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Solution-processed fabrication of highly transparent mono- and tri-colored quantum dot-light-emitting diodes

Chang-Yeol Han [a], Ki-Heon Lee [a], Min-Seok Kim [a], Jong-Woo Shin [a], Jin Soo Kim [a], Jin-Ha Hwang [a], Taesik Kim [b], Min Suk Oh [c], Jiwan Kim [d], Young Rag Do [e], Heesun Yang [a, *]

[a] Department of Materials Science and Engineering, Hongik University, Seoul 121-791, Republic of Korea
[b] Department of Civil Engineering, Hongik University, Seoul 121-791, Republic of Korea
[c] Display Materials and Components Research Center, Korea Electronics Technology Institute (KETI), Seongnam-si, Gyeonggi-do 463-816, Republic of Korea
[d] Department of Advanced Materials Engineering, Kyonggi University, Suwon-si, Gyeonggi-do 16227, Republic of Korea
[e] Department of Chemistry, Kookmin University, Seoul 136-702, Republic of Korea

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ABSTRACT

Analogous to organic light-emitting diode (OLED), quantum dot-light-emitting diode (QLED) possesses a high eligibility with respect to device structure for the transformation to transparent device that may be pursued as a next-generation display. We report the fabrication of a series of highly transparent mono-colored blue, green, and red QLEDs with a standard architecture simply by replacing thermally evaporated Al with sputtered indium tin oxide (ITO) film as a top cathode. To alleviate the sputtering damage on the underlying electron transport layer while securing a reasonable sheet resistance of ITO film, a moderate sputtering power is judiciously chosen to attain high device performance. Fabrication of a transparent tri-colored white or full-color-capable QLED, comprising an emitting layer mixed with three primary colored QDs, is also demonstrated and further implemented on a flexible substrate of polyethylene naphthalate to additionally offer its feasibility toward transparent flexible device.

1. Introduction

Taking full advantage of nearly ideal fluorescent features of semiconductor quantum dots (QDs) including facile emission tunability, high photoluminescent (PL) quantum yield (QY), and exceptional emission color purity, a great deal of work on optically-pumped and electrically-driven QD-based light-emitting diodes (LEDs) has been implemented, primarily aiming at display and lighting industry. In particular, electrically-driven or electroluminescent (EL) QD-LED (QLED), whose device architecture is similar to that of an organic LED (OLED), has progressed sharply for last decade. This was mainly enabled by the adoption of hybrid charge transport layers (CTLs) of organic hole transport layer (HTL) and inorganic electron transport layer (ETL) [1–14] along with the advanced engineering of QD core/shell heterostructure [9–14]. For instance, ~20% of external quantum efficiency (EQE), corresponding to a theoretical limit and also matching the best efficiency of *state-of-the-art* OLED, could be realized from standard- [7] and inverted-structured red QLEDs [4], where charge injections were optimally balanced.

Visible transparency along with flexibility may be a key requirement in the next-generation displays. Analogous to OLED, QLED is also eligible with respect to device structure for the realization of a high degree of transparency. In opaque OLEDs and QLEDs, indium tin oxide (ITO) and metal (*e.g.*, Al, Ag) are the most common electrode combination as anode and cathode (for standard structure) and *vice versa* (for inverted one), respectively. Meanwhile, Ag nanowire (Ag NW) [15,16] and graphene [17,18] have emerged as transparent electrodes alternative to ITO and been applied to the fabrication of non-transparent OLEDs consisting of Al as the other side electrode [16–18]. Processing difficulty in generating patterned electrodes of Ag NW and graphene without damage on the underlying organic layers constrains their use as a top electrode for fully transparent devices. For such a reason, the fabrication of transparent OLEDs have been implemented by introducing thin metals [19,20] or transparent conductive oxides (TCOs) [21–23] as a top electrode. Thermal deposition of metallic film can give little damage on the underlying layer, but the presence of metal top electrode of the resulting OLED inevitably leads to a

* Corresponding author.
E-mail address: hyang@hongik.ac.kr (H. Yang).

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limited transmittance, necessitating additional strategies for the improvement of device transparency such as the introduction of capping layer [19] and oxide/metal composite electrode [20]. Meanwhile, sputter-deposition of TCO top electrode usually gives rise to a highly damaged organic underlayer, substantially deteriorating OLED performance. To address this issue, therefore, organic and inorganic buffer films have been applied as a protection layer prior to TCO sputtering [21–23].

In the initial version of transparent QLED, thermally evaporated Ag film was applied as a top cathode, only showing a semi-transparency with a maximum transmittance of ~45% [24]. Later, a better transmittance of ~60% from all-solution-processed QLED was achievable by spin-depositing Ag NW film as a top cathode [25]. A fully transparent QLED based on transparent Au NP- and Ag NW-graphene composite electrodes was also devised, exhibiting high transmittances of 70–80% but poor EL performances of 358 cd/m^2 in luminance and 0.45 cd/A in current efficiency at best [26]. In standard-structured QLED with hybrid CTLs, the top electrode is formed on top of ETL mostly comprising *n*-type metal oxide (*e.g.*, ZnO or ZrO_2) nanoparticle (NP) layer. Considering the inorganic nature of such an ETL that is likely more resistant against sputtering process compared to organic counterpart, the fabrication of transparent device with a sputtered TCO as a top electrode would be more viable from QLED relative to OLED. Recently, the fabrication of highly transparent red QLEDs with transmittances of 70–74% was attempted through sputter-deposition of TCOs such as ITO and indium zinc oxide (IZO) as top electrodes [27,28]. In particular, one of the above transparent red devices, where the thickness of ZnO NP ETL was optimized toward a thicker direction in order to minimize the ETL damage during the sputtering of ITO top cathode, possessed a moderately high EQE up to 5% [27]. Herein, we explore the fabrication of a series of highly transparent mono-(blue, green, and red) and tri-colored (white or full-color) QLEDs with a standard device architecture, *i.e.*, ITO anode/hole injection layer (HIL)/organic HTL/QD emitting layer (EML)/metal oxide NP ETL/ITO cathode. For the deposition of ITO top cathode an experimentally optimal sputtering power of 150 W is chosen, considering the trade-off between the sheet resistance of ITO film *versus* the sputtering damage on ETL underlayer. All the resulting QLEDs exhibit not only excellent visible transmittances of 75–78% at 550 nm but high device efficiencies of 5–7.4% in maximum EQE, depending on the type of device by color.

2. Experimental details

2.1. Synthesis of blue, green, red QDs and ZnO NPs

Colloidal blue CdZnS/ZnS, green CdZnSeS/ZnS, and red CdSeS/ZnS core/shell QDs for EML formation were synthesized according to our previously reported methods [8,9,13] and a highly transparent ZnO NP dispersion in ethanol for ETL formation were also prepared the recipe in literature [9,13]. Detailed synthetic recipes of QDs and NPs can be also found in Supplementary data.

2.2. Fabrication of transparent mono- and tri-colored QLEDs

All the mono- and tri-colored QLEDs were fabricated *via* all-solution processing with the identical conditions. Onto a patterned ITO glass substrate which was cleaned sequentially with acetone and methanol by sonication and then treated with UV-ozone for 20 min, an HIL of poly(ethylenedioxy thiophene):polystyrene sulphonate (PEDOT:PSS, AI 4083) was spin-deposited at 3000 rpm for 60s and then baked at 140 °C for 30 min. 0.05 g of poly(9-vinylcarbazole) (PVK) dissolved in 5 mL of chlorobenzene was spin-casted on an HIL and then baked at 140 °C for 30 min. On top of PVK HTL the respective mono-colored QD EMLs were spin-deposited as follows; 23 mg/mL of blue QD hexane solution at 2000 rpm for 20 s, 16 mg/mL of green QD hexane solution at 3000 rpm for 20 s, 43 mg/mL of red QD hexane solution at 3000 rpm for 20 s. For the formation of tri-colored QD-mixed EML, 0.75, 0.5, and 0.6 mL of the above blue, green, and red QD coating solutions, respectively, were taken and blended and the resulting QD mixture solution was spin-coated at 2000 rpm for 20 s, followed by drying at room temperature. Subsequently, ZnO NPs dispersed in ethanol with a concentration of ~30 mg/mL were spin-deposited at 3000 rpm for 60 s. Finally, transparent multilayered QLED fabrication was completed by depositing 100 nm thick ITO cathode through a metal mask by a radio frequency (RF) magnetron sputtering with 150 W power for 750 s.

2.3. Characterization

PL QYs of QDs were assessed by an absolute PL QY measurement system (C9920-02, Hamamatsu) in an integrating sphere. Particle transmission electron microscopic (TEM) image of blue, green, and red QDs and cross-sectional TEM image of a transparent tri-colored QLED were collected using a JEOL JEM-2100F electron microscope operated at an accelerating voltage of 200 kV. The chemical compositions of QDs were analyzed by an energy dispersive spectrometer (EDS)-equipped with scanning electron microscope (SEM, JEOL-7800F) operating at 15 kV. The sheet resistance of ITO cathode film deposited on glass substrate was estimated by a 4-point probe system (CMT-SR 1000N, Advanced Instrument Technology). Transmittances of transparent mono- and tri-colored QLEDs were measured with a UV–visible spectroscopy (Shimadzu, UV-2450). EL spectra and luminance–current density–voltage characteristics of transparent QLEDs were recorded with a Konica-Minolta CS-2000 spectroradiometer coupled with a Keithley 2400 voltage and current source under ambient conditions.

3. Results and discussion

Highly transparent QLEDs with a stacking sequence of anode/HIL/HTL/EML/ETL/cathode were fabricated *via* all-solution processing except for ITO anode and cathode deposited by RF magnetron sputtering. Three blue CdZnS/ZnS, green CdZnSeS/ZnS, and red CdSeS/ZnS QD emitters with the respective peak wavelengths of 447, 525, and 603 nm (Fig. S1) used for device fabrication exhibited high-quality fluorescent features such as PL QYs of 84, 76, and 75% and PL bandwidths of 19, 20, and 32 nm, respectively. The average sizes of blue, green, and red QDs were measured by TEM images (Fig. S2) to be 11.2, 12.2, and 8.4 nm, respectively, and the chemical compositions of the respective QDs were also analyzed by an EDS (Fig. S3) and summarized in Table S1. By only varying the type of QD EML within the identical device structure, a full series of highly transparent blue, green, red and tri-colored QLEDs were demonstrated (Fig. 1(a)). Fig. 1(b) shows a representative cross-sectional TEM image of a multilayered tri-colored QLED, which comprises 150 nm ITO anode/28 nm PEDOT:PSS HIL/22 nm PVK HTL/35 nm QD EML/30 nm ZnO NP ETL/100 nm ITO cathode.

A sputtering power is one of the key deposition parameters in determining the qualities of ITO thin film, generally requiring a high power for its high transmittance and low sheet resistance. When ITO film is deposited as a cathode of the present QLED structure, however, its sputtering power should be limited, since an inappropriately high power usually accompanies a sputtering damage on the underlying ZnO NP ETL, consequently deteriorating the device performance. Considering this aspect, we have chosen an experimentally optimized sputtering power of 150 W. The sheet resistance of sputter-deposited ITO film at 150 W (which is used as