

Highly Efficient White Light-emitting Diodes Based on Layered Quantum Dot-Phosphor Nanocomposites as Converting Materials

J. Y. Woo, J. Lee, N. Kim, C.-S. Han

Abstract—This paper reports on the enhanced photoluminescence (PL) of nanocomposites through the layered structuring of phosphor and quantum dot (QD). Green phosphor of $\text{Sr}_2\text{SiO}_4\text{:Eu}$, red QDs of $\text{CdSe/CdS/CdZnS/ZnS}$ core-multishell, and thermo-curable resin were used for this study. Two kinds of composite (layered and mixed) were prepared, and the schemes for optical energy transfer between QD and phosphor were suggested and investigated based on PL decay characteristics. It was found that the layered structure is more effective than the mixed one in the respects of PL intensity, PL decay and thermal loss. When this layered nanocomposite (QDs on phosphor) is used to make white light emitting diode (LED), the brightness is increased by 37 %, and the color rendering index (CRI) value is raised to 88.4 compared to the mixed case of 80.4.

Keywords—Quantum Dot, Nanocomposites, Photoluminescence, Light Emitting Diode

I. INTRODUCTION

COLLOIDAL QDs have attracted much attention due to their unique characteristics, including nanometer scales, high PL quantum yields (QYs), wide absorption spectra toward shorter wavelengths, exquisite color purity, lower light scattering, and size-tunable optical properties [1]-[6]. These advantages make nanocrystals useful for applications in a variety of light-emitting technologies, such as general lighting, display, photovoltaic devices, and lasers [7]-[10].

To tune the wavelength of the absorbed light, QDs have recently been used as fluorescent phosphors for optical devices to make white light or high-quality color light [11]-[16]. Although this has been reported for a white color rendering of LED using QDs, blends of QDs and conventional phosphors are a more typical approach than QDs, only due to optical performance, cost, and stability. QDs often simply tune the color of the LED toward the desired color coordinate along with high CRI. Previous research has only reported the change in optical properties according to simple mixing of QDs and phosphors. It did not consider the optical energy transfer between the QDs and phosphor. There are several optical paths between those, as they are randomly dispersed in space. Therefore, a simple blending structure might show relatively low energy-transfer efficiency because of several intermediate energy-loss steps in the transfer process [17].

This paper systematically analyzes the optical energy transfer between QDs and phosphor. For the first time, a layered structure to QD-phosphor thin films is introduced. Two kinds of composite (layered and mixed) are compared in terms of optical and thermal characteristics. It includes two kinds of layered composites according to the position and concentrations of the QDs.

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The PL decay characteristics are measured to arrive at a feasible reason as to why QDs layer on phosphor layer is more preferable with respect to PL. When an LED device with layered nanocomposite (QDs on phosphors) is fabricated, it shows highest brightness and CRI values among the tested nanocomposites.

II. EXPERIMENTAL

A. Materials and their characterization

For the synthesis, the experiment used Trioctylamine (Aldrich, 98 %), Oleic acid (Alfa, 99 %), Cadmium oxide (Alfa Aesar, 99.998 %), Se powder (Alfa Aesar, 99.999 %), Zinc oxide (Aldrich, 99.99 %), Trioctyl phosphine (Aldrich, 90 %), and 1-octanthiol (Aldrich, 98.5+ %).

An absolute quantum yield was measured through quantum yield measurement system (C-9920-02, Hamamatsu, Japan) composed with integral sphere, PMT, monochromator and Xe lamp. QY was measured under 480 nm excitation wavelength. A sample has 0.02 ~ 0.05 absorption intensity (OD) at the 480 nm. The absorption and photoluminescence were characterized using a UV-vis spectrophotometer (SD-1000, Scinco, Korea) and a fluorometer (Fluorolog, Horiba JOBIN YVON, France) at room temperature. Transmission electron microscopy (TEM) images were obtained using a Tecnai G2 F30 S-Twin model (FEI, The Netherlands) at 300 kV. QDs were dispersed in toluene and dropped on the 300-mesh holey carbon grids to prepare the sample. The decay properties of composite film were characterized with a Ti:Sapphire femtosecond pulse laser (Coherent, USA). The 519 nm green-emitting $\text{Sr}_2\text{SiO}_4\text{:Eu}$ phosphor was purchased from Force4 Co., (Gwangju, Korea) and used as received. InGaN-based blue LED chips (NLX-5 blue power die, $\lambda_{\text{max}} = 455$ nm, non-epoxy molding packages) were purchased from Trikaier (Gwangju, Korea). The dual-component thermal curable silicone resin (OE-6630 A and B) was purchased from Dow Corning.

B. Preparation of QD-phosphor-resin Nanocomposite and LED Device

Composite films were fabricated after the solvent was removed, and PL emission and decay properties from layer-by-layer (LBL) assembly and blending of QD-phosphor-resin film were measured after curing. QD-phosphor-silicone mixture was continuously dropped on blue LED chips to prevent bubble formation. Optical characteristics, such as electroluminescence (EL), luminous efficiency, correlated color temperature (CCT), and the Commission Internationale de l'Éclairage (CIE) color coordinates of WLEDs were evaluated by PR650 spectrascan (Photoresearch, USA) under a 350-mA working current at room temperature. CRI were recorded using a SLMS LED 1060 (Labsphere, USA) at room temperature.

III. RESULTS AND DISCUSSION

Fig. 1a shows the structure of a core-multishell nanocrystal optimized for high luminance efficiency and stability. The synthesized core-multishell QDs (CdSe/CdS/CdZnS/ZnS) are composed of Cd, Se, Zn, and S as shown in Fig. 1b for TEM images. The as-synthesized core-multishell QDs clearly appear on the TEM grid. They are almost monotonically dispersed, without agglomeration. Well-defined lattice fringes for the QD particles can be observed in the high-resolution TEM image (the inset of Fig. 1b), indicating that core-multishell QDs have a well-defined homogenous crystalline structure. Judging from the TEM images, the average particle size of the red-emitting core-multishell QDs is about 6.8 nm. The photograph in Fig. 1c shows the toluene solutions of the QDs in a cuvette under daylight and at 365-nm ultraviolet (UV) excitation. Fig. 1d shows typical UV-vis absorption spectra and the corresponding PL spectra of core-multishell QDs. The core-multishell QDs exhibit high and sharp first absorption peaks at 596 nm and emission peaks at 617 nm, indicating that they are highly monodispersed with a narrow size distribution. The QY of the QDs obtained through the synthetic methods described in Experimental Section, is above 55 % and the full width at half maximum (FWHM) of the QDs is 32 nm. The PL excitation (PLE) and the maximum wavelength of the PL spectrum of green-emitting phosphor are monitored at 450 nm and 519 nm, as reported previously[18]. There is a spectral overlap between the phosphor emission and absorption of the QDs, indicating that photons emitted from the phosphor could definitely be transferred to the QDs. In contrast, the PLE spectrum of the phosphor does not overlap with the QD emission spectrum, indicating that there is no energy transfer via photons from the QD.

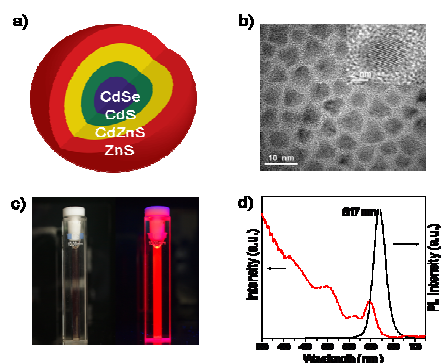


Fig. 1 a) Structure of a core-multishell nanocrystal. b) TEM images of CdSe/CdS/CdZnS/ZnS core-multishell QD (scale bar : 10 nm). The inset shows TEM images with high resolution for QD (scale bar : 2 nm). c) A picture of the QD solutions under daylight and at 365 nm UV illumination. d) UV-vis absorption spectra and corresponding PL emission spectra of core-multishell QDs

Fig. 2 illustrates the emission mechanism and energy transfer between QDs and phosphor in a polymer matrix. When the QD layer on the phosphor layer is exposed to blue light (Fig. 2a), there are three optical paths for the blue light: toward the phosphor, the QD, and the polymer. At this time, emission loss

(absorption, reflection, refraction, scattering, etc.) and heat loss (from QDs, the phosphor, and the polymer) occur during the light transmission. In the next step, the light is converted to green and propagates toward the QDs and the polymer. Accordingly, the red light converted by the QDs is created from green light by the phosphor and blue light source. Energy loss from the QDs also happens during this light conversion. Finally, white light is emitted from the composite layer by the combination of the blue, green-converted, and red-converted light. In the case of the phosphor layer on the QDs (Fig. 2b), the regime of light transmission is apparently similar to that in Fig. 2a, but the light-conversion efficiency is different due to the role of the QDs. In the case of QDs on phosphor, most blue light is first converted by phosphor with high efficiency. QDs are used to convert the blue light and the green light from the phosphor. However, for phosphor on a QD layer, if the QDs absorb most of the blue light, they emit the converted red light at a low conversion efficiency. Considering the overall optical conversion, it seems better to position the QDs on the outermost layer rather than the layer near the light source, as a significant energy loss due to heating occurs during the light conversion. In the phosphor layer, only the blue light that is not converted by the QD layer is absorbed by the phosphor. The red-converted light from the QDs mostly passes through the phosphor layer. In the case of the mixed layer in Fig. 2c, energy transfer and energy loss occurred simultaneously. Emission loss is expected to increase due to the increased optical interference between the QDs and phosphor. Based on the discussion of Fig. 2a and 2b, it can be predicted that the conversion efficiency of the blue light has roughly some value in the interval between Fig. 2b and 2c.

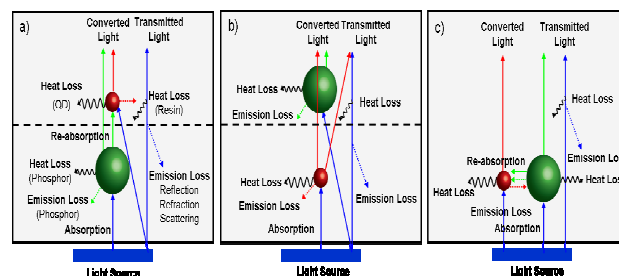


Fig. 2 Schematic illustration of the emission mechanism and the energy transfer between QDs and phosphor in polymer matrix : a) QD layer on phosphor layer, b) phosphor layer on QD layer, and c) mixed layer

Fig. 3 shows the PL emission spectra of the nanocomposite films with core-multishell QDs and phosphors in the silicone resin after thermal curing. The PL intensity and the spectral maximum of QDs does not provide the same value of PL as the QD solutions. The PL intensity could be reduced during film formation by surface defects in the QDs or different side reactions in the silicone resin at high temperature [10], [19]. Fig. 3a shows the PL spectra of both pure phosphor layers and phosphor layers coated by QDs. Blue light (400 nm) from the PL apparatus was used as a light source for these experiments. The phosphor layer alone does not show any red emission upon

excitation with blue light, as expected. After the addition of the QD layer to the phosphor layer, the PL intensity of green emission due to the phosphor is significantly reduced, and the red emission appears in the PL spectrum. The PL spectrum of the red emission results from the blue light transmitted through the phosphor layer and re-absorption of the photons emitted from the phosphor layer. However, Fig. 3b shows the PL spectra of the layer with QD only and of the phosphor layer with QD, respectively. The red emission attributed to the core-multishell QDs shifts slightly to a longer wavelength, from 617 nm to 622 nm, compared with the PL of the QD solution in Fig. 1d. This might be due to the aggregation of QDs which results in a new energy band and the re-absorption of light in the silicone resin [20], [21]. When the phosphor layer is added to the QD layer, the PL intensity of the red emission by the QDs is slightly reduced, and the PL spectrum of the green emission appears at 521 nm. This means that the light converted by the green phosphor is mostly due to blue light, not red. The slight change in PL intensity at the red region is likely due to light scattering at the interface area between the QD and phosphor layer. Also, micron-sized phosphor particles in phosphor layer could cause the light scattering, which would lead to a decrease in PL intensity at the QD emission region. Fig. 3c shows the PL spectra of the phosphor layer on the QD layer, the QD layer on the phosphor layer, and the mixed layer. The QD layer on the phosphor layer exhibits the highest PL intensity of green emission among these three structures, even though they maintain a similar intensity of red emission. This indicates that the layer adjacent to the light plays a major role in the light conversion.

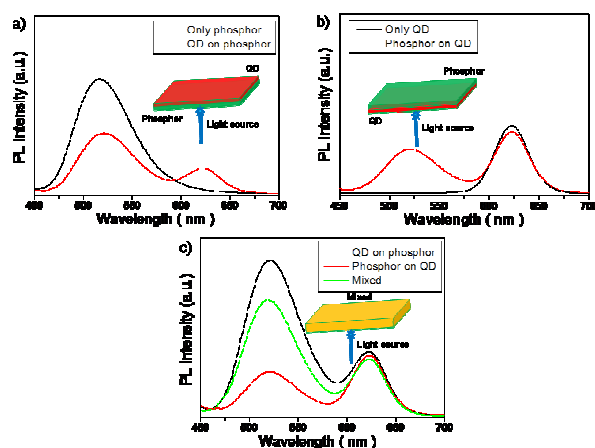


Fig. 3 The PL emission spectra of nanocomposite films composed of phosphors, core-multishell QDs, and resin : a) QD layer on phosphor layer (only phosphor layer : black, QD layer on phosphor layer : red), b) phosphor layer on QD layer (only QD layer : black, phosphor layer on QD layer : red), and c) QD layer on phosphor layer (black), phosphor layer on QD layer (red), and mixed (green) layer.

WLEDs have attracted both scientific and commercial attention. They may be useful for many solid-state illumination applications, including general lighting, backlighting of large displays, and decorative lamps as well as in the automotive

industry due to their environmental friendliness, high efficiency, applicability in a wide range of sizes, and low power consumption [22]-[25]. To fabricate WLEDs, red core-multishell QDs, green phosphor, and thermocurable polymer are coated onto a blue LED chip using a blending and LBL assembly technique (QDs on phosphor and phosphor on QDs). Fig. 4a shows the EL spectra of blue light-pumped LEDs using only phosphor layer and QD layer on phosphor layer. Similar to PL results, only the phosphor layer does not show any red emission and after hybridization of the QD layer on the phosphor layer, a large drop in blue and green emission and a small rise in re-emission appear. These results suggest that both blue and green light can be re-absorbed by QDs. Fig. 4b shows the EL spectra of only the QD layer and phosphor layer on the QD layer. As expected, only the QD layer does not show green emission. However, when the phosphor layer is hybridized on the QD layer, a decrease of blue emission, increase of green emission, and no change of red emission are observed. It is evident that QD emission has no relationship to phosphor emission. Fig. 4c shows the EL spectra of the phosphor layer on the QD layer, QD layer on phosphor layer, and mixed layer on blue light-pumped LEDs. The QD layer on phosphor layer has the most EL peak area, and phosphor layer on QD layer has the least EL peak area. The decrease of the EL peak area corresponds to a reduction in luminous efficiency.

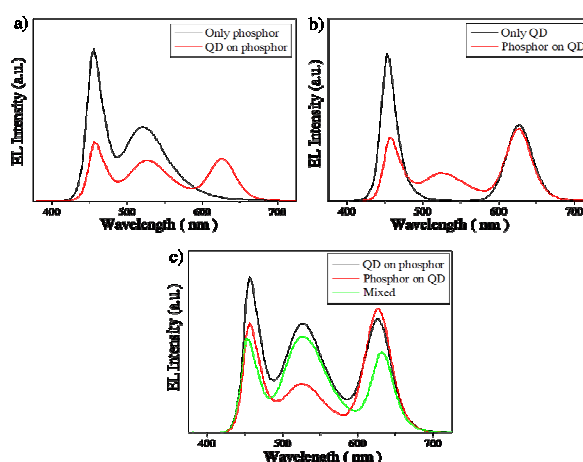


Fig. 4 The EL spectra of blue light-pumped LEDs when operated at 350 mA : a) QD layer on phosphor layer (only phosphor layer : black, QD layer on phosphor layer : red), b) phosphor layer on QD layer (only QD layer : black, phosphor layer on QD layer : red), and c) QD layer on phosphor layer (black), phosphor layer on QD layer (red), and mixed (green) layer

Fig. 5a shows the CIE color coordinates of the chromaticity diagram of the QD layer on phosphor layer, phosphor layer on QD layer, and mixed layer cases on light-pumped LEDs and corresponding photo images at an operating current of 350 mA.

The CIE coordinates of the QD layer on phosphor layer are (0.2889, 0.3627), those of the phosphor layer on QD layer are (0.3651, 0.2869), and those of the mixed layer are (0.3178, 0.3426). For layered structures, the color of the light emitted by

the device shifts to the color emitted by the layer adjacent to the blue light. For the mixed structure, the device emits the color between the QD layer on phosphor layer and the phosphor layer on QD layer. Fig. 5b shows the EL spectra as a function of QD content for a forward current of 350 mA when the QD layer is hybridized on top of the phosphor layer. As the QD content increases, a decrease in blue and green spectral regions and a relative increase in red spectral region are observed simultaneously.

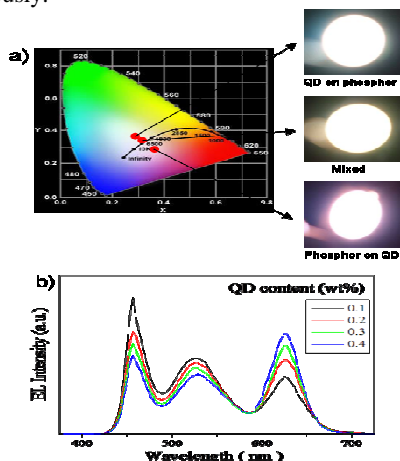


Fig. 5 a) The CIE color coordinates of the chromaticity diagram of QD layer on phosphor layer, phosphor layer on QD layer, and mixed layer on light-pumped LEDs and corresponding photo images at an operating current of 350 mA. b) The EL spectra as a function of QD content for a forward current of 350 mA when QD layer is hybridized on top of phosphor layer.

IV. CONCLUSION

In summary, this paper has developed a novel nanocomposite structure embedding CdSe/CdS/CdZnS/ZnS core-multishell red QDs and Sr₂SiO₄:Eu green phosphors in a silicone resin for a color converting material using various structuring methods (layered and mixed). It is observed that an enhancement of brightness is demonstrated and attributed to effective energy transfer, and that layer structure plays a major role in the light conversion. A two-step change of the QD emission due to the re-absorption of photons emitted from the phosphor layer leads to the broadest PL area and slow decay property of QD layers. When this layered structure is applied to fabrication of WLEDs, the performance of WLED is significantly improved in terms of luminance efficiency and CRI. It can be concluded that this layer-by-layer structuring of QDs and phosphor in WLEDs is a good solution for many optical applications.

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