Highly efficient electroluminescence devices with a mixed layer of SnO₂ and colloidal quantum dots

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ABSTRACT
We demonstrate the high efficiency of quantum dot light-emitting diodes (QLEDs) that consist of a mixed layer of SnO₂ nanoparticles (NPs) and quantum dots (QDs). A stable mixture of SnO₂ NPs and QDs is prepared in chlorobenzene and then applied to QLEDs with no separate electron transport layer (ETL). QLEDs with such a simplified structure produce a maximum luminance of 142,855 cd/m², an EQE of 9.42%, and a current efficiency of 41.18 cd/A that result from the improved charge balance of the mixed layer. This produces one of the best device performances of QLEDs with a non-ZnO inorganic ETL, clearly indicating the remarkable promise of using SnO₂ NPs as an inorganic ETL for QLEDs. Moreover, the reduction of fabrication steps in this solution-based process proves advantageous to next-generation display technology.

1. Introduction
Depending on their size and composition, colloidal quantum dots (QDs) exhibit outstanding properties such as excellent color purity and tunable emission wavelength [1–3]. Therefore, QDs have emerged as the leading next-generation semiconductor emitters in the field of display and lighting. In particular, electrically driven quantum dots light-emitting diodes (QLEDs) are considered the future of display technology owing to their two outstanding characteristics, namely high electroluminescence (EL) and low-cost fabrication that use solution processes. Since the first report on QLEDs in 1994 [4], the performance of QLEDs has been considerably improved with the use of optimized core/shell structures and various charge transport layers. Recently, all red, green, and blue QLEDs with external quantum efficiencies (EQEs) above 20% have been reported [5,6].

The introduction of ZnO nanoparticles (NPs) as the electron transport layer (ETL) constituted a major breakthrough in QLED technology, tremendously improving the brightness and current efficiency of the device. ZnO-based NPs have the superior advantages of (a) coating stability, (b) solution processability, and (c) suitable energy levels for efficient transport of electrons to the emitting layer (EML) [7–9]. For them to compete with organic light-emitting diodes, however, they need to address such issues as the rapid aggregation of ZnO NPs in various organic solvents at room temperature and the inevitable orthogonal process required by multi-layered structures to protect their underlying layers [10,11].

SnO₂ is a promising alternative to ZnO because of its proper band alignment with the QD EML and has a similar electron mobility to ZnO, as well as high chemical stability [12,13]. Still, even though SnO₂ has been intensively studied as one of the most promising ETLs for solar cells, only a limited number of studies on EL devices with SnO₂ as the ETL have been reported. Liu et al have reported a luminance of 12,846 cd/m² and a current efficiency of 11.8 cd/A for QLEDs integrated with SnO₂-based ETL [14]. Likewise, Park et al have reported the improved performance of QLEDs with SnO₂ NPs in terms of lower turn-on voltage and brighter luminance [12]. Both of these findings demonstrate that ZnO-based NPs are highly versatile and easy to synthesize [15–17].

In the present work, we fabricate highly efficient QLEDs with a mixed layer of SnO₂ and QDs (m-QLEDs)
instead of the conventional multi-layered QLEDs (c-QLEDs). Initially, SnO₂ NPs are synthesized by the sol–gel method, and their structural, electrical, and optical properties are investigated. Subsequently, the simplified m-QLEDs are fabricated, and we compared their performance with those of c-QLEDs that use SnO₂ as the ETL. Because unexpected phase separation or non-uniform morphology was observed in the fabricated devices, very few studies have been undertaken on the use of a blended EML with a mixture of QDs and charge-transport materials [18,19].

The m-QLEDs exhibit a maximum luminance of 142,855 cd/m² and a current efficiency of 41.18 cd/A, which are comparable to those of the c-QLEDs with an inverted structure. The electrical and physical properties of the mixed layer were also investigated in detail to clarify the origin of the consistent device performance of m-QLEDs. To date, this is the highest luminance and efficiency reported for QLEDs with SnO₂ as the ETL. Moreover, as earlier mentioned in this report, the use of the mixed layer has proven advantageous for reducing the processing steps.

2. Experimental procedure

2.1. Synthesis of SnO₂ nanoparticles and green quantum dots

The SnO₂ NPs were prepared by the sol–gel method [20], With 5 mmol of tin tetrachloride penta-hydrate (SnCl₄·5H₂O) dissolved in 15 ml DI water. The solution was stirred for a few minutes and then the sodium carbonate (Na₂CO₃) solution was added in a dropwise manner. The mixed solution was stirred with a magnetic stirrer. After they were stirred for 1 h, the SnO₂ NPs were collected via centrifugation of the solution at 10,000 rpm and were dried over 70°C to remove impurities and water molecules. Finally, the collected SnO₂ NPs were redispersed using a solvent – ethanol (for c-QLEDs) and chlorobenzene (for m-QLEDs) – and filtered to remove impurities.

In the recent publication of Yang’s group, Green-emitting CdZnSeS/ZnS QDs were prepared by the synthesis procedure [21]. First, 0.14 mmol of Cd oxide and 3.41 mmol of Zn oxide were placed on 7 ml of oleic acid (OA) in a three-neck flask and the mixture was heated to 150°C with N₂ flowing. Then, 15 ml of 1-octadecene (ODE) was added and heated to 310°C. Subsequently, a Se + S stock solution – 2.2 mmol of Se and 2.2 mmol of S dissolved in 2.2 ml of trioctylphosphine (TOP) – was swiftly injected onto the mixture, and the reaction of composition-gradient CdZnSeS core was carried out at 310°C for 10 min. Then 1.6 mmol of S dissolved in 2.4 ml of ODE was introduced into the reactor, and the reaction was maintained for 12 min. For successive ZnS shelling, 2.86 mmol of Zn acetate dihydrate that was dissolved in 1 ml of OA and 4 ml of ODE was rapidly placed the above reactor, and the reaction was allowed at 270°C for 10 min. Then, 9.65 mmol of S dissolved in 5 ml was added dropwise, followed by the ZnS reaction at that same 270°C temperature for 20 min. The resulting green CdZnSeS/ZnS QDs was purified by centrifugation repeatedly with a solvent/non solvent combination. Then, for the formation of the EML, the purified QDs were redispersed in toluene (for c-QLEDs) or in chlorobenzene (for m-QLEDs).

2.2. Fabrication of QLEDs

The inverted QLEDs were fabricated on indium-tin-oxide (ITO) coated glass substrates, which were then sequentially cleaned with isopropyl alcohol and then rinsed with deionized water. After this, the patterned ITO substrates were treated in ultraviolet-ozone for 15 min. For the c-QLEDs, SnO₂ NPs were spin-coated onto an ITO substrate as the ETL at 1000 RPM for 60 s. For the fabrication of EML, QDs dispersion was spin-cast on top of ITO/SnO₂ substrates at a spin-rate of 2000 RPM for 10 s. For the m-QLEDs, a mixed solution of SnO₂ NPs and QDs was prepared in chlorobenzene, which was then deposited on ITO substrates by spin-casting at a spin-rate of 700 RPM for 60 s. The organic materials and metals were continually deposited by thermal evaporation without breaking the vacuum. For the hole transport layer, 4,4’-bis (carbazol-9-yl) biphenyl (CBP), MoO₃, and Al were thermally evaporated with a deposition rate of ∼ 1 Å/s for CBP, ∼ 0.5 Å/s for MoO₃, and ∼ 3 Å/s for Al electrode.

2.3. Characterization

The current density–voltage-luminance (J–V–L) characteristics of the QLED devices were measured by using a spectroradiometer (CS2000, Konica Minolta) with a Keithley 2400 source meter under ambient conditions. From these J–V–L measurements, the changes in the luminance and current efficiency of the devices as a function of the applied voltage were systematically studied. The high-resolution transmission electron microscopy (TEM) was used to measure the particle sizes of SnO₂ NPs and QDs (JEM-2100F, JEOL). The crystal phase of pristine and SnO₂ NPs was analyzed using an X-ray diffractometer (XRD, MiniFlex2, Rigaku). The surface roughness was measured by atomic force
microscopy (AFM, XE-100, PSIA). The electronic structures of SnO$_2$ NPs were investigated by ultraviolet photoelectron spectroscopy (UPS, ESCALAB 250, Thermo Scientific).

3. Results and discussion

The XRD pattern in Figure 1(a) shows peaks corresponding to the tetragonal structure of cassiterite. The broadening of the characteristic bulk SnO$_2$’s diffraction peaks can be attributed to the absence of high-temperature annealing. The TEM image of the synthesized SnO$_2$ NPs is shown in Figure 1(b). The small particles observed in the image are nearly spherical, with a diameter averaging approximately 5 nm. Figure 1(c) shows the plot of $(\alpha h\nu)^2$ vs. $h\nu$ (photon energy), where $\alpha$ is the absorbance, obtained from the absorption spectrum of SnO$_2$. The bandgap ($E_g$), as determined from the onset of absorption in the linear region, is 3.9 eV.

Figure 2(a) shows the cross-sectional TEM image of the simplified m-QLEDs, which consist of ITO/SnO$_2$ + QDs (60 nm)/CBP (100 nm)/MoO$_3$ (10 nm)/Al (80 nm). Employed as the EML of the QLEDs were highly efficient green CdZnSeS/ZnS QDs of average size of 12.0 nm, emission peak wavelength of 518, and full-width-at-half-maximum of 21 nm (Figure S1). For the m-QLEDs with inverted structure, a stable mixture of SnO$_2$ as the ETL and QDs as the EML was prepared in chlorobenzene and was applied directly to cleaned ITO glasses. As shown in Figure 2(a), the mixed layer appears as a stable single layer in the device. As shown in Figure S2, a mixture in chlorobenzene is transparent without any aggregation at room temperature, and only a slight decrease was observed in its transmittance. The energy band diagram of the m-QLEDs is shown in Figure 2(b). The electronic structure of SnO$_2$ was investigated by UPS; and the secondary electron cut-off and valence-band region spectra are shown in Figure S3.

Using the $E_g$ value obtained from Figure 1(c), the valence band maximum (VBM) position of the SnO$_2$ was calculated to be 8.0 eV below the vacuum level, and the conduction band minimum (CBM) level was estimated to be 4.1 eV below the vacuum level. The similar CBM levels of SnO$_2$ to QDs allows for the smooth electron transport from ITO through the mixed layer, while the deep VBM level of SnO$_2$ leads to the effective hole blocking in the mixed layer. Reducing one layer in the multilayered structure is highly beneficial as it eliminates the heterogenous boundary of the ETL/EML interface and decreases the number of carriers piling up near the interface. As shown in Figure 2(c), there is no difference in the shape and peak position of EL peaks from m-QLEDs and c-QLEDs.

Figure 3 shows the voltage-dependent variations in the luminance, current density, and current efficiency of m- and c-QLEDs. With SnO$_2$ as the ETL, the c-QLEDs exhibit a peak luminance of 143,770 cd/m$^2$, a current efficiency of 36.0 cd/A, and an EQE of 8.33%. These values are superior to those of previously reported QLEDs employing non-ZnO-based inorganic materials as the ETL, and they are comparable to those of QLEDs with a ZnO ETL [12,14]. More importantly, the device performance of m-QLEDs is similar to that of c-QLEDs.
peak luminance of 142,855 cd/m², the maximum current efficiency of 41.18 cd/A, and EQE of 9.42%. The stable performance of the m-QLEDs is attributed to the formation of a cascade VBM alignment that efficiently transports holes into the mixed layer, as shown in Figure 2(b). The injection of holes is less efficient because of the large energy gap between the highest occupied molecular orbital of CBP and the VBM of SnO₂; however, the QDs in the mixed layer facilitate the transport of holes.

Therefore, the injection of holes can be disrupted when the concentration of QDs in the mixed layer is low. As a result, the m-QLEDs with a low concentration of QDs (10 mg/ml) present a low current density over the entire voltage range, degrading the device performance. It is to be noted that the peak efficiency of the m-QLEDs is achieved at a high brightness (over 70,000 cd/m²), which is desirable for practical display applications.

To allow for a detailed investigation of the hole injection to the EML, hole-only devices (HODs) were fabricated that have different concentration of QDs in the...
mixed layer. Their current densities were investigated, and the results are shown in Figure 4. As shown in Figure S4, the electrical characteristic of m-HOD is well matched with that of c-HOD. Since there was no notable difference in the current density–voltage curve after the mixing of the QDs and SnO\textsubscript{2} NPs, the higher concentration of QDs was applied to improve the hole injection to the mixed layer. The current density of the m-HODs with the higher concentration of QDs is higher than that of m-HODs with the lower concentration in the entire voltage range. We assume that packed QDs with higher concentration in the mixed layer become beneficial for the effective control of the hole injection.

The superior performance of m-QLEDs is also due to the suppression of exciton quenching. Figure S5 shows the changes of PL spectra after 4 days of three samples with structures of glass/QDs, glass/SnO\textsubscript{2}/QDs, and glass/SnO\textsubscript{2} + QDs. The PL intensity of QDs drops significantly when they are deposited on SnO\textsubscript{2} NPs. However, by mixing with SnO\textsubscript{2}, the decrease in the PL intensity is reduced, which indicates that the quenching process has been effectively suppressed. Therefore, the m-QLEDs exhibit an excellent lifetime, with the predicted T\textsubscript{50} of 700 h at 100 cd/m\textsuperscript{2} based on the T\textsubscript{50} at 1000 cd/m\textsuperscript{2} with an acceleration factor of 2.0 in Figure S6.

Figure 5 shows the morphologies of the mixed (QDs + SnO\textsubscript{2}) layers and conventional (QDs on SnO\textsubscript{2}) layers that were obtained by atomic force microscopy. The values of their root mean square roughness (R\textsubscript{q}) are similar (mixed: 1.452 nm, conventional: 2.012 nm); however, as shown in Figure 5(a), some microscopic agglomerations are observed in the conventional layers. Surprisingly, the mixed layer’s maximum profile peak height (R\textsubscript{p}) is much smaller than that of the conventional layer. Therefore, the mixed layer is considered to be capable of forming a more homogeneously blended layer. It is well known that a stable interface in the QLEDs is necessary to achieve outstanding device performance. The m-QLEDs show no phase separation or rugged interface that can disturb the efficient charge transport, as shown in Figures 2(a) and 5(b).

4. Conclusion

In summary, SnO\textsubscript{2} NPs that were synthesized under ambient conditions were successfully mixed with QDs to obtain highly efficient QLEDs. The m-QLEDs with a
homogeneous blended layer showed a maximum luminance of 142,855 cd/m² and a current efficiency of 41.18 cd/A, which constitutes one of the best performance of devices reported till date for QLEDs with non-ZnO inorganic ETLs. These results were achieved by optimizing the concentration of QDs to improve the charge balance in the mixed layer. Thus, SnO₂ NPs can be considered as an alternative inorganic ETL material for the fabrication of high-performance QLEDs. Moreover, m-QLEDs have a significant advantage over c-QLEDs in the solution-based fabrication process because the mixed layer of ETL and QDs can reduce the fabrication step in the inevitable orthogonal process.

Disclosure statement
No potential conflict of interest was reported by the author(s).

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