Lifetime Improvement by Organic-doped QD Film in QLED Devices

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Abstract

The electron leakage into hole transport layer (HTL) was proposed to be mainly factor contributing to inferior operating lifetime of quantum dot light emitting diode (QLED). In this paper, a strategy was provided to eliminate electron leakage and improve lifetime by doping conductive organic molecules into QD films. Finally, significant enhancements were observed in all three color devices. We expect our work can provide a general strategy for developing the commercialization of QLEDs.

Author Keyword

QLED; lifetime; conductive organic molecules.

1. Introduction

Quantum dot light emitting diode (QLED) has become a potential candidate for the future of display and lighting with excellent characteristics, including high luminescence, wide color gamut, and low-cost solution-processed technology [1]. In the past few decades, a lot of efforts have been devoted to improving the external quantum efficiency (EQE) and lifetime of QLED. Recently, the EQEs of QLEDs based on red, green, and blue have exceeded the theoretical limit of 25 % [2, 3]. However, the commercialization of QLED is still challenged resulted from its limited lifetime.

At present, most QLEDs with better performances are based on organic hole transport layer (HTL) and inorganic electron transport layer (ETL). The inorganic ZnO nanoparticles exhibit excellent electron-mobility while the hole-mobility of organic HTL is poor. As a result, QDs will be filled with negative charge and the excessive electron leakage into the organic HTL accelerates its deterioration following a chemical reduction reaction ($QD^- + HTL \rightarrow QD + HTL^-$). In order to improve operating lifetime of QLED, a variety of strategies have been made to adjust the charge injection characteristics in QLED. For example, aiming to accelerate hole injection, a suitable HTL molecule with deep highest-occupied molecular orbital (HOMO) could be developed to match the valence band maximum (VBM) of QD. Meanwhile, the HTL molecule with shallow lowest-unoccupied molecular orbital (LUMO) which was higher than the conduction band minimum (CBM) of QD, combined with reduced energetic disorder, was also developed to eliminate electron leakage [3]. Moreover, the Mg-doped into ZnO or additional insulating layer between the QD and ETL could also hinder the electron injection [4, 5]. At the same time, exploiting novel structure of QD with suitable energy levels to match the HTL and ETL is another effective way to achieve charge balance injection [6]. In summary, the above strategies have achieved some improvement of lifetime, and more effective strategies are still expected to be continuously developed.

Here, a novel strategy was proposed to improve lifetime by incorporating conductive organic molecules into QDs. These small organic molecules were selected from the field of organic light-emitting diodes (such as electron transport materials, hole transport materials, et al.). The previous research shows that the diameter of QDs are more than 10 nm, therefore, the arrangement of QD is not compact and there will be gaps between QDs, resulting in poor film quality during the spin-coating progress. Moreover, the size of ZnO nanoparticle is smaller than 2 nm and the gaps in QD film can be filled with ZnO nanoparticles which can even contact the ETL and HTL, resulting in direct channels of electron leakage to accelerate the deterioration of HTL. In this work, these gaps can be filled with small organic molecules and then avoiding the penetration of ZnO into QD film, thereby leading to a compact and high quality film. Meanwhile, the doped QD films exhibit improved hole-mobility which can further inhabit electron leakage into HTL. In addition, inorganic ZnO layer is more stable than organic HTL, so the hole-leakage into ETL caused by the improvement of hole-mobility will not lead to obvious deterioration, which has been confirmed in this study. As a result, the QLEDs based on doped QD films can exhibit more than 4 times lifetime than that of original devices.

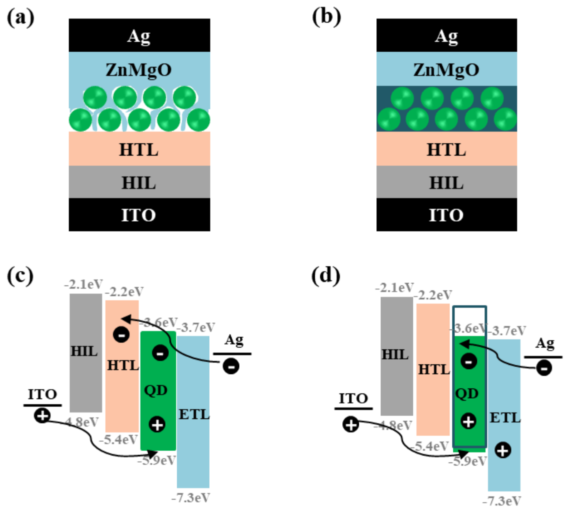

Figure 1. Schematic and energy band diagram of the QLED: (a) and (c) original QD film, (b) and (d) doped QD film.

2. Results and Discussion

2.1 Electron Only Devices and Hole Only Devices

In order to explore the charge transport properties of doped QD films with small organic molecules, the electron only devices (EODs) and hole only devices (EODs) were constructed by different small organic molecules namely doping material 1, doping material 2, and doping material 3. The structures of EQDs were followed by ITO/ZnMgO/QD: small organic molecules/ZnMgO/Ag and HQDs were followed by ITO/HIL/HTL/QD: small organic molecules/HTL/HIL/Ag, while the EML films were fabricated with mixed solutions of green Cd-based QD and small organic molecules.

As show in Fig. 2 (a), the EOD and HOD based on original QD films without small organic molecules shows higher electron-mobility than hole-mobility, caused by the electron leakage of QD film and the inefficient charge-mobility of HTL. The HOD based on doping material 1 displays higher hole-mobility than that of HOD base on original QD film, due to the higher quality of QD film and the excellent hole-mobility of doping material 1. Meanwhile, the hole-mobility of HOD based on doping material 1 is higher than the electron-mobility of EOD based on doping material 1. Since the LUMO of doping material 1 is shallower than CBM of QD and

ETL, which will hinder the electron injection. In this case, the EOD based on doping material 1 can still exhibit comparable electron-mobility to EOD based on original QD film, further confirming the improvement of the film quality. In addition, the devices based on doping material 2 and doping material 3 exhibit similar characteristics with doping material 1. It is worth noting that the HOD based on doping material 3 show highest hole-mobility, indicating smaller electron leakage. As mentioned above, the reduction of electron leakage into HTL has the potential to increase lifetime of QLED.

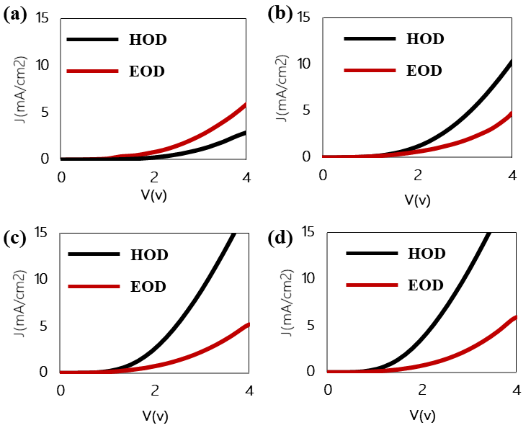

Figure 2. J-V characteristics of HOD and EOD based on: (a) original QD films, (b) QD films with doping material 1, (c) QD films with doping material 2, (d) QD films with doping material 3.

2.2 Performances of Green QLED Devices

To study the performances of green QLEDs based on small organic molecules in QD films, the devices were constructed by structures of ITO/HIL/HTL/QD: small organic molecules/ ZnMgO/Ag, while the EML films were fabricated with different doping materials and green Cd-based QD. The summery performances of green QLEDs were shown in Table 2-1.

As shown in Table 2-1, the QLEDs based on doped QD films exhibit narrowband emission with FWHM of only 27 nm and green emission peaks at 551 nm, which are consistent with QLEDs based on original QD films. In addition, no parasitic emission peaks from small organic molecules in QD films were observed, indicating the complete energy transfer from organic molecules to QDs. All of the devices based on doped QD films show much longer lifetime than that of devices based on original QD films, confirming the key role of small organic molecules in improving the stability of QLEDs. Additionally, the devices with doping material 3 have longer lifetime than others, which may be attributed to their higher hole-mobility. These results suggest that the electron leakage into HTL was successfully suppressed, and illustrate that this green Cd-based QD and ZnMgO with positive charge are more stable states to generate longer lifetime. It is worth noting that the EQE of devices based on doped QD films are slightly lower than that of devices based on original QD film, which may be resulted from the imbalanced charge injection in the devices. These devices exhibit great potential in applications which require long lifetime but are insensitive to low power consumption, such as vehicle display or lighting.

Table 2-1. Performances of green QLEDs.

EML (doping material)	Peak/FWHM (nm)	EQE (%)	T95 (ratio)
GQD	551/27	13.4	100%
GQD (1)	551/27	11.4	439%
GQD (2)	551/27	11.1	454%
GQD (3)	551/27	11.8	478%

2.3 Performances of Red QLED Devices

The red QLEDs devices were also constructed by structures of ITO/HIL/HTL/QD: small organic molecules/ ZnMgO/Ag, and the EML films were fabricated with different doping materials and red Cd-based QD. The summery performances of QLEDs were shown in Table 2-2.

As shown in Table 2-2, the red QLEDs based on doped QD films also exhibit narrow emission spectrum with FWHM of 26 nm~27 nm and peaks at 622 nm which are almost consistent with the original devices, revealing the complete energy transfer from organic molecules to QDs. Obviously, the red QLEDs based on doped QD films show improved lifetimes, indicating the effectiveness of enhanced hole-mobility. In contrast to green QLED devices, the red QLED devices show decreased lifetime with the increase of hole-mobility from doping material 1 to doping material 3. This may be attributed to the too much excessive holes from doping material 2 and doping material 3 and then damages QD and ETL, resulting in a smaller improvement of lifetime. From the above results, it can be seen that the small organic molecules exhibit different effects on various quantum dots.

Table 2-2. Performances of red QLEDs.

EML (doping material)	Peak/FWHM (nm)	EQE (%)	T95 (ratio)
RQD	622/25	19.3	100%
RQD (1)	622/27	13.8	237%
RQD (2)	622/26	14.0	232%
RQD (3)	622/26	14.1	119%

2.4 Performances of Blue QLED Devices

Additionally, the blue QLEDs devices were also constructed by structures of ITO/HIL/HTL/QD: small organic molecules/ ZnMgO/Ag, and the EML films were fabricated with different doping materials and blue Cd-based QD. The summery performances of QLEDs devices were shown in Table 2-3.

Until now, the blue QLED displays the shortest lifetime among three basic colors, which has become the biggest challenge hindering the commercialization of QLEDs. From the Table 2-3, the blue QLEDs based on doped QD films can also exhibit improved lifetime compared to original devices, while the blue QLED based on doping material 2 shows best lifetime. In the future, we believe that the lifetime of blue QLED can be further improved by adjusting charge transfer characteristics of the device accurately *via* selecting more suitable small organic molecules.

Table 2-3. Performances of and blue QLEDs.

EML (doping material)	Peak/FWHM (nm)	EQE (%)	T95 (ratio)
BQD	471/21	10.6	100%
BQD (1)	471/21	7.2	146%
BQD (2)	471/21	6.5	215%
BQD (3)	471/21	8.8	107%

3. Conclusion

In summary, this paper demonstrates a lifetime decay model in QLED, which is followed by the electron leakage into the organic HTL. And then, we proposed an efficient strategy aiming to improve lifetime by incorporating conductive organic molecules into QDs. The doped QD films exhibit enhanced hole-mobility and then eliminate channels of electron leakage. As a result, the green QLEDs based on doped QD films exhibit more than 4 times lifetime than that of original devices. And similar characteristics were also observed in red and blue QLEDs. We believe that our research can provide the method to alleviate the issue of QLED's stability.

4. Reference

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