Electronic Supplementary Information (ESI)

Full-color-capable light-emitting diode based on solutionprocessed quantum dot layer stacking

Ki-Heon Lee,^{a‡} Chang-Yeol Han,^{a‡} Eun-Pyo Jang,^a Jung-Ho Jo,^a Seungki Hong,^b Jun Yeon Hwang,^b Eunsoo Choi,^c Jin-Ha Hwang^a and Heesun Yang^{*a}

 ^a Department of Materials Science and Engineering, Hongik University, Seoul 04066, Republic of Korea. Email: hyang@hongik.ac.kr
^b Institute of Advanced Composites Materials, Korea Institute of Science and Technology (KIST), Jeonbuk
55324, Republic of Korea

^c Department of Civil Engineering, Hongik University, Seoul 04066, Republic of Korea.

Synthesis of blue, green, and red QDs

In a typical synthesis of blue CdZnS/ZnS QDs, a mixture of 1 mmol of CdO, 10 mmol of ZnO, and 7 ml of oleic acid (OA) were placed in a three-neck flask and heated to 150°C with N₂ flowing. And 15 ml of 1-octadecene (ODE) was added to the above mixture and the temperature was elevated to 310°C. Then, the S-ODE solution of 1.6 mmol of S dissolved in 2.4 ml of ODE was injected into the hot mixture and the reaction temperature was kept at 310°C for 12 min for CdZnS core QD growth. For successive overcoating of thick ZnS shell, a S-OA solution containing 8 mmol of S in 5 ml of OA was added in a dropwise manner into the above hot core growth solution and the reaction was maintained at 310°C for 8 h. In a typical preparation of green CdZnSeS/ZnS QDs, a mixture of 0.14mmol of Cd acetate, 3.41 mmol of Zn oxide, and 7 ml of OA was heated to 150°C with N2 flowing. After 15 ml of ODE was added to this mixture, its temperature was elevated to 310°C. Then, a stock solution prepared by 2.2 mmol of Se and 2.2 mmol of S dissolved in 2.2 ml of trioctylphosphine (TOP) was swiftly injected to the above cationic mixture and the reaction proceeded at 310°C for 10 min, yielding CdZnSeS core QDs. Subsequently, a S-ODE solution of 1.6 mmol of S dissolved in 2.4 ml of ODE was injected into CdZnSeS core QD growth solution and the reaction was kept at 310°C for 12 min. Next, 2.86 mmol of Zn acetate dihydrate dissolved in 4 ml of OA and 1 ml of ODE was injected and the reaction temperature was lowered to 270°C. At this temperature, a stock solution containing 9.65 mmol of S dissolved in 5 ml of TOP was dropwisely (~0.5 ml/min) introduced and the reaction was maintained for 20 min for ZnS overcoating. In the case of synthesis of red CdSeS/ZnS QDs, a mixture of 1.1 mmol of Cd acetate and 5 ml of OA was heated to 150°C with N2 flowing, and then 15 ml of ODE was added to the reactor. After the reaction mixture was elevated to 310°C, (Se+S)-TOP solution consisting of 0.27 mmol of Se and 0.03 mmol of S in 0.3 ml of TOP was swiftly injected into the reaction flask. Then, this reaction was held for 90 s at that temperature and the addition of 1.7 mmol of 1-octanethiol was followed, yielding CdSeS core QDs. For the consecutive ZnS shelling, a Zn stock solution containing 2.86 mmol of Zn acetate dihydrate in 4 ml of OA and 1 ml of ODE was first added and then S-TOP solution containing 6.75 mmol of S in 3.5 ml of TOP was injected. This shelling reaction proceeded at 270°C for 10 min. As-synthesized blue, green, and red QDs were precipitated by adding excess nonsolvent (e.g., acetone or ethanol), thoroughly purified via centrifugation-based repeated

precipitation/redissolution using a solvent/nonsolvent (*e.g.*, hexane/acetone or hexane/ethanol) combination, and finally redispersed in hexane for characterization and device fabrication.

Synthesis of ZnO NPs

In a typical synthesis of colloidally stable ZnO NPs, 5 mmol of Zn acetate dihydrate was mixed with 30 ml of dimethyl sulfoxide (DMSO). To this mixture was added 5 mmol of tetramethylammonium hydroxide (TMAH) dissolved in 10 ml of ethanol. Then, the reaction proceeded in an ice bath at ~4°C for 1 h. The resulting ZnO NPs were precipitated by adding excess acetone and clearly redispersed in ethanol.

Fabrication of full-color QLED with stacked B/G/R QD EMLs

First, a wind-mill-patterned ITO glass substrate (with typical sheet resistance of 25 Ω sq⁻¹) was ultrasonic-cleaned sequentially with DI water, acetone, and methanol for 10 min each, and then treated in UV-ozone cleaner for 20 min. Then, 30 nm-thick PEDOT:PSS (AI 4083) as an HIL was spin-casted (3,000 rpm, 60 s) and baked at 150°C for 30 min. Using a solution of 0.05 g of PVK (average MW=25,000-50,000) dissolved in 5 ml of chlorobenzene and applying the same spin-coating and baking conditions as in the above HIL, 20 nm-thick HTL was formed on top of PEDOT:PSS. For the formation of multi-EMLs with a stacking sequence of B/G/R, B-, G-, and R-QD stock solutions (dispersed in hexane) having the respective optimized concentrations of 19, 10, and 31 mg/ml were prepared beforehand. On top of PVK the first B-QD layer was generated by spin-coating and the following buffer layer with a thickness of ca. 3 nm was successively spin-deposited using a dilute ZnO NP ethanol solution with concentration of ~5 mg/ml. Next, the second G-QD layer, ZnO NP buffer, and the third R-QD layer were sequentially stacked. The spin coating conditions for three B-, G-, and R-Q layers and two identical ZnO NP buffer layers were identically 5,000 rpm and 20 s. The respective QD layers and buffers were dried at 60°C after spin-deposition. And then on top of the third R-QD layer 25 nm-thick ETL was deposited by spin-casting ZnO NP ethanol dispersion with a concentration of ~30 mg/ml, followed by drying at 60°C. All deposition procedures from HIL to ETL were conducted in N₂-filled glovebox. Finally, the QLED fabrication was completed by thermally evaporating a 100 nm-thick Al cathode with a deposition rate of \sim 5 Å/s.

Characterization

Absorption and PL spectra of QDs were collected by a UV-visible spectroscopy (Shimadzu, UV-2450) and a 500 W xenon lamp-equipped spectrophotometer (PSI Inc., Darsa Pro-5200). PL QYs of QDs were assessed by an absolute PL QY measurement system (Hamamatsu, C9920-02) in an integrating sphere. The surface roughness of QD layer and QD layer/buffer was analyzed using an AFM (Veeco instruments Inc., Innova). The thicknesses of constituent films such as QD layer and buffer layer were measured by a profilometer (Bruker's DEKTAK-XT Stylus Profiler). To determine the VBM levels of blue, green, and red QD layers, UPS (Thermo Fisher Scientific, ESCALAB 250Xi) work was performed by utilizing a He I photon (21.2 eV) source. For UPS measurements, 40~50 nm-thick QD layers spindeposited on ITO glass substrate were prepared. The UPS spectra were referenced to and aligned at the Fermi level of the system determined by the measurement on Au reference. The VBM level was estimated by using the incident photon energy, the high-binding energy cutoff (E_{cutoff}), and the onset energy in valence-band region (E_{onset}) according to the equation of VBM = $21.2 - (E_{cutoff} - E_{onset})$. And then, the CBM levels were obtained by combining the VBM values and optical band gaps from absorption spectra. Cross-sectional TEM and corresponding EDS compositional mapping images of a multilayered full-color QLED were collected by a Tecnai G2 F20 operating at 200 kV. EL spectra, CIE color coordinates, and luminance-current density-voltage characteristics of QLEDs were recorded with a Konica-Minolta CS-2000 spectroradiometer coupled with a Keithley 2400 voltage-current source unit.

| QD sample | Secondary cut-off (eV) | Fermi level (eV) | Valence band onset (eV) | Valence band maximum (eV) | Band gap (eV) | Conduction band minimum (eV) |
|--------------|------------------------------|------------------------|-------------------------------|---------------------------------|------------------|------------------------------------|
| Blue | 18.14 | 3.06 | 3.27 | 6.33 | 2.79 | 3.54 |
| Green | 18.05 | 3.15 | 3.04 | 6.19 | 2.36 | 3.83 |
| Red | 17.94 | 3.26 | 2.85 | 6.1 | 2.06 | 4.04 |

Table S1 Energetic information on blue, green, and red QD films obtained from UPS and absorption spectra.



Fig. S1 (a) Absorption/PL spectra and (b) TEM images of blue, green, and red QDs.



Fig. S2 Surface profiles of blue QD films (a) without and (b) with ZnO NP overlayer.



Fig. S3 AFM results of height (left) and three-dimensional images (right) of blue QD films (a) without and (b) with ZnO NP overlayer.



Fig. S4 Comparison of EL spectra of green/red bicolored QLEDs (a) without and (b) with buffer layer as a function of applied voltage.



Fig. S5 PL spectra of stacked B/G/R QD layers without and with ZnO NP buffer layers.



Fig. S6 (a) Energy band diagram of B/G/R QD layer-stacked multilayered QLED. UPS spectra showing (b) high-binding energy secondary cutoff and (c) valence-band edge regions of blue, green, and red QD layers.



Fig. S7 Current efficiency and EQE as a function of current density of multilayered QLED (linear scale expression of Fig. 4f).