Improve efficiency of white organic light-emitting diodes by using nanosphere arrays in color conversion layers

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Abstract: The authors demonstrated an efficient color conversion layer (CCL) by using nanosphere arrays in down-converted white organic light-emitting diodes (WOLEDs). The introduced periodical nanospheres not only helped extract the confined light in devices, but also increased the effective light path to achieve high-efficiency color conversion. By applying a CCL with red phosphor on a 400-nm-period nanosphere array, we achieved 137% color conversion ratio for blue OLEDs, which was 2.68 times higher than conventional flat CCL. The resulting luminous efficiency of WOLEDs with patterned CCLs (20.97 cd/A, 1000 cd/m2) was two times higher than the efficiency of the flat device (10.26 cd/A, 1000 cd/m2).

OCIS codes: (220.4241) Nanostructure fabrication; (230.3670) Light-emitting devices.

References and links


1. Introduction

The white organic light-emitting device (WOLED) is of particular importance because of its various applications in solid-state lighting and backlight illumination. It has advantages of excellent electroluminescence performances, good flexibility, and batch fabrication [1–4]. The white light in an OLED is usually generated by the mixture of three primary colors (red, green, and blue, RGB) or two complementary colors. The fabrication of WOLEDs can be classified into three approaches, (1) employing a single emissive layer doped with different kinds of emissive materials, (2) vertical or horizontal stacking of RGB emission structures, and (3) using a color conversion layer on the blue OLED [5]. For a WOLED with a single emissive layer, the device needs careful adjustment of doping concentration and precise control of the exciton distribution [1,3,6]. The emission color would shift due to the different aging lifetime of the emissive materials. The second approach of multiple emissive layer structure can provide a better color homogeneity over the entire emission area. However, the complex manufacturing process results in a higher fabrication cost. Besides, the exciton distribution balance, carrier recombination shift, and different aging rates of individual emissive materials probably result in the problem of color shift [4,7,8]. The last approach is to combine a single blue device with a complementary color conversion layer (CCL) to produce a color-stable white light source [2,3,9–11]. This phosphor converted emission method has been widely used in inorganic LEDs due to its convenient fabrication and good color stability.

Currently, WOLEDs perform at a much lower efficiency than white LEDs. To improve efficiency, some researchers have reported using phosphorescent OLEDs [4–7,12–16] and light extraction techniques [17–20]. An efficiency up to 99 lm/W was achieved by optimizing the internal quantum efficiency and light extraction efficiency [12]. In this paper, the authors proposed a method to make phosphor-converted-emission WOLEDs with light-extraction layers that produced high efficient and color-stable WOLEDs. The authors placed a close-packed polystyrene nanosphere monolayer between the blue OLED and the red phosphor. This monolayer increased the effective light path of blue light in the color conversion layer, producing a large amount of regenerated red photons. In addition, the periodic nanostructure reduced the total internal reflection on the surface of the device. It coupled confined blue and red photons out of the substrate and greatly enhanced the external efficiency of WOLEDs. With this nanosphere monolayer, the authors achieved 137% color conversion ratio and a luminous efficiency of 20.97 cd/A at 1000 cd/m$^2$.

2. Experimental methods

Figure 1(a) showed the schematic diagram of the fabrication process of the polystyrene nanosphere patterned color conversion layer. At first, a solution containing nanometer-scale
latex spheres was spun-coated onto a flexible polycarbonate substrate. By controlling the concentration of nanosphere solution and rotation speed of the spin coater, a close-packed monolayer of nanospheres coated the substrate. After a few minutes of settling down, a hexagonal close-packed monolayer was formed. The period of the hexagonal array was determined by the diameter of polystyrene spheres. The diameters of nanospheres were further reduced by using oxygen plasma etching to form gaps for the filling of MEH-PPV solution. This process also helped the nanospheres stick on the substrate due to the background temperature during the plasma etching. These nanospheres thus were not dispersed during the following MEH-PPV coating process. After etching, these polystyrene spheres turned into isolated polygons as depicted in Fig. 1(b). The MEH-PPV solution with mass concentration 1% was then spun-coated on the patterned substrate and cured at 120 °C for 15 minutes. The MEH-PPV layer formed a smooth surface above the nanosphere monolayer with a thickness around 200 nm. Finally, the patterned color conversion layer was attached on a blue OLED device to generate white emission light. In this color conversion layer, polystyrene nanospheres with different diameters from 400 nm to 800 nm were tested.

Fig. 1. (a) Fabrication process of two-dimensional nanospheres patterned color conversion layer: (Step 1) a monolayer of polystyrene nanospheres was formed on the clean polycarbonate substrate. (Step 2) reduced the nanospheres by oxygen plasma etching and stuck them on the substrate surface. (Step 3) MEH-PPV was spun-coated on the patterned PC substrate. (Step 4) after the thermal curing process, the color conversion layer was attached to the blue device with index matching oil. (b) SEM images of top (up) and cross-sectional (down) views of the reduced nanosphere monolayer with a period of 600nm.
Blue OLEDs were fabricated by a solution process and tested as controlled devices for color conversion. Figure 2(a) shows the device configuration. The emission layer was composed of iridium (III) bis[(4,6-di-fluorophenyl)-pyridinato-N,C2] picolinate (F1rpic) doped into poly(N-vinylcarbazole) (PVK) polymer host containing 1,3-bis[(4-tert-butylphenyl)-1,3,4-oxadiazolyl]phenylene (OXD-7). The luminous efficiency of the blue OLED was 21.7 cd/A or 13.6 lm/W, which was comparable with those reported earlier [21]. The authors prepared color conversion layers with the nanosphere monolayer (patterned CCL) and without nanospheres (flat CCL). Those CCLs were all coated with MEH-PPV under the same conditions. The absorption and relative photoluminescence (PL) spectra of MEH-PPV are shown in Fig. 2(b). The color conversion material showed strong absorption from 450 nm to 550 nm and emission with the peak wavelength at 580 nm. The electroluminescence peak of the PVK-based blue device was approximately 470 nm, which matched quite well with the absorption spectrum of MEH-PPV. The MEH-PPV emits red color which is the complementary color of the blue OLED. White light was generated when the CCL was attached to the blue OLED. Figure 2(c) showed the photographs of the WOLEDs with flat CCL and patterned CCL. The patterned CCL sample showed brighter white light than the flat one.

![Diagram of device structure](image1)

![Normalized EL spectrum and PL spectra](image2)

![Photographs of WOLEDs](image3)

Fig. 2. (a) Device structure of blue phosphorescent device covered with color conversion layer. (b) Normalized EL spectrum of a blue OLED and absorption/PL spectra of the color conversion layer (MEH-PPV). (c) The photographs of WOLEDs without (flat CCL) and with (patterned CCL) the nanosphere array.

### 3. Device modeling and simulations

The nanosphere array played a role for increasing the blue photon intensity in the CCL and helped the coupling of trapped photons into the air. Figure 3 depicted the oblique incidence of blue light and red light in flat and patterned CCLs. With the scattering and grating coupling effect of nanosphere array, the off-angle incident blue light can have an increased light extraction to the air. In addition, part of reflected blue light will be confined in the CCL, because the MEH-PPV has a higher refractive index than the substrate. The waveguide effect...
increased the light path and the excitation possibility of red photons. For red light, only a small portion of red photons can escape to the air because of the total internal reflection. With the nanosphere array, the red photons can be efficiently coupled to the air. To account for the effect of the nanosphere array, the authors used the COMSOL Multiphysics® to solve the electric field distribution in the CCL for different periods of nanospheres. In the simulations, the incident light was incident from the glass substrate (n = 1.5) to the CCL with different incident angles. The CCL was filled with periodic nanospheres (n = 1.57) and MEH-PPV (n = 1.7 + 0.8i). The authors calculated the electric field distribution in a unit cell, which provides all the information on the behavior of the entire patterned CCL. The diameter of the nanosphere was varied from 400 to 800 nm and the incident angle was varied from −90° to + 90°. Figure 3 shows the electrical field distribution of blue emission at different incident angles for 400-nm and 800-nm nanospheres. The incident blue light (λ = 470 nm) was effectively coupled out from the glass substrate and strongly guided in the pattern CCL when the nanospheres period was 400 nm. It is especially obvious at the large incident angle. Such a waveguiding effect increased the effective light path of the blue light and thus enhanced the red light emission. Compared with the 400-nm nanospheres, light in the 800-nm-sphere array only had weak waveguide effect. It followed the light path similar to the flat devices without the nanospheres.

![Electric field distribution of the patterned CCL with periods of 400 and 800 nm.](image)

Fig. 3. (a) The illustration of extraction enhancement for the patterned CCLs. The blue line indicated the obliquely incident light. Light scattering to the air was increased by the nanosphere arrays. In addition, part of reflected light was confined in the CCL layer due to wave guiding effect. It increased the light path and the excitation possibility of red photons. The red line shows the red photons. The nanosphere array also helped coupling red light to the air. (b) Electric field distribution of the patterned CCL with periods of 400 and 800 nm.
Figure 3 showed only single wavelength results. For quantitative estimation of the blue light distribution, the authors calculated electric field intensities by using the emission spectra of blue OLED for the incident light. The intensities for different wavelengths and different incident angles were plotted in Fig. 4(a). The 400-nm-nanosphere CCL showed that the larger intensity occurs near 45° incident angle. It was due to the coupling of the incident wave to the MEH-PPV waveguide by the periodic nanospheres. On the other hand, the larger intensity for the 800-nm-nanospheres occurred near 0° due to the weak coupling effect of the large-period array. The overall blue light enhancement can be estimated from the summation of intensities for different incident angles and wavelengths. It is assumed that the red emission is proportional to the overall blue light intensity. Figure 4(b) showed the calculated red emission in the CCL as a function of nanosphere period. The best red light enhancement was observed with nanospheres of 400-nm period. The intensity decreased with the period. The enhancement from 700 nm to 400 nm was about 1.6 times. It was noted that there was a small intensity increase in the 800-nm-period nanospheres. The authors attributed this increase to the second order coupling effect because the grating vector for 800-nm nanosphere was one half of 400-nm nanospheres.

![Angular resolved absorption spectra in the patterned CCL](image1)

![Calculated relative red emission intensity of the patterned CCL with periods from 400 to 800 nm](image2)

**4. Measurement results and discussion**

Figure 5(a) showed the measured emission spectra of the down-conversion light of the devices at a constant operation current density, 30 mA/cm². Compared to that of a MEH-PPV layer on a smooth surface, the effective light path length in the CCL was increased due to the waveguide effect, which led to a distinctly enhanced red emission and total color conversion efficiency.
The red emission peak of the down-conversion white light was increased 2.16 times when a 400-nm-nanosphere monolayer existed in the CCL. It was noted that the blue emission also increased 1.34 times when compared with the flat MEH-PPV layer. It confirmed that by introducing nanosphere monolayer on the surface also led to an enhanced extraction of light from the substrate. The increased blue and red photons were dissimilar for different diameters of nanospheres. The resulting CIE coordinate thus also shifted with different nanospheres as seen in Fig. 5(b). For 700 nm and 800 nm nanospheres, the improvement of blue light extraction ability exceeded the optical path increase for the red photons. Therefore, a blue shift in the CIE coordinate was found. When the diameter of the nanosphere was decreased, the red photons increased more than the blue photons. A red shift in the CIE coordinate was measured. The down conversion color was turned from warm white ($x = 0.3849, y = 0.4002$) for 400-nm-diameter nanosphere to cool white ($x = 0.3099, y = 0.3909$) for 800 nm nanosphere. By varying the period of the assembled nanosphere monolayer, the x-coordinate of the white emission can be adjusted, while the y-coordinate was not significantly affected. It provided an efficient down-conversion approach for adjusting different white emission.

To study the conversion ratio from blue light to red light, the authors divided the emission spectra with individual photon energy for different wavelength to avoid the effect of Stokes loss. The photon energy spectrum was fitted by using two-peak Gaussian functions to calculate the photon densities for red and blue light in the white emission. Figure 6 shows the calculated conversion ratios for the patterned CCL device with different diameters of nanospheres. The introduction of nanosphere monolayer increased the conversion from blue light to red light. The enhancement was decreased with the increase of nanosphere size. For the size larger than 800 nm, there was no enhancement. When the size was down to 400 nm, the conversion ratio was increased up to 1.37. According to the model proposed by Duggal et al. in 2002, the conversion efficiency should always be less than one due to the ðnite quantum yields of the down-conversion layer [2]. The authors attributed the extraordinary color conversion ratio of the devices to the good light extraction and scattering ability of the periodical nanostructures.
To account the extraordinary color conversion, the down-conversion mechanisms for both flat and patterned CCLs were illustrated in Fig. 7. The color conversion ratio is defined as the photon density of converted red light divided by the decrease of blue light. The decrease of blue light is calculated by comparing the difference between blue OLEDs with and without the CCL. The color conversion ratios for flat and patterned CCLs are expressed as

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\text{Color conversion ratio} = \frac{\text{generation of red photons}}{\text{decrease of blue photons}} = \frac{\eta_1 \cdot B_0}{\eta_{\text{ext}0} B_0 - \eta_{\text{ext}1} B_0} \quad \text{(for flat CCL)}
\]

\[
= \frac{\eta_{1,2} \cdot B_0}{\eta_{\text{ext}0} B_0 - \eta_{\text{ext}2} B_0} \quad \text{(for patterned CCL)}
\]

Where \(B_0\) is the blue photon density generated in the substrate, \(\eta_{\text{ext}0}\), \(\eta_{\text{ext}1}\), and \(\eta_{\text{ext}2}\) show the extraction efficiency of the glass substrate, flat and patterned CCL, respectively. The extraction efficiency is greatly influenced by the index difference between substrate and air and the corresponding patterned structures on the substrate surface. Due to the better light extraction ability of the periodical nanospheres, the \(\eta_{\text{ext}2}\) is larger than \(\eta_{\text{ext}1}\). On the other hand, \(\eta_{1,1}\) and \(\eta_{1,2}\) are the red photons generation efficiency in the flat and patterned CCLs. The scattering of light in the patterned nanostructure increases the coupling of red photons to the air. Therefore, \(\eta_{1,2}\) is higher than \(\eta_{1,1}\). The \(\eta_{\text{ext}2}\) and \(\eta_{1,2}\) are simultaneously increased. From Eq. (1), the denominator is decreased and numerator is increased. Therefore, the conversion ratio can be larger than one as compared with flat sample. If we compare the overall enhancement ratio, the increase of conversion efficiency (blue + red) for 400 nm nanospheres is 2.68 times higher than the flat CCL as seen in Fig. 6.
Figure 8 shows the current efficiency of the down-conversion devices with and without nanospheres patterned (period: 400 nm) under different operation brightness. For 1000 cd/m$^2$, the corresponding current efficiency was 20.97 cd/A for CCL with nanospheres and 10.26 cd/A for the flat surface. Due to better light extraction and higher conversion ratio, the device with nanospheres patterned CCL showed a great improvement when compared to the device with flat CCL.

4. Conclusions

In summary, a high color conversion efficiency for down-converted WOLEDs was achieved by making a close-packed nanosphere monolayer on the CCL. By coating MEH-PPV on the patterned CCL and using a PVK-based phosphorescent blue OLED, 137% color conversion ratio was measured, which was 2.68 times higher than flat CCL. The resulting luminous efficiency of the white device with nanospheres patterned CCL (20.97 cd/A, 1000 cd/m$^2$) was higher than the efficiency of the original blue light source (19.66 cd/A, 1000 cd/m$^2$). The luminous enhancement was attributed to the strong light-coupling effect of the periodical nanostructures. Furthermore, the periodical nanospheres also increased the effective light path and provided an efficient approach to adjust the CIE coordinate.
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