Nanocrystalline $Y_3Al_5O_{12}$:Ce Phosphor-Based White Light-Emitting Diodes Embedded with CdS:Mn/ZnS Core/Shell Quantum Dots

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Abstract

Yellow-emitting $Y_3Al_5O_{12}$:Ce nanocrystalline phosphor and orange-emitting CdS:Mn/ZnS core/shell quantum dots were prepared by a modified polyol and a reverse micelle chemistry, respectively. To compensate a poor color rendering index of YAG:Ce nanocrystalline phosphor due to the lack of red spectral component, CdS:Mn/ZnS quantum dots were blended into YAG:Ce. Based on spectral evolutions in the blended systems, hybrid white light emitting diodes are fabricated and characterized.

1. Introduction

Development of InGaN-based light-emitting diodes (LEDs) has led to rapid growth in the solid-state lighting industry [1,2]. Typically, blue LED-pumped white LEDs use one or two phosphors for white light generation. From the viewpoint of luminous efficiency and fabrication cost, a yellow-emitting $Y_3Al_5O_{12}:Ce^{3+}$ (YAG:Ce) phosphor is most often used one [3,4]. Despite its advantages, YAG:Ce phosphor shows a red spectral deficiency, resulting in relatively low value of color rendering index [5]. For an effort to improve color rendering properties of YAG:Ce phosphor-based white LEDs, highly luminescent orange-emitting quantum dots (QDs) were blended with nanocrystalline YAG:Ce phosphor. Orange-emitting CdS:Mn/ZnS core/shell QD-assisted nanocrystalline YAG:Ce phosphor-based white LED are fabricated and evaluated.

2. Experimental

Nanocrystalline YAG:$Ce_{0.06}$ phosphors were synthesized via a modified polyol process and annealed at 1400°C for 6hr in an air atmosphere. ~3.6 nm sized 2 mole% Mn^{2+}-doped CdS quantum dots capped with 0.45 nm thick ZnS shell (CdS:Mn/ZnS core/shell) were prepared using a reverse micelle route, where Cd acetate, Zn acetate, Mn acetate, and Na_2S are used as starting materials and reverse micellar solution consisting of water, surfactant (AOT), and heptane is made under water-to-surfactant (W) ratios of 10.

3. Results and discussion

PL excitation and emission spectra of YAG:$Ce_{0.06}$ and CdS:Mn/ZnS QDs are shown in Fig. 1(a) and (b), respectively. Yellow band emission of nanocrystalline YAG:$Ce_{0.06}$ phosphor, peaking at 520 nm, is due to Ce^{3+} ^2D–$^2F_{5/2,7/2}$ transition, and orange band emission of CdS:Mn/ZnS QDs, peaking at 585 nm, is originated from Mn^{2+} $^4T_1$–$^6A_1$ transition. The quantum yield of CdS:Mn/ZnS core/shell quantum dots was measured to be ~30%. The high quantum yield of those quantum dots is a direct result of effective surface passivation by ZnS shell, by which nonradiative recombination paths at the surface of CdS:Mn core are considerably reduced. Significant spectral overlapping of two excitation spectra in Fig. 1(a) and (b) might indicate that both yellow and orange emission can be realized efficiently with a single excitation wavelength.

Average sizes of nanocrystalline YAG:Ce phosphor and CdS:Mn/Zns quantum dot were determined to be ~120 and ~4.5 nm, respectively, as shown in Fig. 2(a) and (b). CdS:Mn quantum dots without ZnS shell had a 3.6 nm in diameter, thus the thickness of the shell layer was estimated to be ~0.45 nm (1.5 monolayers).

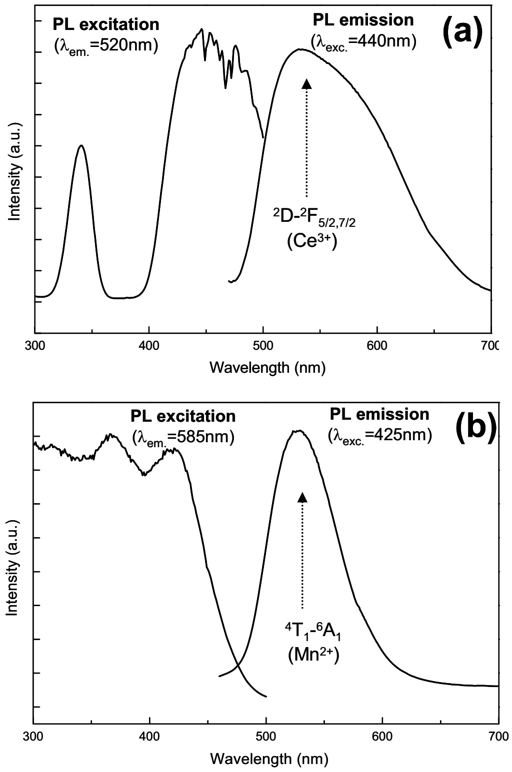

Fig. 1. PL excitation and emission spectra of (a) nanocrystalline YAG:Ce$_{0.06}$ phosphor and (b) CdS:Mn/ZnS core/shell quantum dots.

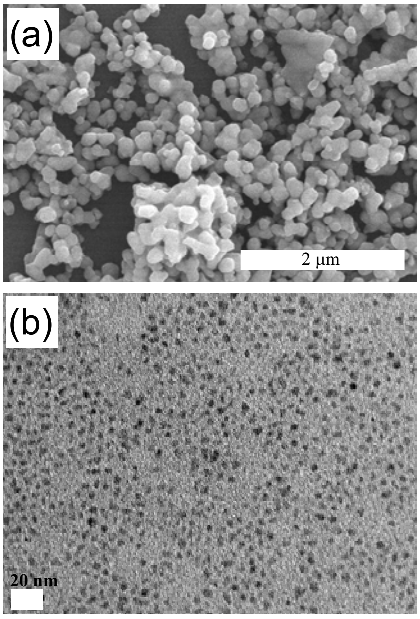

Fig. 2. (a) Scanning electron microscopic image of YAG:Ce$_{0.06}$ nanophosphors and (b) transmission electron microscopic image of CdS:Mn/ZnS quantum dots.

Blends of YAG:Ce nanocrystalline and CdS:Mn/ZnS QDs with different weight ratios were prepared, and PL emission spectra (excitation wavelength of 440 nm) of each blend are presented in Fig. 3. For 10:1 blend with a small content of quantum dots, its PL emission spectrum was little changed compared to that of pure YAG:Ce. With an increasing content of quantum dots, two spectral distinctions are observed between PL emission spectra of blends versus that of pure YAG:Ce, i.e., a small drop in green spectral region and a protruding rise in red spectral region. Using spectral tunability induced by the incorporation of quantum dots, the limited color rendering index of YAG:Ce phosphor might be improved.

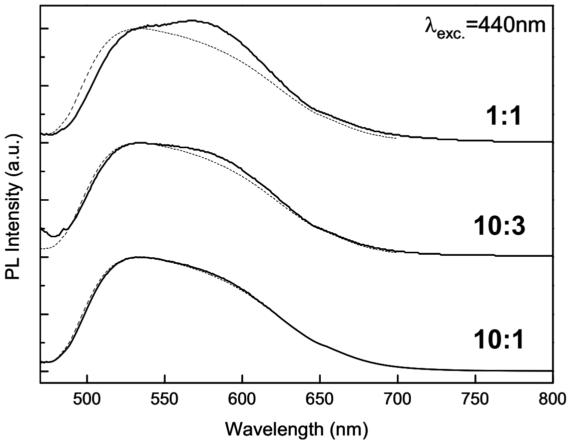

Fig. 3. Variation of PL emission spectra of blends of nanocrystalline YAG:Ce phosphor and CdS:Mn/ZnS core/shell quantum dots with their weight ratios (YAG:Ce vs. quantum dots) from 10:1, 10:3 to 1:1. YAG:Ce emission spectrum is referenced with dotted curve for comparison.

Hybrid white LEDs were fabricated using InGaN-based blue (450 nm) LED chips. Fig. 4(a) shows the electroluminescence (EL) spectra of various white LEDs under a forward current of 20 mA using from pure CdS:Mn/ZnS QDs, mixtures of (QDs + nano-YAG:Ce) to pure nano-YAG:Ce. With an increasing content of QDs, the spectral variation in the yellow region is observed as verified in Fig. 2. From a QD-nano YAG:Ce blend with a weight ratio of 1:1, EL spectra of the white LED were collected as a function of applied forward currents from 5 to 60 mA as shown in Fig. 4(b). Note that no luminescence saturation was observed up to a forward current of 60 mA. The CIE chromatcity coordinates of the fabricated white LEDs

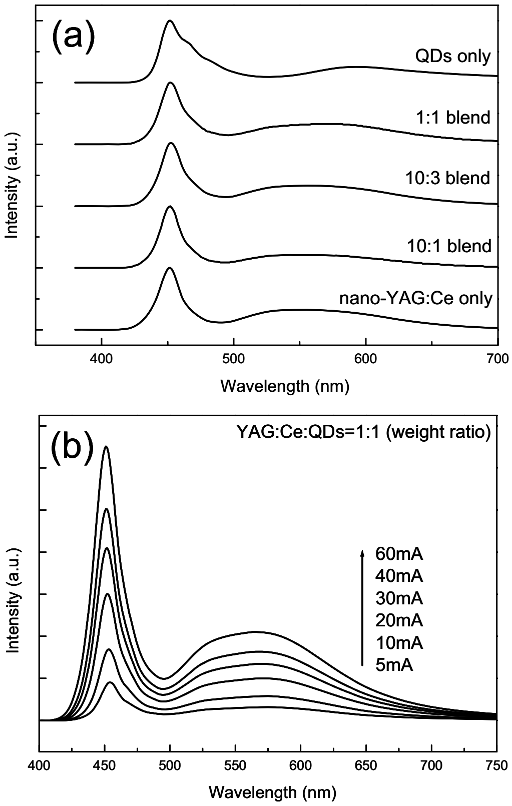

Fig. 4. (a) EL spectra of blue light-pumped white LEDs using the various mixtures of nano-YAG:Ce and QDs and (b) evolution of EL spectra of white LEDs as a function of applied forward current from nano-YAG:Ce and QD blend with 1:1 weight ratio.

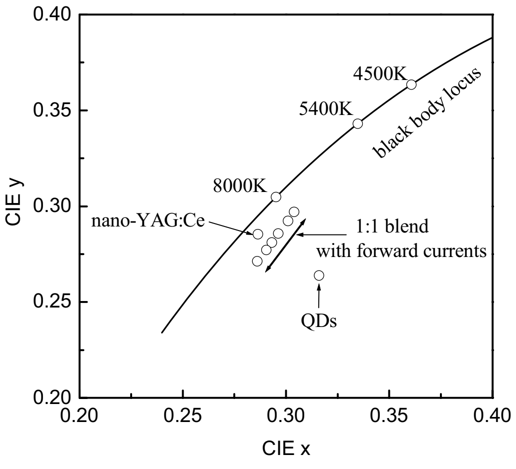

Fig. 5. CIE chromaticity coordinates of the fabricated white LEDs.

are presented in Fig. 5. The CIE coordinates and color temperatures for nano-YAG:Ce- and QD-based white LEDs under a forward current of 20 mA are (0.2864, 0.2855) and 9482K, and (0.3159, 0.2638) and 6939K, respectively. The chromaticity coordinates of the white LEDs using a 1:1 blend lie in (0.3039–0.2861, 0.2971–0.2713) with the variation of applied current. Nano-YAG:Ce- and QD-based white LEDs exhibited the CRI values of 78 and 62, respectively. Low CRI value from QD-based white LED is attributed to the deficiency of green spectral region. However, with the gradual addition of QDs into nano-YAG, the white LEDs using 10:1, 10:3, and 1:1 blends displayed the improved CRI values of 80, 82, and 85, respectively, suggesting that the QDs are effective in improving the red spectral deficiency of YAG:Ce phosphor.

4. Summary

120 nm-sized yellow emitting $Y_3Al_5O_{12}$:Ce nanocrystalline phosphor and 4.5 nm-sized orange emitting CdS:Mn/ZnS core/shell quantum dots were synthesized by a modified polyol and a reverse micelle chemistry, respectively. To improve a poor color rendering index of YAG:Ce nanocrystalline phosphor CdS:Mn/ZnS QDs were blended into YAG:Ce. Nano-YAG:Ce- and QD-based white LEDs exhibited the CRI values of 78 and 62, respectively. Hybrid white LEDs using the blends of nano-YAG:Ce and QDs exhibited an improved color rendering property. With increasing QD content in the blends the white LEDs from 10:1, 10:3, and 1:1 blends showed the CRI values of 80, 82, and 85, respectively. Better CRI values from the hybrid white LEDs indicate that the QDs are effective in supplementing a red spectral region that is lacking in YAG:Ce phosphor.

5. Acknowledgment

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6. References

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