Device Physics and Material Chemistry of Quantum-Dot Light-Emitting Diodes

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ABSTRACT

The past decades witness tremendous progress of quantum-dot light-emitting diodes (QLEDs). These encouraging facts foreshadow the commercialization of QLEDs, promising an unprecedented generation of cost-effective, large-area, wide-color-gamut, ultra-thin and flexible displays. Here we review our activities associated with QLEDs, including exciton-generation mechanisms, material chemistry of charge-transporting layers and device engineering.

1 Introduction

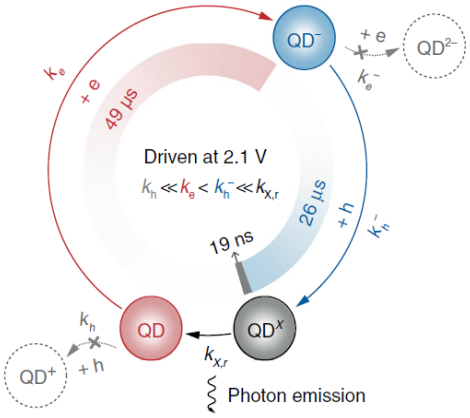
Quantum dots (QDs) are a unique class of emitters with size-tunable emission wavelengths, saturated emission colors, near-unity luminance efficiency, inherent photo- and thermal-stability and excellent solution processability.[1] These amazing luminescence properties stimulated commercial applications of QDs in display industry. Giants in display industry (e.g. Samsung, Hisense, TCL and BOE) worked together with start-up companies in the QD field (e.g. Najing Tech, QD vision and Nanosys) to produce the so-called QD-television, which uses QD-enhanced back-lighting.

Electroluminescence (EL) of QDs provides another attractive route to harness their superior emission properties for display applications. We highlight that both efficiency and lifetime of quantum-dot light-emitting diodes (QLEDs) achieved dramatic improvements in the past few years. [2-14]

This article aims to provide a comprehensive review on our recent progress of QLEDs. We begin with addressing a fundamental question of how the excitons are electrically generated in individual QDs.[5] Next, we analyze the mechanism of device degradation in QLEDs operation. [6] Based on these understandings, we develop material chemistry of charge-transporting layers, including the treatment of an oxygen plasma on the PEDOT:PSS films, [6] the fabrication of the NiO_x films with a high and stable work function,[7] and the design of bi-layer structured electron-transporting layers (ETLs).[8] These efforts enable QLEDs with significantly improved operational performance.

2 Results

In the studies of how excitons are electrically generated in individual QDs, we reveal a nanoscopic mechanism of sequential electron-hole injection for exciton generation in nanocrystal-based EL devices (Fig. 1). [5] We develop electrically-pumped single-nanocrystal spectra to decipher the corresponding elementary processes. While hole injection into neutral quantum dots is generally considered to be inefficient, we find that the intermediate negatively charged state of quantum dots triggers confinement-enhanced Coulomb interactions, which simultaneously accelerate hole injection and hinder excessive electron injection. In-situ/operando spectroscopy on state-of-the-art quantum-dot light-emitting diodes demonstrates that exciton generation at the ensemble level is consistent with the charge-confinement-enhanced sequential electron-hole injection mechanism probed at the single-nanocrystal level.



The identification of the long-lived intermediate QD^- state for exciton generation inspires us to hypothesize a side reaction of $QD^- + TFB \rightarrow TFB^- + QD$, i.e., electron transfer from the negatively charged QD to the hole-transporting layer (HTL) of TFB polymer. To confirm this hypothesis, we conduct a comprehensive investigation on the molecular-level degradation mechanism of the HTLs.[6] Mechanism studies reveal that in the operation of QLEDs, the leakage electrons into HTLs induce in-situ electrochemical reduction reactions of the HTLs, which in consequence degrade the charge-transport properties of the HTLs and deteriorate the device performance.

A feasible approach to minimize the side reaction of

electron transfer to TFB is via accelerating the main reaction for exciton generation, which require more efficient hole injection at the hole-injection layer (HIL)/HTL interface to increase the hole concentration at the HTL/QD interface. Thus, we invoke an oxygen plasma treatment on the PEDOT:PSS films, resulting in enhanced hole injection efficiency at the HIL/HTL interface. This simple modification leads to more holes injected into QDs and fewer electrons leakage into the HTLs, enabling QLEDs with improved operational performance, i.e., high external quantum efficiency (EQE) of >20.0% and outstanding T_{95} lifetime of 5,600 h at 1,000 nits. Furthermore, we develop NiO_x films with a high and stable work function of ≈5.7 eV achieved by a simple surface modification strategy as HILs (Fig. 2), which offer efficient hole injection into the polymeric HTLs.[7] In consequence, QLEDs based on the surface-modified NiO_x HILs show driving voltages of 2.1 and 3.3 V to reach 1000 and 10 000 nits, respectively, both of which are the lowest among all solution-processed LEDs and vacuum-deposited OLEDs.

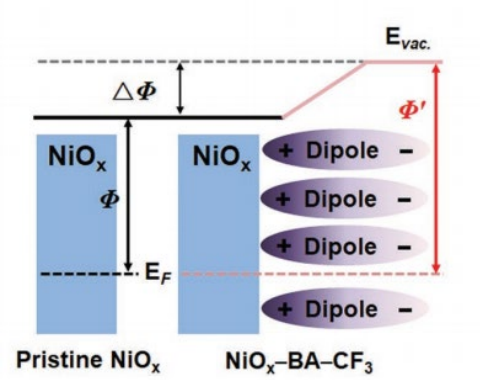


Fig.2 Schematic diagram showing the surface dipole-induced change of the work function of the NiO_x film.[7]

The design of ETLs is guided by mechanism studies of the shelf ageing behaviors of QLEDs.[8] Remarkably, a so-called positive ageing behavior, i.e., improvements in device performance including efficiency, electrical conductance, and operational lifetime after a short storage time of within several days, is generally observed for the state-of-the-art QLEDs.[9,11] Unfortunately, the QLEDs benefiting from the positive ageing behaviors would inevitably undergo gradual deterioration of device performance, which we refer to as negative ageing. We reveal that the in-situ reactions induced by organic acids in the commonly used encapsulation acrylic resin lead to positive ageing and, most importantly, the progression of in-situ reactions inevitably results in negative ageing. In-depth studies focusing on the correlations between the in situ chemical reactions and the shelf-ageing behaviors of QLEDs inspire the design of bi-layered oxide ETLs consisting of optical ZnO and conductive ZnO, which delivers both improved electrical conductivity and suppressed interfacial exciton quenching. This material innovation enables shelf-stable, high-efficiency, and long operational lifetime red QLEDs, exhibiting neglectable changes of EQE (>20.0%) and long lifetime (T_{95}: 5500 h at 1000 nits) after storage for 180 days (Fig. 3).

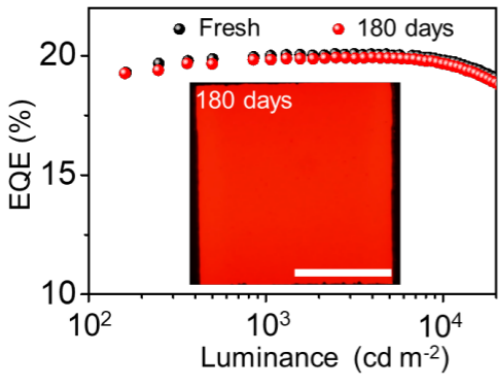


Fig.3 The corresponding EQE-L relationships of a fresh device and a device shelf-aged for 180 days. Inset of an electroluminescence image of a device shelf-aged for 180 days. Scale bar: 1 mm.[8]

3 Discussion

To date, the operational lifetime of blue QLEDs is still inferior to those of the state-of-the-art green and red QLEDs. Based on our research experience on the red QLEDs, we suggest that high-performance blue QLEDs can be achieved by further work on crystal engineering and surface engineering of blue QDs, surface chemistry of CTLs guided by in-depth device physics studies.

4 Conclusions

We have achieved progress in operational mechanism, material chemistry of QDs and charge-transporting layers and device engineering of QLEDs. Combining the considerable advances already made and the excellent properties of QDs, we believe that QLEDs offer unique advantages for future display and lighting applications.

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