Electronic Supplementary Information (ESI)

High-Performance Tricolored White Lighting Electroluminescent Devices Integrated with Environmentally Benign Quantum Dots

Chang-Yeol Han, Suk-Young Yoon, Sun-Hyoung Lee, Seung-Won Song, Dae-Yeon Jo, Jung-Ho Jo, Hyun-Min Kim, Hyun-Sik Kim* and Heesun Yang*

Department of Materials Science and Engineering, Hongik University, Seoul 04066, Korea

*Corresponding Author E-mail: hyunsik.kim@hongik.ac.kr; hyang@hongik.ac.kr

Experimental Section

Synthesis of blue and green ZnSeTe and red ZCIS core/shell QDs.

Both blue- and green-emitting multi-shelled ZnSeTe/ZnSe/ZnSeS/ZnS QDs were synthesized in the following same manner except for Te/Se feed ratio (0.0235 for blue and 0.2352 for green) and growth temperature (300°C for blue and 270°C for green). As anionic precursor solutions, Se stock solutions (2 mmol of Se dissolved in 1 ml of diphenylphosphine (DPP)) and a Te stock solution (0.235 mmol (for blue) and 1.176 mmol (for green) of Te dissolved in 5 ml of trioctylphosphine (TOP)) were prepared in advance. In a typical synthesis of ZnSeTe cores, 2 mmol of Zn acetate dissolved in 2 ml of oleic acid (OA) and 15 ml of 1-octadecene (ODE) were placed in a three-neck flask. In the course of degassing this mixture was heated up to 120°C and held at that temperature for 1 h. Then, the reaction temperature was further elevated to 210°C under N₂ purging. At 210°C 0.5 ml of Se-DPP and 0.5 ml (for blue) versus 1 ml (for green ZnSeTe cores) of Te-TOP were co-injected into the reactor and the reaction was held at 210°C for 30 min. For full growth of cores, the reaction temperature was further elevated to 300 and 270°C for blue and green ZnSeTe cores, respectively, followed by the same growth time of 1 h at the respective temperatures. To consecutively generate ZnSe inner shell a Zn stock solution (3 mmol of Zn acetate dissolved in 2 ml of OA and 1.2 ml of ODE) and a Se stock solution (1.265 mmol of Se dissolved in 1 m of TOP) were slowly introduced to the ZnSeTe core growth solution. After that, ZnSeS intermediate shell was formed by adding 3.2 ml of the above Zn stock solution and an anionic mixture containing 0.6325 mmol of Se and 0.625 mmol of S in 1 ml of TOP. Then, 3.2 ml of the Zn stock solution and 1.25 mmol of S dissolved in 1 ml of TOP were injected into the flask for the ZnS outer shelling.

The above multishelling processes were carried out at fixed temperatures of 300 and 270°C for blue and green QDs, respectively, while the reaction time for each shelling step was fixed at 1 h. 2.63 mmol of Zn stearate with 5 ml of ODE was additionally injected to ensure the formation of thick ZnS shell, followed by 30 min of reaction time. Finally, 1 ml of 1-octanethiol was added, and the reaction was held at 230°C for 30 min.

For a typical synthesis of red-emitting ZCIS/ZnS core/shell QDs, 0.5 mmol of Zn chloride, 0.25 mmol of Cu iodide, 0.5 mmol of In acetate, and 1.1 mmol of S were mixed with 5 ml of oleylamine and 1.5 ml of 1-dodecanethiol (DDT) in a three-neck flask. The reactor was first heated up to 120°C while degassing. Then, the temperature of the mixture was further increased to 240°C under N₂ purging, and the target temperature was maintained for 5 min to grow ZCIS cores. To consecutively form ZnS shell on the ZCIS core, 8 mmol of Zn acetate dihydrate dissolved in 8 ml of OA, and 4 ml of ODE were put into the reactor with an injection speed of 1ml/min. The reaction was held at 240°C for 75 min. Subsequently, 4 mmol of Zn acetate dihydrate dissolved in 4 ml of OA, 2 ml of ODE, and 2 ml of DDT were introduced with the same injection speed. This ZnS shelling process proceeded at 240°C for 10 h. As-synthesized blue and green ZnSeTe/ZnSe/ZnSeS/ZnS and red ZCIS/ZnS QDs were repeatedly purified by centrifuging them with the combinations of hexane/acetone for the former two and hexane/ethanol for the latter. Then, these purified QDs were dispersed in hexane for characterization and EML formation.

Device fabrication.

A patterned ITO glass substrate was cleaned by sonication sequentially with acetone and methanol, and then UV-ozone-treated. An HIL of PEDOT:PSS (AI4083) was spin-casted at 3000 rpm for 30 s and baked at 150°C for 30 min. Using 10 mg/ml of PVK dissolved in chlorobenzene, an HTL was formed by the same spinning and baking conditions as in HIL. To fabricate an EML architecture of configuration I (for the configuration II, the stacking sequence of QD layers was reversed), a single ZCIS QD layer was first spin-deposited at 3000 rpm for 20 s and baked at 70°C for 10 min by using ZCIS QD dispersion with a concentration of 5 mg/ml. The same baking condition was applied to all the layers in QD EMLs. Subsequently, an ultrathin ZnMgO NP buffer layer was generated by spin-casting ZnMgO NPs dispersion (which was prepared according to ref. 27) in ethanol with a concentration of 5 mg/ml at 3000 rpm for 30 s. On top of ZnMgO NP buffer layer, blue and green ZnSeTe QDs-mixed solutions with three different blend ratios specified in Table 1 were spin-casted at 3000 rpm for 20 s. The following ETL was formed by spin-casting the ethanol dispersion of the same ZnMgO NPs as in the above buffer layer with a concentration of 30 mg/ml and drying it at room temperature. The whole spin-coating and baking processes from HIL throughout ETL were conducted in N₂-filled glove box. Finally, QLED fabrication was completed by thermally depositing a 100 nm-thick Al cathode.

Characterization.

Absorption and PL spectra of QDs were recorded by a UV-visible spectroscopy (Shimadzu, UV-2450) and a 500 W Xenon lamp-equipped PL spectrophotometer (Darsa Pro-

5200, PSI Inc.), respectively. PL QYs of QDs were measured with an absolute PL QY measurement system (QE-2000, Otsuka) equipped with an integrating hemisphere. TEM images of QDs and cross-sectional TEM image of multilayered QLED were obtained from JEM-2100F (JEOL Ltd.) and Tecnai G2 F20, respectively. The elemental compositions of blue, green ZnSeTe, and red ZCIS core QDs were assessed by an EDS (X-MAX 80, Oxford instruments)-equipped field emission-scanning electron microscope (JSM-7800F, JEOL) operating at 15 kV. PL decay profiles of QDs in the form of solid film were collected by a time-correlated single-photon counting method on a spectrophotometer (FS5, Edinburgh Instruments) with a picosecond pulsed laser diode (EPL-375), and fitted with a triexponential function with the parameters of amplitude (A) and decay time constant (τ), i.e., $f(t) = A_1 \exp(-\frac{1}{2} \exp($ t/τ_1 + $A_2 \exp(-t/\tau_2)$ + $A_3 \exp(-t/\tau_3)$. The surface roughness of QD layer versus QD layer/buffer was analyzed using an AFM (Veeco instruments Inc., Innova). XPS (Thermo VG) with Al Ka x-ray (E=1486.6 eV) was used to further verify the presence of ZnMgO NP buffer on top of QD layer. The VBM levels of blue and green ZnSeTe QDs were estimated by a UPS (AXIS Ultra DLD, Kratos Inc.) with a He I (21.2 eV) radiation source. The VBM levels of QDs were calculated by using the incident photon energy, high-binding energy cut-off (E_{cut} - $_{off}$), and the onset energy in the valence-band region (E_{onset}) according to the equation of VBM = $21.2 - (E_{cut-off} - E_{onset})$. The corresponding conduction band minimum (CBM) levels of QDs were determined by combining the above VBM results and optical band gaps obtained from their absorption spectra. EL spectra and luminance-current density-voltage characteristics of the QLEDs were recorded with a spectroradiometer (CS-2000, Konica Minolta) equipped with a voltage-current source unit (Keithley 2400).



Figure S1. EDS spectra and elemental compositions (right insets) of (a) blue, (b) green ZnSeTe, and (c) red ZCIS cores.



Figure S2. PL decay profiles of (a) blue, (b) green ZnSeTe, and (c) red ZCIS QDs in the forms of solid-state film.



Figure S3. TEM images of a series of (a) blue, (b) green, and (c) red QDs as a function of shelling stage. Average diameter and thickness values for each shell are specified in the images.



Figure S4. Device performances of monochromatic (a,b) blue, (c,d) green, and (e,f) red QLEDs; (a,c,e) luminance–current density characteristics as a function of voltage and (b,d,f) current efficiency–EQE characteristics as a function of current density.



Figure S5. PL spectra of three blue and green QDs-mixed solutions of blend A, B, and C used for device fabrication.



Figure S6. Spectral comparison of PL of blue ZnSeTe QDs and absorption of green ZnSeTe QDs, showing a substantial spectral overlap.



Figure S7. AFM results of height (left) and three-dimensional images (right) of blue and green QDs-mixed layer (a) without and (b) with ZnMgO NP buffer atop, showing room-mean-square roughness (R_{rms}) values of 2.4 and 1.9 nm, respectively.



Figure S8. High-resolution XPS scans of Mg 1s photoelectron signal of blue and green QDsmixed layer (a) without and (b) with ZnMgO NP buffer atop.



Figure S9. PL decay profiles of blue and green emission components measured from blue and green ZnSeTe QDs-mixed film.



Figure S10. Variations of (a) luminance-current density and (b) current efficiency-EQE as a function of voltage and current density, respectively, of blend B- and C-based bichromatic QLEDs. Voltage-dependent as-recorded EL spectra of (d) blend B- and (d) blend C-based bichromatic QLEDs.



Figure S11. UPS spectra of blue ZnSeTe QDs showing (a) secondary-electron cutoff and (b) valence-band edge regions and (c) their original and the second derivative absorption spectra.



Figure S12. UPS spectra of green ZnSeTe QDs showing (a) secondary-electron cutoff and (b) valence-band edge regions and (c) their original and the second derivative absorption spectra.



Figure S13. Comparison of current density–voltage characteristics of (a) EODs and (b) HODs with different EML configurations of I versus II. EODs and HODs consisted of ITO/ZnMgO NP ETL/QD EMLs/ZnMgO NP ETL/Al and ITO/PEDOT:PSS HIL/PVK HTL/QD EMLs/4,4'-Bis(N-carbazolyl)-1,1'-biphenyl (CBP) HTL/MoO_x HIL/Al, respectively. Note that CBP and MoO_x were thermally evaporated with rates of 1 and 0.2 Å/s, respectively.



Figure S14. Normalized EL spectra (relative to the blue emission) of blend A-, B-, and C-based white QLEDs collected at driving voltages corresponding to the respective peak luminances.



Figure S15. Lifetime result of blend C-based tricolored white QLED evaluated at an ambient condition under a constant current density of 1.9 mA/cm^2 at an initial luminance of 220 cd/m².

QD composition		PE	EQE	Luminance (cd/m ²)	ССТ	CRI	Ref.
		(lm/W)	(%)		(K)		
Cd- based	CdZnSeS	1.5	0.9	5340	5521-8642	92.8	16
	CdZnSeS		10.9	23352	6126-7719	95	17
	CdSe	3.9	5.0	3554	5029-8924	67	18
	CdZnSeS		6.8	16241			19
	CdZnSeS		23.88	65690		80	21
	CdSe	10.55	27.39	115000			22
	CdZnSeS	10.92	28.0	20320	3769-4926	75	23
Non- Cd- based	CuGaS	1.9	1.9	1007	7494-8234	88	24
	ZnCuGaS:Mn		4.2	1352			25
	ZnCuGaS, CuInS	5.4	4.6	2172	3995-6046	82	27
	ZnSeTe, ZnCuInS	8.4	5.8	5461	3866-4628	95	This work

Table S1. Comparison of device performances of white lighting QLEDs reported in literature with those from this work.