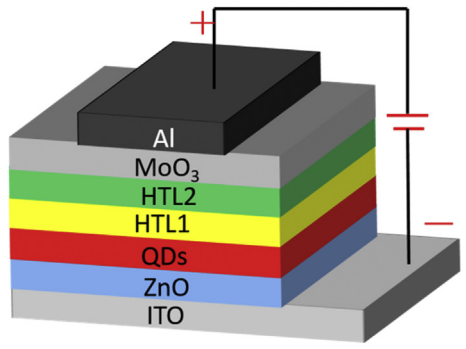

Fig. 1. Multilayer QD-LEDs devices structure.

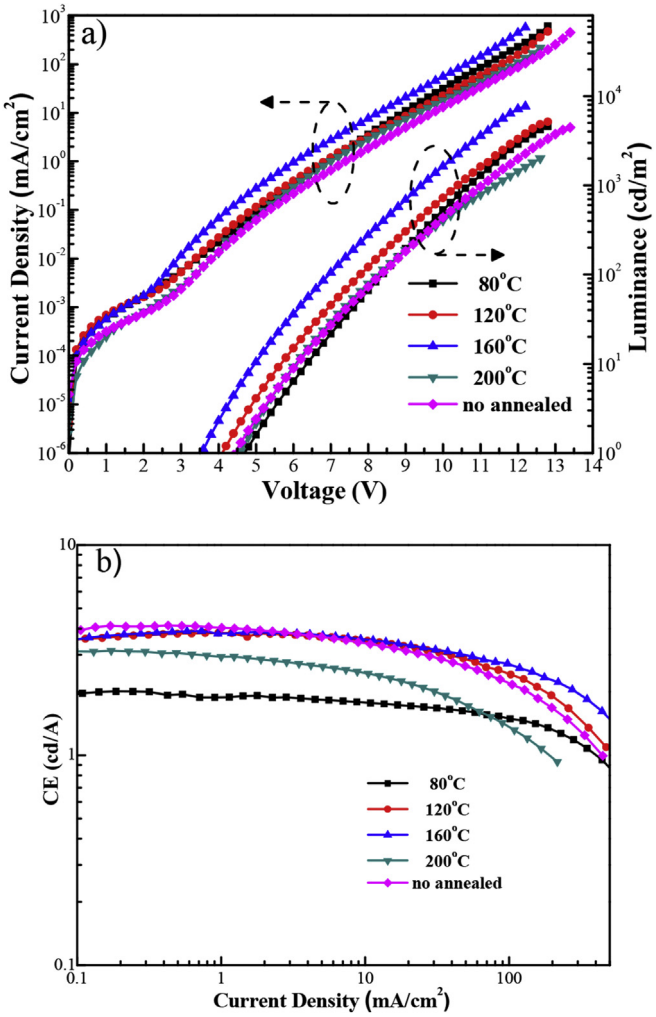

Fig. 2. Current density and luminance verse voltage (J-V-L) curves a) and current efficiency verse current density (CE-J) curves b) with structure ITO/ZnO (35 nm)/CdSe–CdS–CdZnS QDs (35 nm)/CBP (60 nm)/MoO_3 (8 nm)/Al (200 nm) (Devices A) annealed at different temperatures.