Nanoparticle scattering layer for improving light extraction efficiency of organic light emitting diodes

Chur-Hyun Shin,[1] Eul Yong Shin,[1] Min-Hoi Kim,[2] Jae-Hyun Lee,[2,3] and Yoonseuk Choi[1,*]

[1]*Department of Electronics and Control Engineering, Hanbat National University, Daejeon, 305-719 South Korea*
[2]*Department of Global Convergence Studies, Hanbat National University, Daejeon, 305-719 South Korea*
[3]*Co-corresponding author: jhyunlee@hanbat.ac.kr*
[*]*ychoi@hanbat.ac.kr*

Abstract: Nanoparticle scattering layer based on polymer-metal oxide composite is successfully introduced to enhance the light extraction efficiency of organic light emitting diodes (OLEDs). We find that the density and the distribution of nanoparticles is the key factor to maximize the light extraction efficiency of pristine OLEDs by out-coupling the unusable light with the scattering film. In our experiment, 71 wt% of Al_2O_3 mixed with polymer matrix shows the increase of light extraction efficiency of 40%. This method is expected to play a critical role to create the low-power OLED application such as OLED lightings with simple fabrication process and low cost.

OCIS codes: (160.4236) Nanomaterials; (230.3670) Light-emitting diodes; (160.5470) Polymers; (290.5880) Scattering, rough surface; (310.6860) Thin films, optical properties.

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1. Introduction

Organic light emitting diodes (OLEDs) are now widely commercialized in the display market due to many advantages such as wide color gamut, possibility of making thin device and high contrast ratio. Nevertheless there are still several things to improve for obtaining high quality OLEDs and one of the most important issues is the light extraction efficiency of the device. Since OLEDs are composed of many sub-layers with different refractive indices, it is known that the typical light loss is almost 80% [1]. This is inevitable in general OLED system since the light emitting layer lies in the middle of the device and when the light travels throughout the multi-layers it suffers the various optical effects such as internal reflection, refraction, surface plasmon to prevent the light coming out from the device [2].

To reduce this intrinsic internal light loss, various optical solutions so-called light extraction techniques are viably studied to derive a maximum light from the device [3]. The basic concept of light extraction techniques is the addition of an optical structure to reduce the refractive indices mismatch between the layers. It helps to guide the leaked light at each interfaces of the device into the normal direction (front viewing point) which results in a high light efficiency. Various light extraction techniques has been developed so far. The representative techniques are using microlens array [4,5], silica microsphere [6,7], random surface [8], micro-cavity structure [9,10], photonic crystal [11], and scattering layer [12–17]. However, from the viewpoint of practical application, it is important to achieve a simple and large area adaptable process with high light extraction efficiency.

In this paper, we demonstrate the nanoparticle based light scattering films with simple one step process. Metal oxide particle and polymer matrix composite is used to create a thin and effective light scattering film as varying the mixing parameters. We found that the maximized light extraction efficiency can be obtained by optimizing the scattering film's haze and thickness properly. This is because that large haze can help to extract the trapped light at the interface while the thicker film is better to achieve a well-dispersed scattering film with higher haze. In our research, the density of nanoparticle and its distribution is the key factor to make the optimized scattering film. This approach shows that it can simply increase the efficiency of OLEDs up to 40% with simple fabrication process. We believe this technique could be highly applicable for large size OLED application such as the lighting system.

2. Fabrication of nanoparticle scattering film

Figure 1 shows the fabrication process of suggested scattering film with nanoparticles. At first, we mixed the nanoparticles, a polymer matrix and a solvent with different mixture ratio then it is spin-coated on the substrate and subsequently baked at 65°C for 1hour.This simple process is easily applicable for the flexible substrate due to its low temperature adaptability. Detailed fabrication process is depicted in Fig. 1. We had chosen alumina (Al_2O_3) as the fundamental metal oxide nanoparticle and a typical polystyrene as the polymer matrix. The material selection rule is that the refractive indices of Al_2O_3 and polystyrene (Sigma Aldrich, M_w: 192,000) are 1.7 and 1.6, respectively, which is suitable for increasing an out-coupling efficiency [18]. Furthermore, the degree of scattering is proportional to both scattering cross section (σ) and the number density (ρ) of scatterers. Hence the present condition may be enough to create the sufficient scattering effect as long as the product of sigma and rho is large enough [19]. The difference in refractive indices between nanoparticles and the host medium is relatively small at 0.1 from the material sheet, but the ‘effective’ difference could be bigger than 0.1 because of pores present in out film which eventually lower the effective refractive index of a host medium [16]. The basic diameter of nanoparticles is 50 nm, but without any treatment it easily aggregates which results in making a bigger lump. To prevent this aggregation, we have treated the surface of nanoparticles with n-octadecyltrimethoxysilane which has a high hydrophobicity in the solvent of 2-butanone (methyl ethyl ketone, MEK) [20]. The polystyrene was separately dissolved in MEK at 90 °C for 1 hour with the concentration of 0.5 wt% and these two solutions were mixed with ultrasonic vibration for 15 min. When it is cured, the thickness of films can be controlled precisely by the spin-coating speed and time.

We have made several nanoparticle scattering films on the glass substrate with different weight percentages (54, 71, 85, and 94 wt%). By varying the mixture ratio of solutions, we can obtain various scattering films with different optical characteristics. The key factor for making a good scattering film is that the mixture concentration and the thickness of the film. In order to get a well dispersed and flat scattering film, we should optimize the fabrication process with delicate selection of parameters. Details will be discussed in the next section.

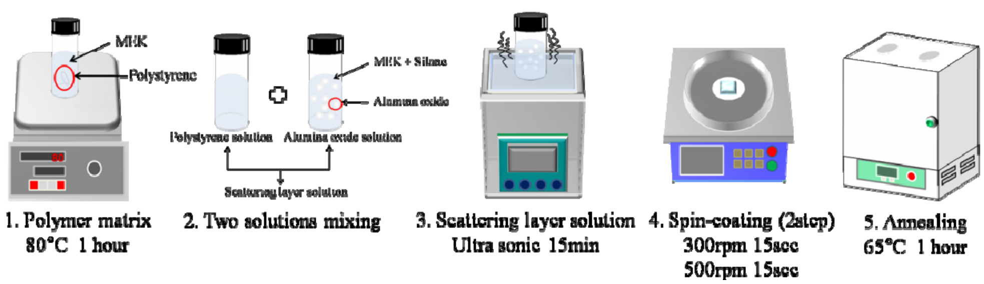

Fig. 1. Fabrication process of nanoparticle scattering film.

3. Analysis of nanoparticle scattering film

At first, we have checked the basic film characteristics of our nanoparticle scattering film. Figure 2 shows the optical microscopic images of the scattering films on the glass substrate which has a different mixture ratio (54, 71, 85, and 94 wt%). The images were taken by using the reflection mode of polarizing optical microscope (Olympus BX-43F).

At the low density of nanoparticle (54 wt%), the total volume fraction of nanoparticle is calculated as 22 vol% based on the material data. In this case the nanoparticle is rather not uniformly distributed and sometimes aggregates which results in the connected structure in the polymer matrix as shown in Fig. 2(a). However, this aggregation phenomena is exceedingly decreased as the volume fraction of nanoparticle is increased (i.e., more higher wt%). We believe that this is because the surface of silane-treated nanoparticles is tend to expel each other and higher volume fraction can help a well-dispersion of nanoparticles in the scattering film.

In our experiment, we can generally get a well-dispersed flat nanoparticle scattering film after certain high density (roughly over 71 wt% case). This is confirmed by the measured rms roughness value from atomic force microscopy observation. The roughness of the 71 wt% film is 131.7 nm. We also confirmed that this film can be easily made on the flexible substrate such as polyethylene terephthalate (PET) and polyethylene naphthalate (PEN). Thus, this method can be play a critical role in next-generation flexible OLED lighting devices.

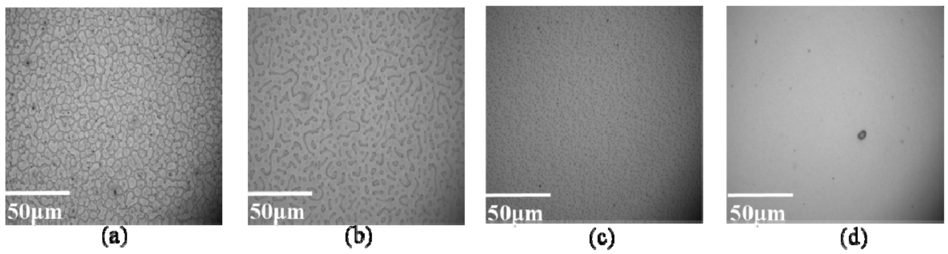

Fig. 2. Optical microscopic images of nanoparticle scattering films on bare glass substrate with different mixture ratio. Nanoparticle composition of each mixture is (a) 54wt%, (b) 71wt%, (c) 85wt%, and (d) 94wt%, respectively.

To investigate the optical characteristics of the scattering film, haze meter (NDH-5000) was used. In this experiment, we formed the nanoparticle scattering film on a bare glass substrate (without ITO). Note that the haze meter is equipped in an integrating sphere.

Table 1. Optical characteristics of nanoparticle scattering film

Nanoparticle Concentration	Total Transmittance (%)	Parallel Transmittance (%)	Diffused Transmittance (%)	Haze (%)	Thickness (μm)
Reference	91.4	90.7	0.7	0.8	
54wt%	89.2	41.6	47.5	53.3	0.7
71wt%	88.5	28.7	59.8	67.5	1.9
85wt%	87.2	19.9	67.3	77.2	2.7
94wt%	81.7	11	70.7	86.5	3.4
97wt%	76.9	7.1	69.8	90.7	7.5

Table 1 shows the optical characteristics of nanoparticle scattering film with different mixture ratio. In this table, total transmittance means the amount of measured transmitted light after passing through the sample gathered at the half-sphere integrator. Thus it represents how much absorption and reflection is occurred at the sample including a glass substrate. Total transmittance is decreased as the concentration of nanoparticles is increased since the thickness of the film is increased. In the case of 97 wt%, total transmittance was measured as 76.9% which means that there is some considerable light loss for using this film. To increase the light efficiency of OLED, higher transmittance is better. Total transmittance of reference sample was measured as 91.4% which means the reference film is highly transparent. Note that the reference sample is composed of the glass substrate and polymer film only.

Haze of the film can be calculated based on the ratio between concentrated and diffused light intensity. In principle, haze is defined as the measured diffused transmittance divided by total transmittance. To get a large scattering effect, the haze is the most important factor. It is known that the large haze can increase the light extraction efficiency of OLED by guiding the leaked light at the interface due to internal reflection [9, 12]. In our experiment, the haze is increased as the concentration of nanoparticle is increased as depicted in the Table 1. It is completely understandable since the nanoparticles in the film scatter the incident light. Thus, from the viewpoint of optical analysis, scattering film with 97 wt% is the most appropriate

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one. However, we found that this is not true in our experiment since the bigger concentration of nanoparticle lowers the total transmittance of the film as we discussed previously. Thus there exist an optimized condition (71 wt% in our experiment) to maximize the light extraction efficiency.

The maximum haze we get from our scattering film was the 90.7% which is very high compared to the other researches [15]. It means that various scattering films with large optical characteristic tunability (haze variation from 50 to 90%) can be obtained by using our technique. From the previous researches for internal light extraction techniques, various complicated manufacturing process or expensive high refractive index nanoparticle is required to get a large haze film. But in our method, we can easily get a rather large (~90%) haze in a simple manner and it is also tunable by simply changing the mixture ratio.

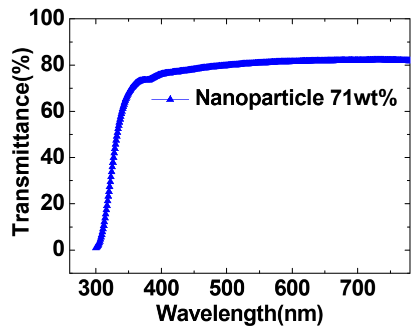

Fig. 3. Transmittance of nanoparticle scattering film with 71 wt% nanoparticle (Inset is the photograph of nanoparticle scattering film on the glass substrate).

Figure 3 shows the transmittance spectrum of 71 wt% nanoparticle scattering film on the glass substrate. In the visible range, the spectrum is almost flat which means the optical property does not change when it used as the lighting sources. If you put the scattering film on the alphabet letters as shown in the inset, the image is blurred due to the haze of the film.

4. Implementation for OLED and analysis

To check the light extraction effect of our scattering film, we have implemented the fabricated film onto the typical bottom-emission OLED device and measured the OLED characteristics.

The bottom anode substrate is the transparent indium tin oxide (ITO) glass which is patterned to have four sub-pixels by typical photolithography and etching process. On the ITO patterned glass, molybdenum oxide (MoO_3) of 2 nm thickness and N,N'-bis(1-naphthyl)-N,N'- diphenyl-1,1''-biphenyl-4,4'-diaminne (NPB) of 90 nm thickness were deposited as the hole injection layer and the hole transport layer, respectively. We chose a well-known tris(8-hydroxyquinolinato) aluminum (Alq_3) as the emissive material which has a center wavelength of 522 nm. The thickness of Alq_3 layer is 60 nm. We used aluminum of 100 nm as the top cathode material and a very thin lithium fluoride (LiF) layer (1.2 nm) was placed between the cathode and the emitting layer as the electron injection layer. This configuration is very typical one and we easily optimize the fabrication parameters for maximized light efficiency. All organic and metal layers were deposited by thermal evaporation in a vacuum chamber and the pressure in vacuum chamber was kept always between 10^{-6} and 10^{-7}Torr. The deposition rate of organic layers was between 0.5Å/s ~2Å/s and the metal layer was deposited through shadow mask, with the deposition rate of 4Å/s.

After the fabrication of OLED device, the scattering film was spin-coated on the opposite side of substrate. Fabrication of nanoparticle scattering film is same as we described in the previous chapter. Low annealing temperature of scattering film at 65°C doesn't make any

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change OLED device characteristics. We first measured the current density-voltage-luminance (*J-V-L*) characteristics of the devices to check the light emission property of the device (Photo Research PR-650). Especially, to examine the light scattering and gathering effect, the electroluminescence (EL) was measured with an integrating sphere. For the measurements, the emitting side of OLED devices were faced on the edge of the port of integrating sphere. Therefore the emission from the edge of glass substrates cannot enter into the integrating sphere.

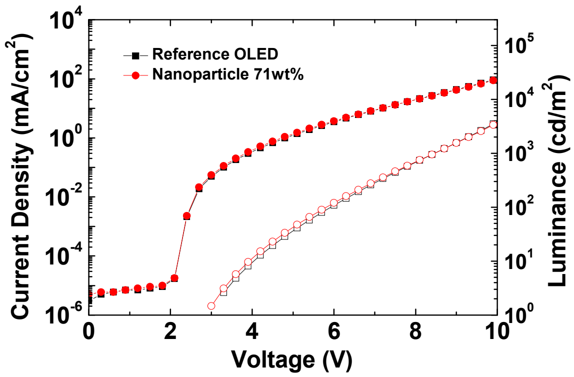

Fig. 4. The current density-voltage-luminance (*J-V-L*) characteristics of OLED devices with (red circle) and without (black square) scattering film.

Figure 4 shows the *J-V-L* characteristics of bottom-emission OLEDs with or without nanoparticle scattering film. Hole injection barrier between ITO and hole transporting layer can be effectively reduced by MoO_3 layer insertion due to the large vacuum level shift by the interface dipole formation [21,22]. Two characteristic curves in Fig. 4 showed almost identical *J-V-L* characteristics. It means that the additive process for the formation of scattering film on OLEDs doesn't change the electrical characteristics of pristine OLED devices. From the measured luminance on vertical direction, turn-on voltage at 1 cd/m^2 and operating voltage at 1000 cd/m^2 were determined as 3.0 V and 8.5 V, respectively. This *J-V-L* characteristic is very typical one compared to the conventional OLED devices. The current efficiency of reference OLED was 3.8 cd/A at the current density and luminance of 53 mA/cm^2 and 2000 cd/m^2, respectively.

In the vertically measurement setup, luminance of OLEDs with nanoscattering film wasn't enhanced because the parallel transmittance of scattering film is decreased as shown in Table 1. For the detailed measurement of luminance, we used an integrating sphere setup to compare the OLEDs with or without nanoparticle scattering film. This is because the typical vertical measurement cannot include the angular distribution of extracted light from OLEDs.

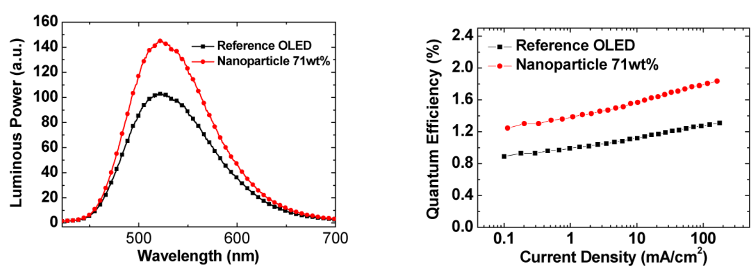

Fig. 5. (a) EL spectrum (b) EQE of OLEDs with (red circle) and without (black square) the nanoparticle scattering film (with 71 wt% nanoparticle).

Figure 5(a) shows the EL spectra of OLED devices with or without nanoparticle scattering film which was measured by an integrating sphere measurement setup at the applied voltage of 8 V. Two EL measurements show same spectrum with center wavelength of 524 nm since the nanoparticle scattering film has a nearly flat transmittance at the visible range as shown in the Fig. 3. As shown in Fig. 5(a), total light emission of OLED was increased at the peak of spectra almost 40%. We could achieve the maximized increase of outcoupling efficiency (i.e., the enhancement factor [4–6]) at the 71 wt% of nanoparticle concentration. If we increase the concentration of nanoparticle up to 97 wt%, for instance, only 24.5% of enhancement factor was achieved because the total transmittance of film is reduced as we discussed in the previous section. External quantum efficiency-current density of OLED devices is shown in Fig. 5(b). EQE of OLEDs with or without the scattering film at 53 mA/cm^2 was 1.2% and 1.8%, respectively. Enhanced EQE is calibrated with the enhancement factor which is measured with the integrating sphere measurement setup.

Figure 6 shows the normalized angular intensity distribution of OLED with nanoparticle scattering film. Typical angular intensity distribution of OLED devices with ITO/NPB/Alq_3/Al layers has been reported as the Lambertian distribution because these devices have low reflectance at ITO electrode side and large recombination zone [9,16]. The angular emission intensity of OLED with scattering film in our experiment was nearly Lambertian distribution because the nanoparticles have a random distribution in the film. This means the use of our film can make a Lambertian-like plane light source which is usually considered as the best lighting source.

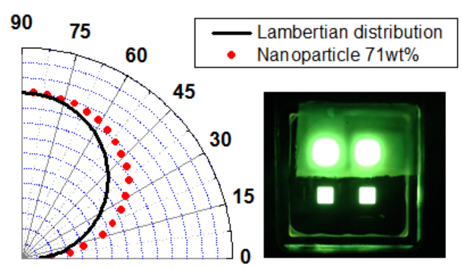

Fig. 6. Angular intensity distribution of OLEDs with (red circle) or without (black square) nanoparticle scattering film. (Solid line is Lambertian distribution) Inset photograph is the OLEDs with (upper devices) and without (lower devices) nanoparticle scattering film.

5. Summary

In summary, we investigated the OLED light extraction method based on the polymer-metal oxide composite scattering film. Uniform and transparent composite film was successively fabricated with polystyrene and Al_2O_3 nanoparticles in the various mixing concentration to control the haze of scattering film. The maximized enhancement factor of 40% at 524 nm was achieved by the proposed scattering film with the concentration of 71 wt% Al_2O_3 nanoparticles. The fabrication process is very simple and also easy to control the characteristic of the film which can be adapted to various applications for the large-sized, flexible OLED lighting devices.

Acknowledgments

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