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# Time-resolved photoluminescence study of tris(8-hydroxyquinolinato) aluminium with surface plasmon resonance of Ag nanoparticles

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ABSTRACT

Surface plasmon resonance (SPR) of Ag nanoparticles (NPs), and its emission enhancement properties are investigated by time-resolved photoluminescence spectroscopy using tris(8-hydroxyquinolinato)aluminium ($Alq_3$), which is generally applied in organic light-emitting diode, as the emitter. 5-nm-thick Ag island-films were fabricated, and annealed at various temperatures to vary the size of the Ag NPs. The peak position of the SPR band in the absorption spectra of Ag NPs blue-shifts with increasing annealing temperature, that is, the SPR frequency is controlled by the NP size. Comparison of the photoluminescence (PL) spectra of $Alq_3$ with and without Ag NPs annealed at 150 °C indicates 1.2-fold enhancement of PL for $Alq_3$ with Ag NPs compared to the reference $Alq_3$. From the temperature dependence of the PL intensity and lifetime of $Alq_3$ with Ag NPs, we evaluated the degree of enhancement of the radiative recombination rate in the presence of the localized surface plasmon of Ag NPs, in comparison with the competitive non-radiative quenching process.

## 1. Introduction

Localized surface plasmon (LSP) is the collective vibration of free electrons in metal and LSPs are generated when metal nanoparticles and nanostructures are irradiated with the electromagnetic waves. In case of an ideal metal thin film with a perfectly flat surface, it is impossible to generate the LSP, because there is no coupling between the surface plasmon polaritons and radiative mode in space. But the real surface of a metal thin film fabricated by physical vapor deposition has a certain roughness, and therefore, LSP generation at the metal film interface and the extraction of the light from LSP mode are also possible by the scattering event which induces change in momentum. When the frequency of the external electromagnetic wave coincides with the surface plasmon resonance (SPR) frequency, effective coupling between the light and LSP occurs, leading to enhancement of the local electric field and emission amplification [1–4]. The basic principle of luminescence enhancement due to LSP coupling can be explained as follows: (1) When an emissive material (without plasmonic material) is excited by light source, a part of the absorbed energy is emitted and the other part is dissipated as heat by non-radiative processes; in this case, the internal quantum efficiency of the emissive material is not equal to 1. (2) If there is a plasmonic material such as metal nanoparticles in the vicinity of the emissive material, the absorbed energy can be transferred to the LSP states at a rate much faster than the non-radiative processes in case the emission and the LSP energies are in resonance condition. (3) The energy transferred to the LSP, in other words, the excited LSP, can be extracted as light with a scattering event which induces a change in momentum. Therefore, the overall emission can be enhanced using LSP, instead of getting spent by the non-radiative quenching process.

Fukuura reported the enhancement effect of the surface plasmon on tris(8-hydroxyquinolinato)aluminium ($Alq_3$) emission using large (~300 nm) Ag nanoparticles (NPs) with various interparticle separations, which were changed by a suitable annealing and deposition method, and demonstrated 4.5 times enhancement of luminescence efficiency for an organic light-emitting diode with closely packed Ag NPs. The results suggested the possibility of long-range interaction inducing the enhancement of photoluminescence (PL) in case of larger NPs [5]. Salah et al. synthesized pure $Alq_3$ nanoparticles doped with various metal ions and studied their PL properties from the viewpoint of surface plasmonic enhancement. The Ag-doped $Alq_3$ NPs showed 2 times stronger emission than that of pure $Alq_3$, which is attributed to the SPR of Ag ions [6].

Although there have been several studies on the amplification of emission of $Alq_3$ combined with a metal surface or nanostructure [7], the enhancement dynamics including the competition between the

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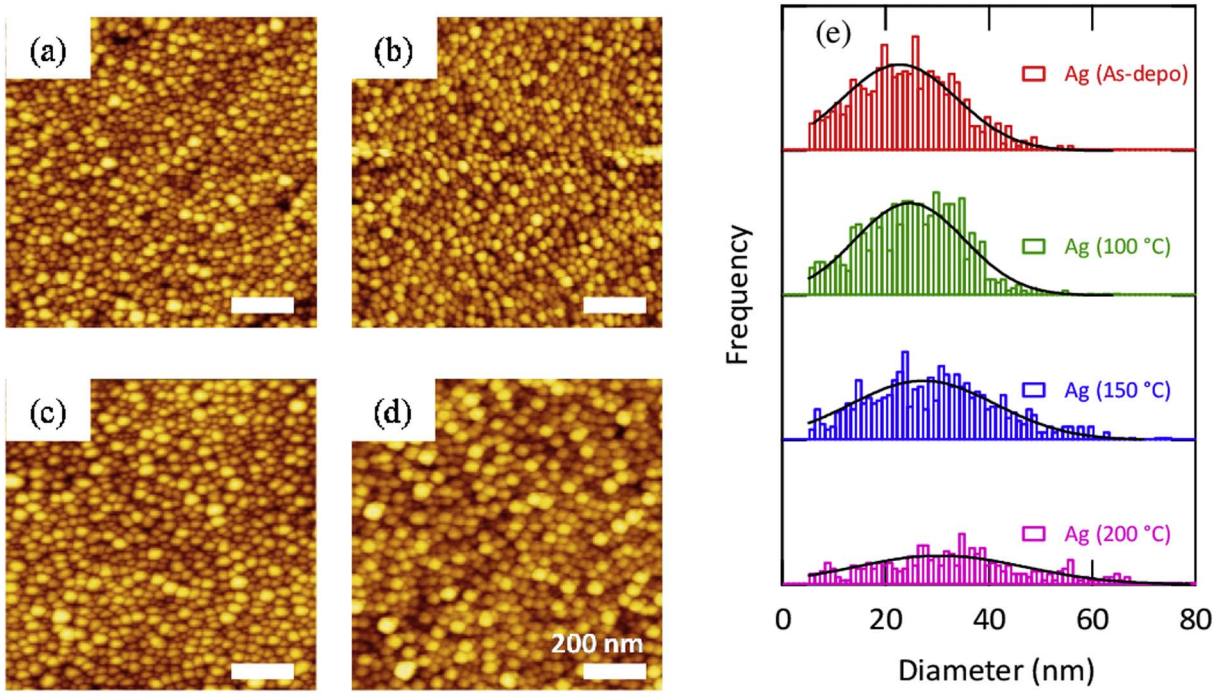


**Fig. 1.** AFM images of (a) as-deposited Ag NPs, and Ag NPs annealed at (b) 100 °C, (c) 150 °C, and 200 °C. (e) Histogram of the average particle diameter of Ag NPs for each sample obtained by the AFM image analysis.

energy transfer to the LSP mode and other non-radiative quenching processes, which can be probed by time-resolved photoluminescence (TRPL) measurements is still not clear. In many cases, the observation of a fast PL lifetime in the presence of metal can be treated as an evidence for the LSP-induced PL enhancement. However, this kind of lifetime acceleration might also be caused by the rapid non-radiative relaxation towards metal states acting as a heat bath. Therefore, the distinguishing the radiative and non-radiative contributions from the observed PL lifetime using temperature-dependent PL intensity and lifetime is necessary to discuss the LSP-induced PL enhancement.

In this work, TRPL studies of $Alq_3$ with Ag NPs fabricated by annealing an Ag island film was carried out and the balance between the PL enhancement by LSP and non-radiative quenching process was investigated. The sample was annealed at various temperatures for varying the size and shape of the Ag NPs, so as to control the energy of the SPR. The trends of temperature dependence of PL intensity of $Alq_3$ with and without Ag NPs samples are significantly different, suggesting that the LSP states of Ag NPs play a key role in the enhancement or quenching of emission.

## 2. Experimental method

$Alq_3$ with Ag NPs films and reference $Alq_3$ films were deposited on synthetic quartz substrates via resistive thermal evaporation of 99.99% pure Ag wire and $Alq_3$ powder, respectively, at room temperature. A 5 nm-thick Ag film, which was still an island-like film was treated as layers of “Ag NPs” and used as a plasmonic material. The thickness of the $Alq_3$ film used as the emissive material was 60 nm. The thicknesses of Ag and $Alq_3$ films were monitored by a quartz crystal oscillator. The base pressure of the Ag NPs deposition process was below $4.4 \times 10^{-4}$ Pa, and that of the $Alq_3$ film deposition was $4.0 \times 10^{-4}$ Pa. After deposition, the Ag NP film was annealed at 100, 150, 200 °C for 1 h in the deposition chamber, without breaking the vacuum. The surface morphology of the Ag NPs was observed over an area of 1 μm × 1 μm using an atomic force microscope (AFM, Hitachi, AFM5100N). Absorption spectra were obtained in the range of 200 nm to 800 nm using a spectrophotometer. The TRPL spectra were collected using a streak-camera (Hamamatsu, C4334) equipped with a monochrometer. The samples were mounted on a cold-finger of a closed-cycle He cryostat, and they were excited by second-harmonics of a mode-locked Ti:Sapphaire laser (400 nm), the time duration of which was approximately 100 fs. The excitation power density was 1.2 W $cm^{-2}$. The time-resolution of this measurement was founded to be 50 ps after deconvolution analysis.

## 3. Results and discussion

Fig. 1 shows the AFM images exhibiting the surface morphology of (a) as-deposited Ag NPs, and those annealed at (b) 100 °C, (b) 150 °C and (d) 200 °C. It was found that the grain size of Ag increased after annealing [8,9]. Ag NPs are expected to have a flat and oblate shape because there is almost no change in height between these samples. The melting point of Ag NPs becomes lower than that of bulk when their physical thickness is less than 10 nm [10]. According to previous reports, the melting point of 5-nm-thick Ag NPs is estimated to be ~300 °C. The highest annealing temperature used in this study was 200 °C, which is lower than the estimated value. However, Ag atoms diffused between adjacent particles when the temperature is close to their melting point, resulting in the coalescence of particles to yield larger particles than those of the as-deposited sample. The AFM images were analyzed using an image processing software, to separate, count, and evaluate each particle. The histogram of the particle diameter distribution is shown in Fig. 1(e). From the fit of the diameter histogram assuming a Gaussian distribution, the average particle diameter of 22.7 nm is estimated for as-deposited Ag NPs; however it increased to 24.6, 27.8, and 30.5 nm for the sample annealed as 100, 150, and 200 °C, respectively.

Fig. 2(a) shows the absorption spectra of various Ag NPs. The peak position of the absorption blue-shifted as the annealing temperature was increased [11]. The observed absorption originated from the LSP resonance, according to previous reports on similar Ag NPs [5]. Further, the spectrum became sharp as the annealing temperature was increased. The obtained absorption peak of various Ag NPs is plotted as a function of annealing temperature (data of the as-deposited sample at