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Spectral broadening of Cu–In–Zn–S quantum dot color converters for high color rendering white lighting device

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ABSTRACT

We report the synthesis of quaternay Cu–In–Zn–S (CIZS) core/ZnS shell quantum dots (QDs) that possess the emission wavelengths suitable as color converters for white light-emitting diode (LED) fabrication. For the demonstration of high color rendering white QD-LEDs enabled by a more complete white spectral coverage, the synthetic effort on CIZS QDs exhibiting the photoluminescence (PL) as broad as possible is made. The amount of 1-dodecanethiol (DDT) used in CIZS core synthesis is found to critically affect the spectral shape and consequent bandwidth of QD emission. The QD PL is systematically, progressively broadened with increasing DDT amount, achieving an unprecedented bandwidth up to ~240 nm. The CIZS/ZnS QDs that are synthesized with different DDT amounts are indiviually tested as color converters for the fabrication of white QD-LEDs and thier performance is compared. The resulting devices exhibit color rendering index (CRI) values in the range of 74–95, depending on CIZS/ZnS QDs used. This exceptional CRI of 95 is a record quantitiy obtainable by use of a single QD color converter.

1. Introduction

I–III–VI chalcogenide quantum dots (QDs) with various multinary compositions including Cu–In–S (CIS) [1–12], Ag–In–S (AIS) [13], Cu–In–Zn–S (CIZS) [14–16], and Cu–In–Ga–S (CIGS) [17, 18] have gained appreciable attention owing to their useful optical properties suitable for the application to optoelectroinic devices. In particular, since the above QDs can possess a high photoluminescence (PL) efficiency, facile visible-emission tunabilitiy, and high absorption capability in the near UV-blue region, they have been strongly regarded as potential color converters in light-emitting diodes (LEDs) [19–28]. The charges photo-excited in those QDs recombine radiatively *via* intra-gap states stemming from the intrinsic presence of defects, typically affording Stokes-shifted, broad photoluminescence (PL), even though their accurate transition pathway is still open to dispute. Owing to such a broad band emission lacking color purity, I–III–VI QDs may not be the candidates suitable for the fabrication of dispaly-targeted white LEDs that require a high color reproduciblity. Instead, they can be beneficially employed as color converters for the construction of general lighting devices, where the QD emission as broad as possible is favored to secure a wide spectral coverage and thus achieve a high color rendering white light, as long as the emission wavelength is appropriate for the generation of white light through color-mixing with a blue light from LED pumping source.

For an attempt to replace the conventional yellow bulk phosphor of Ce^{3+}-doped $Y_3Al_5O_{12}$ (YAG:Ce), CIS or AIS QDs that were wisely synthesis-tailored to possess key fluorescent attributes (*i.e.*, emission wavelength and bandwidth) silimiar to those of YAG:Ce were successfully utilized as blue-to-yellow color converters in white QD-LEDs [19,23]. However, the devices fabricated above exhibited only moderate color rendering index (CRI) values of 72–75, primarily ascribable to a limited white spectral coverage from still insufficiently broad QD emissions. To improve the color rendering property of CIS-based QD-LEDs through a spectral extension, two types of QD emitters instead of a single type of CIS QDs have been adopted with an approriately optimized quantity ratio. For instance, CIS and CIGS QDs with peak emission wavelengths of 578 and 546 nm, respectively, were co-packaged with a blue LED chip, and the resulting device showed a somewhat enhanced CRI of 76–78, depending on the driving current [26]. Later, Zou and coworkers reported an even higher CRI of 94–95 by blending two color converters of green (535 nm) CIZS and red (615 nm) CIS QDs [25], which were spectrally more separate than the above CIS–CIGS QD combination, thus enabling a more distinctly tricolored white spectrum. Another tricolored white device was also demonstrated by reinforcing a green (536 nm) emission of CIGS QD with a red (617 nm) emission of InP QD that is another class of promising non-Cd emitters, showing high CRI of 89–94, depending on the blending weight ratio of CIGS-to-InP QDs [27]. In the present work, we propose a colloidal synthesis enabling a substantial

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spectral broadening of CIZS QDs, where the spectral shape and bandwidth of QD emission are systematically varied simply by controlling an amount of a key reactant of 1-dodecanethiol (DDT) that serves as both sulfur (S)-feeding source and surface ligand species. PL of the resulting CIZS QDs ranges from green to deep-red region, resulting in an extraordinarily broad emission bandwidth, and subsequently they are employed as effective color converters for the fabrication of an exceptionally high CRI white QD-LED.

2. Experimental

Prior to CIZS/ZnS core/shell (C/S) QDs, CIS/ZnS C/S QDs were preliminarily synthesized as follows; 0.125 mmol of Cu iodide, 0.5 mmol of In acetate, 0.8 ml of DDT, 5 ml of oleylamine (OLA), and 1.75 ml of trioctylphosphine oxide (TOPO) were placed in 50 ml of three-neck round flask, and the mixture was sequentially degassed, N_2-purged, and heated to 180 °C. Then, a S mixture of 3 mmol of S powder dissolved in 3 ml of 1-octadecene (ODE) was swiftly injected to the above mixture and the reaction proceeded at that temperature for 4 min for core QD growth. For the consecutive ZnS shelling, a shell stock solution consisting of 8 mmol of Zn acetate, 8 ml of oleic acid (OA), 4 ml of DDT, and 4 ml of ODE was slowly introduced to the core growth solution, and then the reaction proceeded at a further elevated temperature of 240 °C for 1 h. Lastly, another fresh shell solution of 8 mmol of Zn stearate, 4 ml of DDT, and 8 ml of ODE was successively added and reacted at that temperature for 1 h. Keeping the same core reaction details as in the previous CIS QD growth, CIZS QDs were synthesized only by including a fixed amount of 3 mmol Zn acetate and applying various DDT amounts of 0.8–2.0 ml. A series of CIZS QDs were individually overcoated with a ZnS by applying the same shelling conditions as in CIS/ZnS QDs. CIS/ZnS and CIZS/ZnS QDs were thoroughly purified by the repeated precipitation/re-dispersion processing with a solvent combination of acetone/chloroform, and finally dispersed in chloroform.

Analogous to the conventional bulk phosphor-converted LED, white QD-LED was fabricated as follows; the QD-chloroform dispersion with a concentration of ~50 mg/ml was blended with the mixture of commercial thermo-curable epoxy resin plus hardener with an equivalent weight ratio, and then the remaining chloroform was removed by heating at 70 °C for 2 h. The resultant QD-resin paste was dispensed into the mold of a 50×50 mm^2 surface mounting device typed InGaN-based blue-emitting LED (λ_{peak}=455 nm, Haewon Semiconductor, Korea) and then placed in a two-step thermal curing process of 80 °C for 30 min and 110 °C for 1 h.

UV–visible absorption spectroscopy (Shimadzu, UV-2450) and a 500 W Xe lamp-equipped spectrophotometer (PSI Co., Ltd., Darsa Pro-5200) were employed to record absorption and PL/PL excitation (PLE) spectra of QDs, respectively. For time-resolved PL decay data, the QD dispersion was excited at 410 nm by 3 ps pulses from Ti:Sapphire laser operating at a repetition rate of 76 MHz and PL decay dynamics were resolved using a time-correlated single photon counting method. PL quantum yield (QY) of QDs was assessed in an integrating sphere with an absolute PL QY measurement system (C9920-02, Hamamatsu). Crystallographic structure of QDs was analyzed by employing a powder x-ray diffraction (XRD) (Rigaku, Ultima IV) with Cu K_α radiation. Transmission electron microscopic (TEM) images of QDs were collected using a Tecnai G2 F20 operating at 200 kV. Various electroluminescent (EL) data such as EL spectrum, luminous efficacy, correlated color temperature (CCT), Commission Internationale de l'Eclairage (CIE) color coordinates, and CRI of white QD-LEDs were obtained at a driving current of 60 mA in an integrating sphere with a diode array rapid analyzer system (PSI Co. Ltd.).

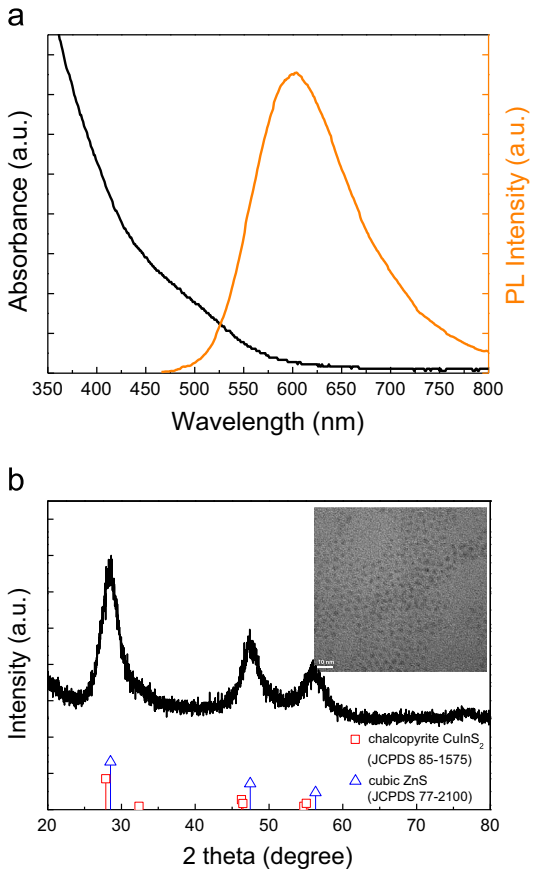

Fig. 1. (a) Absorption and PL spectra and (b) XRD pattern of CIS/ZnS QDs. The reflection peaks of chalcopyrite $CuInS_2$ and cubic ZnS phase are indexed in (b) for comparison and TEM image of CIS/ZnS QDs is also shown in the inset of (b) (scale bar: 10 nm).

3. Results and discussion

As shown in the absorption spectrum of CIS/ZnS QDs (Fig. 1(a)), I–III–VI type QDs generally exhibit an ill-defined absorption feature, primarily attributable to the combined effects of QD size/shape inhomogeneity plus compositional variation [3,28,29]. Their defect-associated radiative recombination leads to an appreciably broad PL typically with an emission bandwidth of >100 nm. The present CIS/ZnS QDs possessed a PL bandwidth of 119 nm (Fig. 1(a)) along with a peak wavelength of 604 nm and a PL QY of 64%. As shown in XRD pattern of Fig. 1(b), the overall reflection peaks of CIS/ZnS QDs somewhat deviated from those of tetragonal chalcopyrite $CuInS_2$ and closely approached those of cubic ZnS phase, proving that the ZnS overlayer was suitably formed onto CIS core surface [19,26,29]. The size of CIS/ZnS QDs was found by a TEM measurement (inset of Fig. 1(b)) to be widely distributed in the range of 1.7–3.3 nm with a mean diameter of 2.5 nm. These CIS/ZnS QDs were preliminarily tested as color converters for the fabrication of white QD-LED. However, due to the red-weighted emission of such QDs, the resulting bi-colored EL spectrum exhibited a significant green spectral gap between transmitted blue emission and color-converted QD emission component. As a combined result of inappropriately long wavelength and moderate bandwidth of QD emission, the CRI value of CIS/ZnS QD-LED reached ~65 at best.