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High Color Rendering White LED Based on Silicate/Dye-Bridged Siloxane Hybrid Phosphor Encapsulant

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White light-emitting diodes (LEDs) attract much attention as next generation lighting. Among many components constructing white LED, phosphors have a key role to generate white emission combining with blue LED. We report a red dye-bridged siloxane hybrid (DBH) as a red emitter and white LEDs based on red DBH mixed with green silicate phosphor. Red DBH has a potential to alternate inorganic phosphors and quantum dots used as red emitter in white LEDs because it has merit on cost and broad emission and absorption. The silicate/DBH phosphor encapsulated white LEDs exhibit high color rendering index up to 90 and easy color tunability.

Introduction

White light-emitting diodes (LEDs) are widely used because of their eco-friendly characteristics such as low energy consumption, lead-free and no harmful gas and also their high performance on efficiency, brightness and lifetime. White LEDs are generally used on signals and small lightings and demands for white LEDs are suddenly increased after it is applied to backlighting for TVs and laptop displays. And it is expected that white LEDs will be next generation lighting instead of incandescent and fluorescent lights. To be applied to room lighting, white LEDs should have high color rendering and low initial price.

Di-chromatic white LEDs consisted with blue LEDs and yellow phosphors are the most commercialized type and they have merit on brightness and cost. But they have poor color rendering to be applied to room lighting because of lack of red and green emissions. Recently, di-chromatic white LEDs develop into tri-chromatic white LEDs using red and green phosphors to achieve high color rendering index (CRI). But the problem is it is hard to find sufficient red phosphors because most oxide-based phosphors have low absorption in the blue-light range and sulfide-based phosphors have low chemical stability (1). Nitride phosphors have earned interest for high stability and good red emission but their high cost due to crucial synthesis conditions of high temperature and nitrogen pressure becomes one reason of high initial price of white LED (2, 3).

Quantum dots (QDs) can be a candidate for phosphors because they have high luminescence efficiency, color purity and color tunability by controlling the particle size (4-6). There are several researches on QDs based white LEDs which have high color rendering (7, 8). However, the usage of QDs is limited because many of QDs are consisted with toxic material such as cadmium and the price is still too high compare to inorganic phosphors.

Previously, we have reported dye-bridged siloxane hybrid (DBH) phosphor encapsulant as an alternation of inorganic phosphor (9-12). The fluorescent dyes are good emitting material for their broad absorption and emission spectra, easy structure modification and moderate cost. But the low stability on heat, light and oxygen causes the limitation. R-DBH is a single component of red dye and sol-gel derived oligosiloxane encapsulant that dye is covalently bridged to oligosiloxane to increase thermal stability.

In this study, a red DBH is synthesized through a sol-gel reaction and mixed with green silicate phosphors. And white LEDs are fabricated using the mixture and blue LED chips.

Experiment

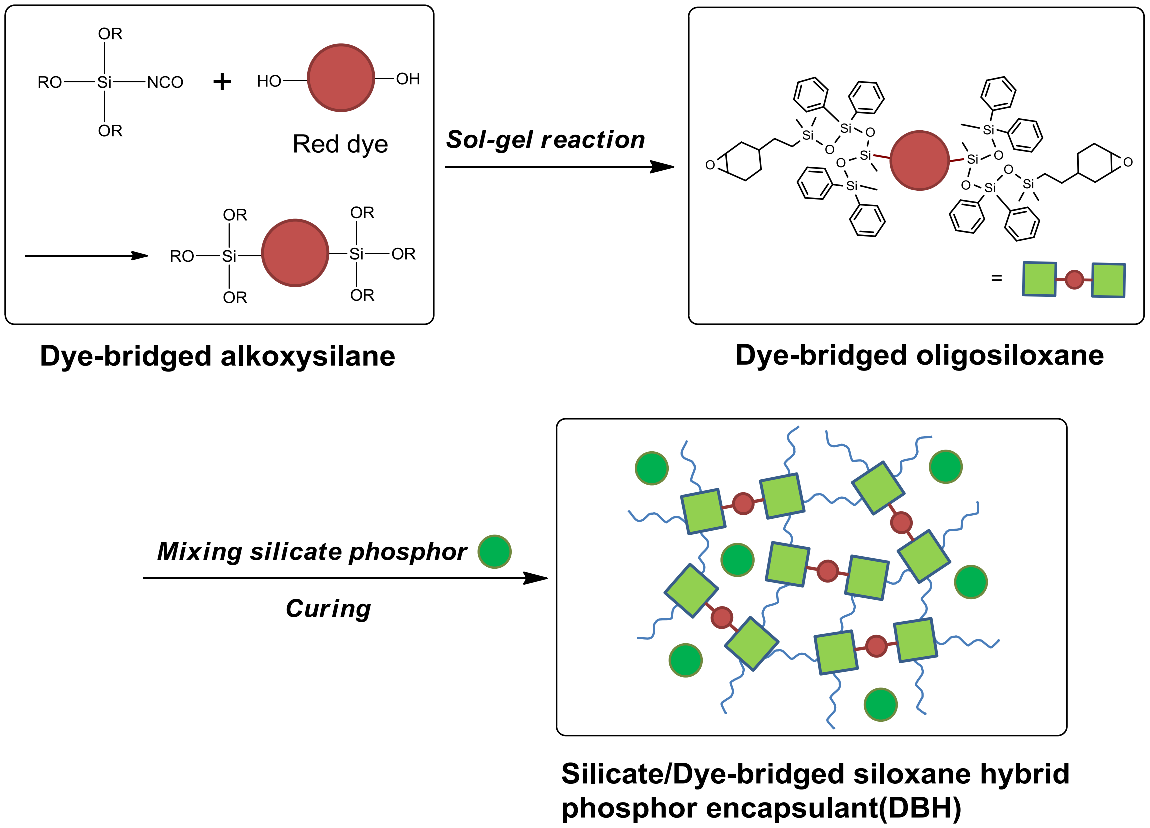

Figure 1. Fabrication of green silicate/red dye-bridged siloxane hybrid (DBH) phosphor encapsulant through sol-gel reaction and thermal curing (10).

Synthesis of Dye-Bridged Alkoxysilane. Three steps are required to synthesize silicate phosphor mixed red DBH as presented in Figure 1. First, hydroxyl-functional red dye was synthesized by following the reference (9, 10). Then 3-(triethoxysilyl)propyl isocyanate was added to red dye by double molar ratio over red dye. The mixture was stirred for 6 h at 80 °C to be dye-bridged alkoxysilane.

Synthesis of Dye-Bridged Oligosiloxane. Diphenylsilanediol and 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane were added to the synthesized dye-bridged alkoxysilane with barium hydroxide monohydrate as catalyst. The mixture was reacted at 80 °C for 4 h to procced condensation via sol-gel reaction in the nitrogen atmosphere. The synthesized dye-bridged oligosiloxane was filtered using 0.45 μm teflon filter to eliminate powdered catalyst. The concentration of red dye in dye-bridged oligosiloxane was controlled to be between 0.02 mM and 0.1 mM.

Fabrication of Dye-Bridged Siloxane Hybrid (DBH) Mixed with Green Silicate Phosphor. The silicate phosphor purchased from Intematix was dispersed in red dye-bridged oligosiloxane by 10 wt%. And 40 wt% of hexahydro-4-methylphthalic anhydride was used as an epoxy hardener and 2 mol% of tetrabutylphosphonium methanesulfonate was used as an initiator for thermal curing. The curing occurred at 150 °C for 2 h. The final product became a hard solid state.

Fabrication of White LEDs and Characterization. Above mixture before curing was dispensed on blue LED chip which is not encapsulated and thermally cured as the same method as fabricating DBH solid sample. We analyzed curing condition of the DBH using FT-IR spectrometer (FT/IR-680 Plus, Jasco). And photoluminescence of samples was measured using DARSA PRO 5100 PL System (PSI Trading Co., Ltd). Characteristics of the white LEDs such as electroluminescence, color coordinates, color rendering index and color temperature are measured using DARSA PRO 5100 PL System (PSI Trading Co., Ltd) and integrating sphere under a forward bias current of 20mA at the air atmosphere.

Result and Discussion

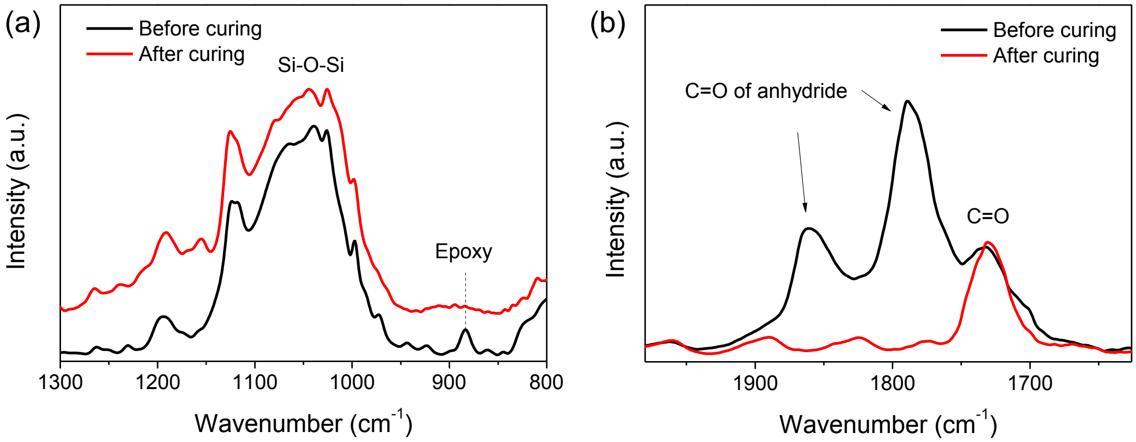

Figure 2. FT-IR spectra of DBH before and after curing for analyzing (a) epoxy group of DBH, and (b) C=O stretching vibration of hexahydro-4-methylphthalic anhydride.

The structure of the DBH before and after curing was analyzed using FT-IR to assure it is cured well. It can be a one reason of unreliable performance if it is not fully cured due to the unreacted organic parts. Figure 2 (a) represents absorption spectra of siloxane bonding of the DBH in the range of 1120~1040 cm^{-1}. On the right side of siloxane stretching, the epoxy peak is seen at 883 cm^{-1} before curing the DBH and it disappears after curing which means epoxy curing is occurred. In the range of 1900~1700 cm^{-1} (Figure 2b), we can analyze the C=O stretching vibration of anhydride originated from epoxy hardener in the DBH. Before curing, the cyclic anhydride C=O is observed at 1860 cm^{-1}, 1788 cm^{-1} and then it turns to ester carbonyl at 1730 cm^{-1} because cyclic ring has been opened after curing. And unreacted cyclic anhydride C=O of hardener is not observed at the cured DBH sample. This result demonstrates that red DBH is well fabricated through thermal curing.

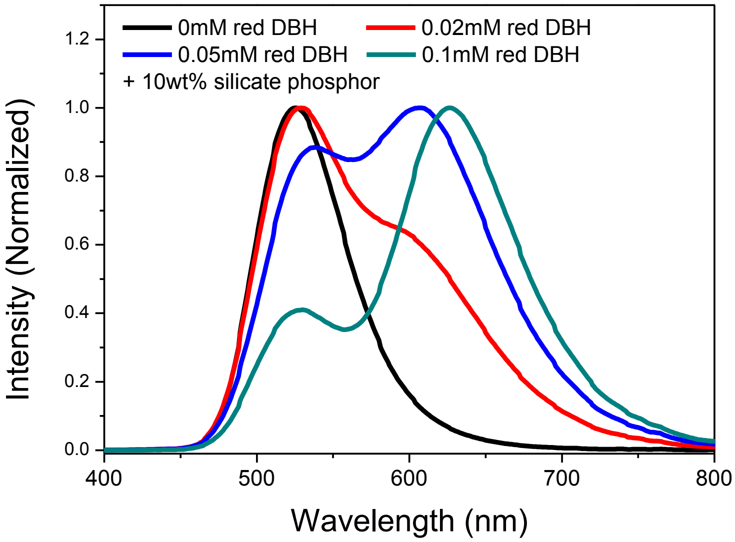

Figure 3. Emission spectra of green silicate and red DBH mixture with various dye concentrations from 0 mM to 0.1 mM.

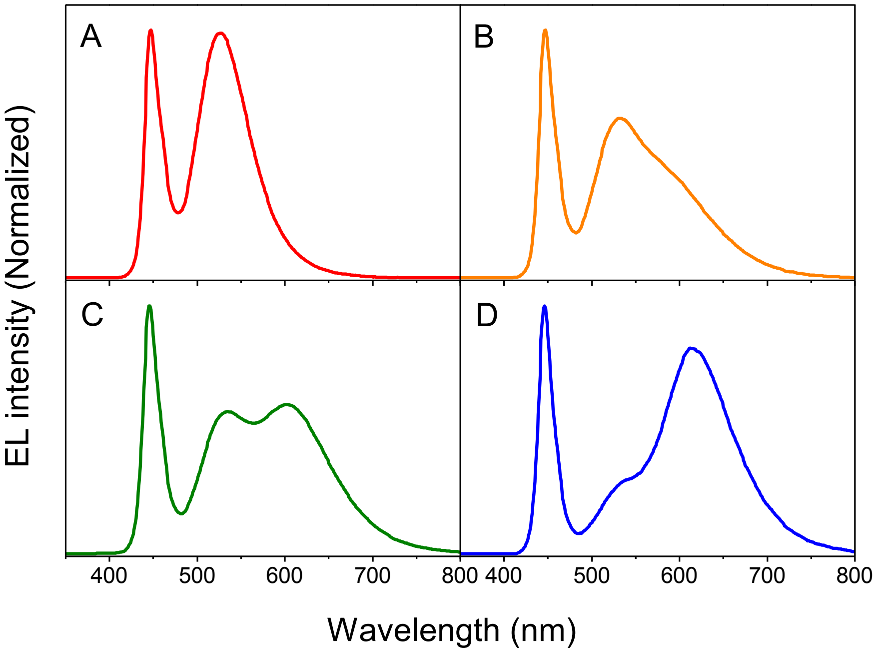

Figure 4. Electroluminescence (EL) spectra of various white LEDs based on red DBH and silicate phosphor (12).

We used Eu doped silicate which has main emission peak at 525 nm for the green phosphor. The absorption range of silicate phosphor is between 200 nm and 490 nm, so it matches with emission of blue LED around 450 nm. And the main emission of fabricated red DBH with concentration of 0.1 mM is 644 nm and broad absorption spectrum is seen in the range of 350~600 nm. The amount of silicate phosphor was fixed at 10 wt% and the concentration of red dye in DBH was changed to generate proper yellow emission. Figure 3 shows the emission spectra of green silicate and red DBH mixture with various dye concentrations. The original emission peak of silicate phosphor is shifted from 525 nm to 535 nm and the emission of red DBH is also shifted from 644 nm to 610 nm after red DBH and silicate phosphors are mixed with each other. It seems it is due to the superposition of two red and green emission spectra. The color coordinates (x, y) on Commission Internationale de l'Eclairage (CIE) 1931 color space are (0.3905, 0.5443), (0.4547, 0.5033), and (0.5167, 0.4483) for dye concentration of 0.02 mM, 0.05 mM, and 0.1 mM, respectively. These are proper yellow emission to be combined with blue LED.

According to the above mixing ratio, various white LEDs are fabricated by controlling the dye concentration and silicate phosphor amounts to adjust CRI and color temperature. Figure 4 shows electroluminescence (EL) spectra of various white LEDs based on red DBH/silicate phosphor. And their color coordinates, CRI and color temperature are listed in the Table I. The A/B/C/D samples are for the 0/0.02/0.05/0.1 mM red DBH with 10 wt% silicate phosphor, respectively. Color temperature is easily tuned from cool white (7600 K) to warm white (2700 K) to be applicable to room lighting.

TABLE I. CIE color coordinates, CRI and color temperature of various white LEDs based on silicate/DBH phosphor encapsulant (12).

Sample	CIE (x,y)	CRI	Color Temperature (K)
A	(0.2247, 0.3723)	-	-
B	(0.2921, 0.3360)	75	7600
C	(0.3341, 0.3237)	90	5400
D	(0.3917, 0.2877)	82	2700

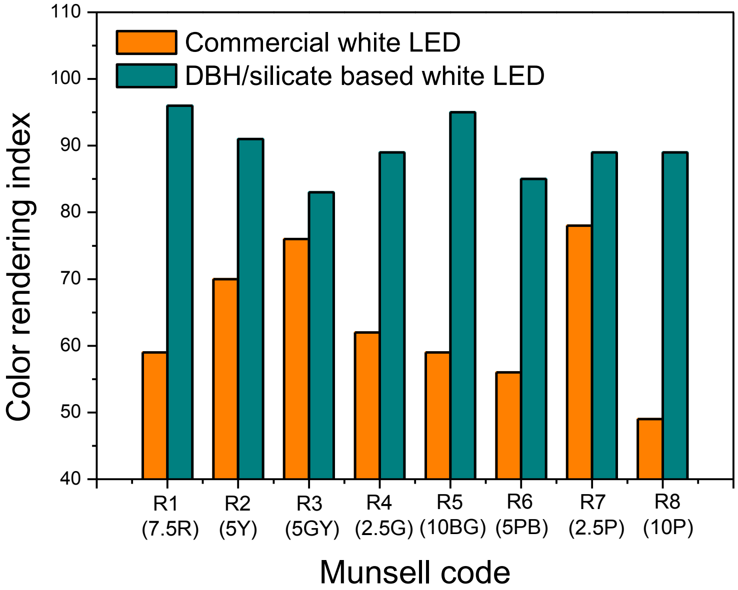

Figure 5. Color rendering index (CRI) comparison of DBH/silicate phosphor based white LED (sample C) to commercial white LED in Munsell code.

The sample C shows the best CRI of 90 among four samples and the color temperature is 5400 K. Generally, commercial white LED based on inorganic phosphor has CRI of 60~70. Because the emission in the region of red and green of red DBH/silicate phosphor based white LED is stronger than inorganic phosphor based white LED, it can achieve much higher CRI. The CRI values of the DBH/silicate phosphor based white LED (sample C) and a commercial white LED depending on the eight color components were compared (Figure 5). The commercial white LED has a di-chromatic source and the CRI is 64. As presented in Figure 5, color rendering at 7.5R and 10P has been increased by about 40 points. 7.5R and 10P represent light greyish red and light reddish purple. These results indicate that the red emission of the DBH/silicate phosphor encapsulated white LED is stronger than that of an inorganic phosphor based white LED. Also color rendering at 2.5G and 10BG which are related to green emission, are increased by about 30 points due to the silicate phosphor. But still additional work is necessary to make white light that is close to the blackbody (Planckian) locus.

Conclusion

In summary, we have fabricated red DBH based white LEDs mixing with green silicate phosphor. The red DBH and green silicate phosphor based white LEDs show high color rendering index up to 90 and facile color temperature tuning by controlling the dye concentration to be used for solid-state lighting. We expect red DBH has a potential to substitute inorganic red phosphors.

Acknowledgments

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