

Enhancement of radiative efficiencies of near-ultraviolet organic light-emitting diodes by localized surface Plasmon resonance enhancement effect

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Abstract. Near-UV emission organic light emitting diodes (OLEDs) containing silver (Ag) nanoparticles (NPs) were fabricated to improve their radiative efficiencies by the localized surface plasmon resonance (LSPR) enhancement effect. The samples studied were simple bi-layer structures consisting of an active layer and a hole-transporting layer (HTL). Poly[(9,9-dihexylfluoren-2,7-diyl)-co-(1,4-dimethyl-benzene-2,5-diyl)] (PF-DMB) was used as a UV emission material, whose emission peaking-wavelength is about 395 nm. Ag NPs were inserted between ITO and HTL, whose absorption peaking wavelength is corresponding to about 395 nm. Thus, the electroluminescence (EL) intensity of UV OLEDs containing Ag NPs was enhanced to about 2.5 times as large as that without Ag NP by the LSPR enhancement effect.

1. Introduction

Most of the research topics on organic light-emitting diodes (OLEDs) concentrate on the OLEDs operating in the visible light regime, because they are applied to flat panel displays and white light sources [1]. On the other hand, some research on OLEDs operating in the ultraviolet regime were reported [2, 3]. However, their radiative efficiencies are not excellent because high efficient carrier injection into large-bandgap emissive materials is difficult. In addition, they were fabricated using a vacuum evaporator because they consisted of low-weight molecular materials. Thus, it is easy to fabricate multiple-layer structures containing electron- and hole-transporting layers plus electron- and hole-injection layers for improving carrier injection into the wide-bandgap emissive materials. On the other hand, polymer-based OLEDs are fabricated using wet-process. It has an advantage to reduce the production-cost lower than that using vacuum evaporators. However, it is very difficult to fabricate multiple-layer structure OLEDs. Recently, localized surface plasmon resonance (LSPR) enhancement effect was energetically studied because LSPR was effective to improve the radiative efficiencies of LEDs [4-7]. LSPR is known that if the nanostructure is smaller than the wavelength of light and the free electrons can be displaced from the lattice of positive ions and collectively oscillate in resonance with the light. LSPR is also used in solar cells to enhance the energy conversion efficiencies [8].

In this research, near-UV emission polymer-based OLEDs containing silver (Ag) nanoparticles (NPs) were fabricated to improve their radiative efficiencies by the LSPR enhancement effect. Ag NPs have the potential to improve UV radiative efficiencies from OLEDs because the LSPR wavelength of

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Ag NPs depends on the diameter of Ag NPs, thus LSPR wavelength can be tuned to the near-ultraviolet and visible regions [7].

2. Experimental

2.1 Extinction spectra of Ag NPs

Ag NPs were deposited on indium-tin-oxide (ITO)-coated glass substrates using 3-(Aminopropyl) triethoxysilane (APTES) [9]. The diameter of Ag NPs was 10 nm. Figure 1 shows atomic force microscope (AFM) images of the two sample surfaces; one contains only APTES, while another contains APTES and Ag NPs. The averaged surface roughness of the sample without APTES was less than 1 nm, while that of the sample with APTES was about 10 nm. This indicates that Ag NPs were uniformly deposited on the sample surface using APTES because the averaged roughness is equal to the diameter of Ag NPs. Figure 2 shows extinction spectra of the two samples; one contains APTES and Ag NPs, another contains only APTES. It is very clear that the absorption peak at around 390-nm was caused by Ag NPs in the sample containing Ag NPs. Thus, we concluded that Ag NPs were uniformly deposited on the ITO electrode and revealed absorption peaking wavelength at around 390 nm.

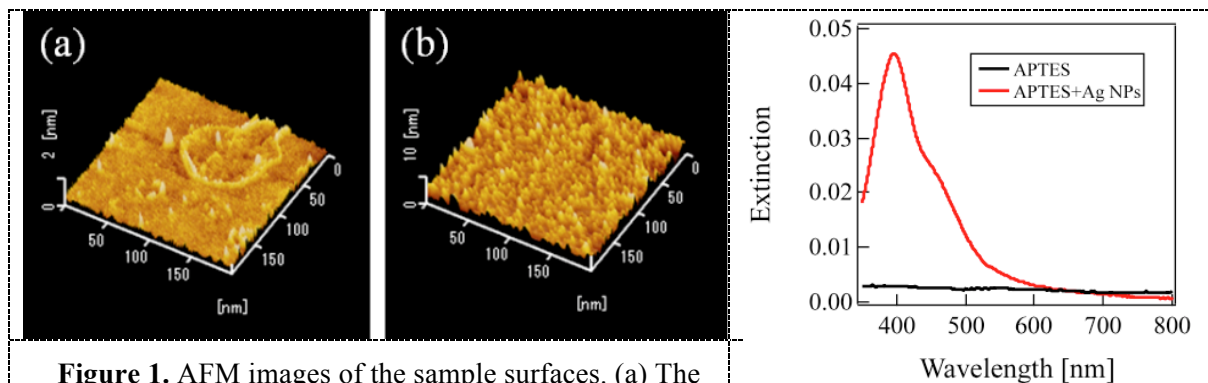


Figure 1. AFM images of the sample surfaces. (a) The sample contains only APTES, while (b) contains APTES and Ag NPs. The averaged surface roughness of (b) corresponds to the diameter of Ag NPs

Figure 2. Extinction spectra of samples. Red line denotes the sample containing APTES and Ag NPs, while black line is only APTES

2.2 Fabrication of OLEDs

An emissive layer and a hole-transporting layer (HTL) were fabricated on the Ag NPs sheet by using spin-coating method. Thus, the samples studied were simple bi-layer structures. The following two polymer emissive materials were used in each OLED: Poly[(9,9-dihexylfluoren-2,7-diyl)-co-(1,4-dimethyl-benzene-2,5-diyl)] (PF-DMB) reveals a UV emission at 395 nm, while poly[(m-phenylenevinylene)-alt-(2,5-dihexyioxy-p-phenylenevinylene)] (PPV) reveals a green emission at around 500 nm. This enables us to evaluate the LSPR enhancement effect because the emission of PF-DMB corresponds to the extinction peak of Ag NPs. Thus, the UV emission of PF-DMB should be enhanced by LSPR, while the emission of PPV should not be changed. In addition, poly(3,4-ethylenedioxythiophene)-polystyrenesulfonic acid (PEDOT:PSS) was used as a hole-transporting material. Finally, aluminium (Al) was vacuum deposited on the emissive layer as cathode metal. Consequently, two kinds of OLEDs were fabricated as follows and compared their emissions affected by LSPR enhancement effect.

Sample A ITO/PEDOT:PSS/PF-DMB/Al,

Sample B ITO/PEDOT:PSS/PPV/Al.

Ag NPs were inserted between ITO and PEDOT:PSS layers. To evaluate the LSPR enhancement effect originating from Ag NPs, we fabricated the samples A and B without Ag NPs. Note that Ag NPs are known to suffer oxidation, which leads to degradation of the LSPR enhancement effect in OLEDs. However, OLEDs are usually sealed not to expose to the air because organic materials are easily

destroyed due to the oxidation and moisture. Thus, Ag NPs in OLEDs are also protected against the oxidant effect by the sealing effect. Consequently, the oxidant effect has little effect on Ag NPs.

3. Results and discussion

Figure 3(a) shows the injection current density dependence of luminance of sample A. It is very clear that the luminance of the sample containing Ag NPs rapidly increased when the injection current was more than 220 mA/cm^2 . Figure 3(b) shows EL spectra of the sample A when the injection current density was 270 mA/cm^2 . UV-EL signals from PF-DMB were clearly observed in the both samples. In addition, the shape of both EL spectra is very similar. These results indicate that the OLEDs operating in the near UV regime were successfully fabricated. In this case, it is worthy of notice that the EL intensity of UV OLEDs containing Ag NPs was enhanced to about 2.5 times as large as that without Ag NPs. Consequently, this leads to an increase of the external quantum efficiency from $2.27 \times 10^{-4}\%$ to $5.42 \times 10^{-4}\%$ at the current injection of 270 mA/cm^2 . Thus, the near UV EL emission was enhanced by the LSPR enhancement effect originating from Ag NPs.

In order to verify the above result, EL properties of sample B were shown in Fig. 4. Sample B should emit green light from PPV, which does not correspond to the extinction wavelength of Ag NPs. The luminance-current density properties shown in Fig. 4(a) reveal that the luminance did not drastically increase in the sample containing Ag NPs. In addition, EL spectra when the injection current density was 370 mA/cm^2 were not affected by the LSPR enhancement effect originating from Ag NPs as shown in Fig. 4(b). These results clearly demonstrate that the green emission was not enhanced by the LSPR enhancement effect. Thus, we conclude that the near UV emission was successfully enhanced by the LSPR enhancement effect because the extinction peaking-wavelength of Ag NPs corresponds to the emission wavelength of PF-DMB.

4. Conclusions

The localized surface plasmon resonance (LSPR) enhancement effect was applied to the near UV emission from polymer-based OLEDs for enhancing the near UV emissions. The extinction peaking-wavelength of Ag NPs whose diameter is about 10 nm was tuned to the near UV regime. As a result, the EL intensity of the UV OLEDs containing the Ag NPs was enhanced about 2.5 times as large as that without Ag NPs. This demonstrates that the LSPR enhancement effect is simple and useful method to enhance the UV emission from polymer-based OLEDs because the high-efficient carrier injection into wide-bandgap emissive materials is difficult in the polymer-based OLEDs.

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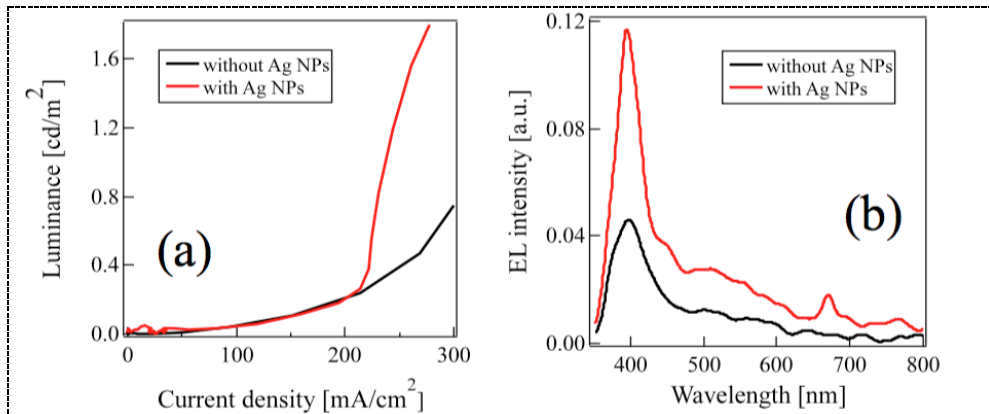


Figure 3. (a) Injection current density dependence of luminance of sample A. Red line denotes the sample containing Ag NPs, while black line denotes the sample not containing Ag NPs. (b) EL spectra of sample A when the same current density of 270 mA/cm^2 was injected. Red line denotes the sample containing Ag NPs, while black line denotes the sample not containing Ag NPs.

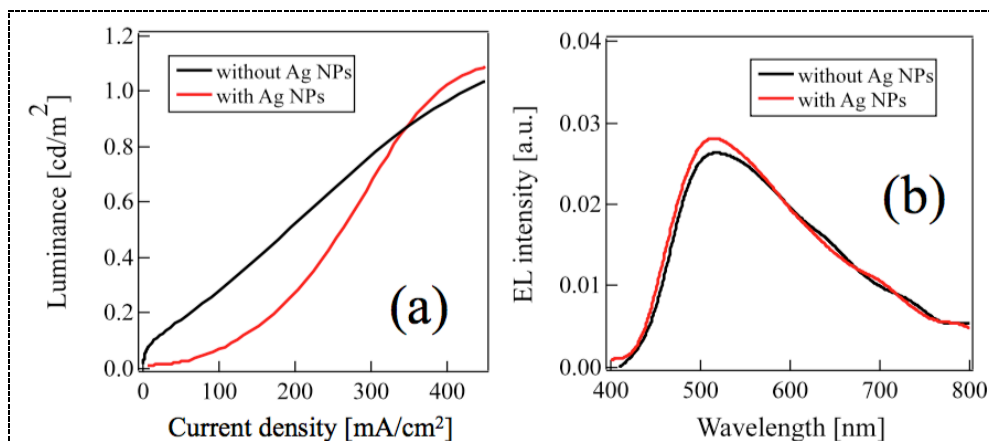


Figure 4. (a) Injection current density dependence of luminance of sample B. Red line denotes the sample containing Ag NPs, while black line denotes the sample not containing Ag NPs. (b) EL spectra of sample B when the same current density of 370 mA/cm^2 was injected. Red line denotes the sample containing Ag NPs, while black line denotes the sample not containing Ag NPs.