Synchronized surface plasmon generation and scattering in organic light emitting diodes: measurements removing optical interference effect

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Abstract. It has been believed that the energy transfer of one exciton arising in an organic layer creates one SPP on a proximally-positioned metal surface. However, because excitons in the organic layer are close to one another, there is the possibility that multiple SPPs are generated in phase, entering an appearance of constructive interference among the scattered electromagnetic waves. This should lead to an increase in SPP scattering probability effectively. To investigate the possibility and light enhancement associated with this, we prepared a device consisting of Alq₃ on a quarter-wavelength dielectric multilayer film/glass as a reference instead of the usual Alq₃/glass substrate. This reference device eliminated the influence of complicated optical interference, and made it possible to calculate SPP-mediated light enhancement accurately. The contributions of SPPs and non-radiative components to light emission were adjusted in the calculation as the results corresponded with the measured enhancement dependence on Alq₃ thickness. As a result, it was found that the SPP scattering rate was larger than the ordinary calculation based on the assumption that excitons create SPPs randomly. In-phase energy transfer from excitons to SPPs is supported by evidences obtained from this study.

1. Introduction
Surface plasmon polariton (SPP)-mediated light emission which occurs in organic light emitting diodes is of considerable practical concern. SPPs essentially become ohmic loss on the surface of a metal electrode. SPPs are essentially light waves arising from the strong interaction between electromagnetic fields and the free electron collective oscillations along the metal–dielectric interface. In addition to the intrinsic Ohmic losses of metals, scattering can be a major loss factor that limits the propagation length of SPPs. This scattering occurs at naturally formed submicrometre-scale roughness on the metal surface, and SPPs could be extracted as light again.

So far, we have investigated the possibility of the generation and scattering of SPPs in phase in organic light emitting diodes [1]. Due to excitons in the organic film being in close proximity to each other, SPPs can be generated simultaneously, and scattered synchronously, which should lead to an increase in the scattering probability of SPP due to the constructive interference of the electric fields of SPPs. In examining this possible phenomenon, the optical interference of fluorescence occurring in the organic film on a glass which was used as a reference was rather complicated, because emitted light from the organic layer entered the glass substrate, and it was difficult to calculate the influence. That is, optical interference occurring in the reference device stood in the way of the experiments. Consequently, ambiguity has remained concerning the probability of constructive SPP generation and scattering. In
this study, we eliminated this obstacle by using a quarter-wavelength dielectric multilayer film (DMF) as a reference. It was found that the SPP generation in phase was probable in organic layers through the experimentally obtained enhancements and calculations.

2. Device fabrication and measurements of the enhancement
To avoid the optical interference effect, we deposited Alq3 on a quarter-wavelength DMF/glass substrate as a reference. The DMF consisted of quarter-wavelength thick alternating SiO2 and TiO2 layers. The reflectivity of the DMF was set at almost 100% at 530 nm where Alq3 had the maximum intensity. We made Alq3/Ag/glass to investigate the SPP-mediated enhancement. Angle dependence of the luminescence was measured by rotating devices with the use of a 405-nm laser diode and a luminance meter. Fluorescence emitted up to a rotating angle of 15 degrees from the frontal direction was summed up with all devices. The coefficient of reflectance of the dielectric multilayer mirror could be assured to be -1 in the range of those angles. Input and reflection light power of the laser diode were measured, and the correction of the absorptance was performed for each measurement result. Following this step, light enhancement was acquired by dividing the total light output up to 15 degrees measured for Alq3 on an Ag/glass by that of Alq3 on a DMF/glass while the Alq3 thickness was changed. At the same time, using an integration sphere, we measured the internal quantum efficiency of Alq3 formed on frosted glasses. The surface of a glass substrate was treated with sand-blasting, and was unlevelled because the internal quantum efficiency of organic film on a flat glass was subject to an optical interference effect inside the organic layer. Measured enhancements are shown in figure 1. They were 1.2, 1.0, and 0.6 for 90 nm, 110 nm, and 145 nm, respectively, on Ag.

3. Results and discussion
3.1. Enhancement based on an ordinary picture that one exciton creates one SPP
To know the contribution of SPP-mediated emission, we calculated theoretical values corresponding to the measured enhancements. Thus, the sum of original radiation and that originating from the scattering of SPP created by energy transfer of an exciton was obtained first for the structure of an organic layer on a metal film.

In obtaining energy transfer from an exciton to radiation \((b_T)\), SPP \((b_{sp})\), and lossy wave \((b_{isw})\) in the organic layer/metal film structure, they are calculated from the following equations [2].

\[
b_T(k_1, z) = \int_0^{k_1} W(k_1, k_{jj}, z) dk_{jj},
\]

\[
b_{sp}(k_1, z) = \int_{k_1}^{2k_{sp}-k_1} W(k_1, k_{jj}, z) dk_{jj},
\]

\[
b_{isw}(k_1, z) = \int_{2k_{sp}-k_1}^{\infty} W(k_1, k_{jj}, z) dk_{jj},
\]

where \(k_1\): wavenumber in the organic layer (in this case, wavenumber corresponding to 530 nm), \(k_{jj}\): \(x\) component of \(k_1\) that is parallel to the metal surface, \(k_{sp} = \frac{\omega_p}{c} \sqrt{\frac{\varepsilon_i \varepsilon_m}{\varepsilon_i + \varepsilon_m}}\) (\(\varepsilon_i\) and \(\varepsilon_m\) are the permittivity of the organic material and metal, respectively), and \(W\): dissipation of exciton energy per unit time, \(z\): position of exciton in the direction normal to the metal surface, the origin of which was defined at the interface of the metal and organic layer, and \(d\): thickness of the organic layer. Experimentally obtained light output in this study is given by eq. (4), where \(k_h\) is the value of \(k_{jj}\) corresponding to the maximum rotating angle (i.e. 15 degrees).

\[
b_{rh}(k_1, z) = \int_0^{k_h} W(k_1, k_{jj}, z) dk_{jj}.\]

With respect to the emission based on SPP scattering, we used the following eq. (5) instead of eq. (2), because the use of eq. (2) results in \(k_{jj}\) being larger than \(k_1\), meaning that the wavelengths of SPP scattering-based radiation become shorter than the wavelength set in the enhancement measurements. Thus, it is necessary to calculate the contribution from SPPs to light output using eq. (5), and not by eq. (2).

\[
b_{sp}(k_1, z) = \left\{1 - (1 - P_{scat})^N\right\} \frac{T_0}{T_{max}} \int_{2k_{sp}-k_1}^{\infty} W(k_1', k_{jj}, z) dk_{jj}'.\]
In eq. (5), $\lambda_{\text{max}}$ is the maximum emission wavelength, which we assumed 670 nm for Alq3 in the calculation. The intensities of Alq3 became comparatively weak at the wavelength compared to the peak intensity. The scattering rate of SPPs at the wavelength, $P_{\text{scat}}$, was calculated using the average height and full-width at half-maximum of a bump, and the average period between the bumps measured by AFM [2], which were 5 nm, 50 nm, and 100 nm, respectively. $N$ is the number of scattering, which was obtained from the propagation distance of the SPP attenuating to $1/e$ due to ohmic loss divided by the measured average period. The propagation distance of Ag was calculated to be 4.2 $\mu$m at 530 nm. $T_0$ is the average transmissivity of light between 0 to 15 degrees emitted at $z = 0$ and appearing in the air. SPP scattering occurred at $z = 0$, and the extracted light in the air was assumed to be affected by the optical interference inside the organic film.

The portion of light emission over the original total exciton energy $R_m$ is given by eq. (6).

$$ R_m = \left( \frac{1}{d} \right) \int_0^d \frac{R_{\text{bph}}}{(b_{r}+b_{\text{bph}}+b_{\text{lw}})} \, dz. \quad (6) $$

Next, we calculated radiation for Alq3 on the DMF/glass not having such losses as SPP generation and lossy surface wave. The portion of light emission over the original total exciton energy $R_d$ is given by the radiation summing up to the maximum rotation angle to the total radiation, as is shown in eq. (7).

$$ R_d = \left( \frac{1}{d} \right) \int_0^d \frac{b_{\text{ph}}}{b_{r}} \, dz. \quad (7) $$

Because the original exciton energy was the same with respect to two structures, the ratio of $R_m$ and $R_d$ becomes theoretical enhancement. Figure 1 shows the calculated values (solid diamonds), and we found that numerical calculations could not account for the measured enhancements. In the case of no existence of SPP-mediated light emission of non-radiative components, the aforementioned discussion holds true, even when the internal quantum efficiency of Alq3 is not 100%.

![Figure 1: Measured and calculated enhancements of Alq3 at 530 nm. Output light of Alq3 on Ag emitted to a cone with the half-angle of 15 degrees was divided by that of Alq3 on DMF. Original radiation and that originating from the scattering of SPP created by energy transfer of an exciton were taken into account in the calculation of $R_m$.](image)

3.2. Calculation taken into account of possible generation of SPP in phase and scattering

It is understood that one SPP is created on a metal surface by energy transfer from one exciton in an organic layer. There is a possibility that multiple SPPs are generated in phase, leading to constructive interference occurrence among the scattered electromagnetic waves. The distance between the closest organic molecules is of the order of ~nm. It is possible that SPPs are generated simultaneously rather than separately, and the scattering rate of SPPs should become high compared with the case of individual SPP creation. Assume a system consisting of $N$-SPPs. The total electric field is expressed as $\sum_{j=1}^{N} E_j e^{i\theta_j}$ using individual phase $\theta_j$ of generated SPPs. When SPPs have the same phase, total scattering energy is proportional to $P_{\text{scat}} N^2 E^2$ (i.e. $E = E_j$). This is $P_{\text{scat}} N^2 E^2$ in the case of no phase
synchronization, meaning that the substantive scattering probability results in \( N \) times the probability with out-of-phase in association with in-phase SPP creation.

In addition, we allowed for SPP-mediated light emission of non-radiative components, which can be converted to light after becoming SPPs, and by their scattering on the metal surface. We assumed that these two processes occurred in the experiments. In that case, \( b_{\text{sph}} \) and \( R_m \) is given by eqs. (8) and (9).

\[
b_{\text{sph}}(k_1, z) = \{1 - (1 - XP_{\text{scat}})^N\} \times T_0 \times \int_{2\pi m/\lambda_{\text{max}}}^{k_1} W(k_1', k_1, z) \, dk_1',
\]

\[
R_m = \eta \left( \frac{1}{d} \right) \int_0^d \left( \frac{b_{rh} + b_{\text{sph}}}{b_{rh} + b_{\text{sph}} + b_{\text{low}}} \right) \, dz + (1 - \eta)YT_0,
\]

where \( \eta \) is the internal quantum efficiency, which was estimated to be 20% from an integration sphere used-measurements using Alq\(_3\) on a sand-blasted glass as a sample. The process of energy conversion from non-radiative components to photon included an unknown factor. Namely, the probability of energy transfer from the non-radiative components to SPPs was unclear. Thus, the non-radiative component-to-SPP energy transfer rate times subsequent SPP scattering rate at bumps was represented by \( Y \). \( R_d \) was the same as shown in eq. (7), because the internal quantum efficiency was multiplied for both \( b_{rh} \) and \( b_r \) in the integral in the right-hand side of eq. (7).

Figure 2 shows the calculated results (solid squares) assuming that \( X = 10 \), and \( Y = 8 \times 10^{-3} \), and they favoured the measured results. \( X = 10 \) meant that 10 excitons created SPPs simultaneously. Here, a question arises as to what determines the number of in-phase excitons. The answer to the question might be in random lasers. Random lasers based on a suspension containing dyes and silver nanoparticles in methanol was reported by et al., the properties of which were dominated by an enhanced photon scattering mechanism induced by the surface plasmons [4]. Although we don’t use such a suspension containing silver particles, multiple energy exchange between excitons and SPPs has the possibility of generating the local coherence.

![Figure 2. Measured and calculated enhancements of Alq\(_3\) at 530 nm. It was assumed that SPPs were created synchronously from excitons, and that the non-radiative components were converted to light through SPP generation and scattering. Assuming that \( X = 10 \) and \( Y = 8 \times 10^{-3} \) (solid squares), calculated data corresponded reasonably well with the experimental data. Open squares show calculated results on the assumption that \( X = 1 \) and \( Y = 3 \times 10^{-2} \).](image)

4. Conclusion
The contributions of SPPs and non-radiative components to light emission were adjusted as the result corresponded with the measured enhancement dependence on the Alq\(_3\) film thickness. As a result, it was found that the SPP scattering rate was larger than the ordinary calculation based on the assumption that excitons create SPPs randomly. In-phase energy transfer from excitons to SPPs is supported by evidences obtained from this study.

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