Quantum-dot light-emitting diodes with NiO and NiO:Mg as hole injection layer

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ABSTRACT

Quantum-dot light-emitting diodes （QLED） have attracted great attention due to their impressive optoelectronic properties and stability. The most common used hole injection layer (HIL) material Poly(3,4-ethylenedioxytiophene):polystyrene sulfonate (PEDOT:PSS) is acidic and causes corrosion of indium-tin-oxide (ITO) anodes. Nickle oxide (NiO) are widely used as the hole transport layer (HTL) in QLED due to their suitable electrical properties. For the large energy gap between QD and HTL, there is unbalanced charge injection in QLED device when NiO is used. The energy band structures of NiO can be adjusted by Mg doping, which is an effective strategy to improve charge injection and mobility. Compared to undoped HIL, device with doped NiO give rise to higher EQE. In this work, our results suggests that Mg-doped NiO serve as a good hole injection layer materials for QLED and other optoelectronic devices.

Keywords: *QLED, hole injection layer, Mg-doped NiO*

1. INTRODUCTION

Colloidal quantum dot light-emitting diodes (QLED) is one of the most promising candidates in display applications because of their unique advantages on high color purity, tunable emission wavelength and low-cost fabrication. A number of approaches for improving device performance have been reported, including colloidal quantum dot (QD) synthesis, multilayer engineering, and surface engineering, and good progress has been made in last two decades[1,2]. In most QLEDs, a planar sandwich-like structure[3] where the emission layer (EML) is clamped by hole transport layer (HTL) and electronic transport layer (ETL) is used. Despite steady research progress, the unbalanced charge injection in QLED, caused by the large energy gap between EML and HTL[4,5,7], made it lagging behind Organic Light-Emitting Diode (OLED).

In QLED, Poly(3,4-ethylenedioxytiophene):polystyrene sulfonate (PEDOT:PSS) is widely used as hole injection layer (HIL) in a combination with indium tin oxide (ITO) as an anode. During the device operation, PEDOT:PSS will react with ITO, resulting in metal ion diffusion in applied electric field and exciton quenching[8]. On the other hand, inorganic materials is more stable than organic materials so using inorganic materials as HIL to replace PEDOT:PSS is an approach to improve the device performance. Nickel Oxide (NiO) is a good candidate because it is an intrinsic p-type semiconductor with a wide bandgap[6]. Additionally, NiO is solution-processable and can prevent In or Sn in ITO anodes from migrating to EML. However, the performance the devices using NiO are not satisfied, further work needed.

In this work, we report a QLED with NiO film as HIL made by solution-process. The resulting QLEDs with NiO HIL shows better stability and higher external quantum efficiency (EQE) than the ones without. We also show the improved performance of devices with Mg:NiO as HIL.

2. EXPERIMENTIAL SECTION

Materials: All the chemicals were supplied or bought and used without any further purification. Nickel Oxide (NiO, 0.05mol/ml), Mg-doped NiO (15mg/ml, 15%), Zinc oxide (ZnO, 50mg/ml) and CdSe/CdS/ZnS core-shell-shell quantum dots (QD, 10mg/ml), were made in Guangdong Poly Opto-Electronics Co., poly(N,N-bis(4-butylphenyl)-N,N-bis(phenyl)benzidine) (poly-TPD, 99.99%), was purchased from Xi'an Polymer Light Technology Corp., Analytical grade ethanol, acetone, isopropanol are from Hangzhou Shuanglin Chemical Reagent Co.

Device fabrication: Patterned ITO coated glass substrates were cleaned by sequential sonication in detergent (5% of Decon90), deionized water, ethanol, acetone and isopropanol. The cleaned ITO substrates were treated by UV for 15min immediately before use. All the following operating procedures were performed in nitrogen-filled glove box. On cleaned ITO, a 30-nm of NiO layer, a 30-nm of poly-TPD, a 18-nm of QD layer and a 30nm of ZnO was spin-coated sequentially. Each of above layers were annealed at 270℃ for 30 min., 150℃ for 20 min., 150℃ for 5 min. and 90℃ for 20 minutes Then, patterned Ag electrode was deposited in a thermal evaporator using a metal mask. Devices are encapsulated in N_2 environment with UV glue.

Measurement: Electroluminescence (EL) spectra for QLEDs were measured with a Photo Research PR670 spectra scan spectrometer and the current density-voltage (J-V) and luminance-voltage (L–V) characteristics were measured using an IVL-test-2400-2000. The test equipment mentioned here were purchased from Guangzhou Crysco Equipment Company Limited. All the measurements were carried out in the air at room temperature.

3. RESULTS AND DISCUSSION

The schematic energy diagram of device is shown in Fig. 1(a) where the NiO layer is inserted between the ITO and Poly-TPD HTL and the architecture of our QLED is in Fig. 1(b). The device consists of an ITO anode, a NiO for HIL, a Poly-TPD as HTL, a QD EML, a ZnO as ETL, and an Ag layer as cathode. From the energy level diagrams, it can be seen that the hole is easier to inject when NiO is used.

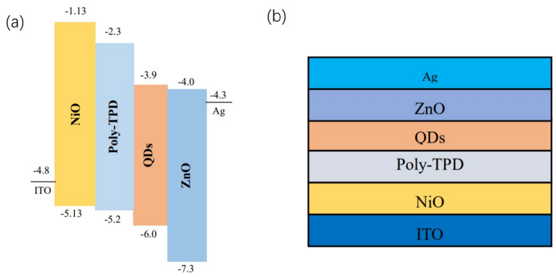

Fig.1 (a) Energy level diagrams of QLED. (b) Device structure of ITO/NiO/Poly-TPD/ QDs/ZnO/Ag.

Fig.2 (a) shows the normalized EL spectra of the device peaking at the 630nm with a narrow full width at half-maximum (FWHM) of 30nm. When the PEDOT:PSS is replace by NiO as HIL in the QLED architecture, there is no change in EL emission. The current density and the luminance of the NiO device and the device with PEDOT:PSS are shown in Fig.2 (b) . Both devices show a steady increase in current density with voltage, and a similar turn-on-voltage (≈ 2.2V). Of interest is that although PEDOT:PSS and NiO are both used as HIL, there are large difference between their current-voltage behavior that current density of device with PEDOT:PSS is much higher than the device with NiO. We speculate this result can be solved by film thickness optimization. The relationship of current efficiency (CE) and external quantum efficiency (EQE) with luminance for both QLED are shown in Fig2. (c). Overall, when NiO is used to replace PEDOT:PSS, the maximum EQE increased from 2% to 2.81%, and the highest CE increased from 1.6 cd/A to 2.29 cd/A. This was explained by the fact that NiO does not have diffusion of ion from PEDOT:PSS into the EML when there is applied electric field, thereby effectively reducing the effect of exciton quenching. Also NiO HIL prevent ITO surface from presumed reaction by acid from PEDOT:PSS.

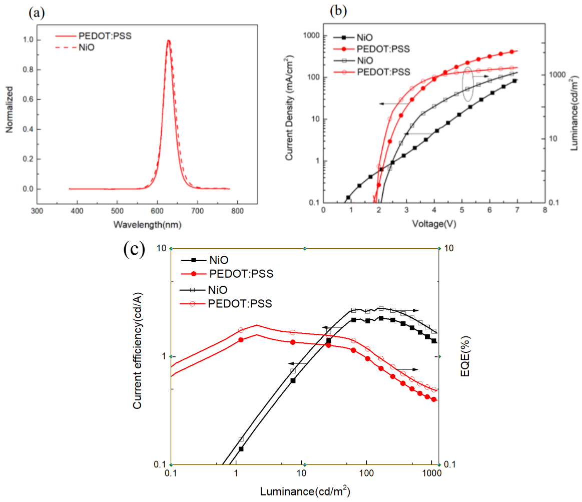

Fig.2 (a) EL spectra, (b) IVL, and (c) current efficiency (CE) and external quantum efficiency (EQE) vs luminance for devices with NiO and PEDOT:PSS as HIL.

For QLEDs, the imbalanced charges severely affects their performance. A better charge balance can reduce the Auger recombination and increase the formation of exciton. When NiO is doped with Mg, the device performance has improved as shown in Fig.3.

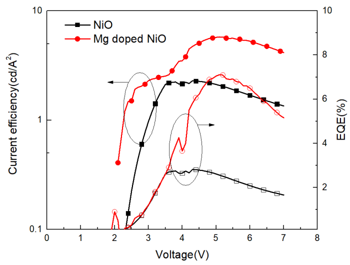

Fig3. Current efficiency and external quantum efficiency vs drive voltage for device with NiO and Mg doped NiO.

It can be seen that the EQE is increased to 7.1% and CE to 5.5cd/A with Mg doped NiO (NiO:Mg) is used. The improved device EQE and CE is attributed to the Magnesium doping, which is an effective way to improve charge injection and mobility.

4. CONCLUSION

In this study, QLED performance were improved via a NiO as a HIL instead of PEDOT:PSS. The improved performance can be largely attributed to the use of the NiO HIL that avoid etching react between PEDOT:PSS and ITO. We also report an Mg-doped NiO HIL which facilitates the charge injection and mobility, thus improves further the performance of QLED. These results provide a strategy using NiO or NiO:Mg as an alternative and effective material for HIL for efficiency QLED.

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