

Distance-dependent plasmonic enhancement via radiative transitions of Europium complex

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We elucidated the distance-dependent plasmonic effects on radiative transitions from an Eu^{3+} ion-doped phosphor by varying the thickness of the dielectric spacer. Magnesium oxide prepared by electron-beam evaporation was chosen for the dielectric spacer. Spectral overlap between emission from Eu^{3+} ions and the plasmon band of Ag nanoparticles led to improved luminescence intensity. This luminous enhancement was effective within the area of influence by localized surface plasmon resonance. At a long distance, the plasmon-enhanced luminescence was not effective. In addition, the numerical analysis results were in good agreement with the distance-dependent decay characteristics of plasmon resonance. © 2013 Optical Society of America

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Localized surface plasmon resonance (LSPR) can be described as the resonant and collective oscillation of surface electrons in a nanoscaled structure stimulated by incident electromagnetic waves [1]. LSPR in a resonant condition with visible wavelength has attracted much interest from researchers of display devices using phosphor materials, because light-matter interaction under LSPR is known to enhance the fluorescence and phosphorescence intensities from luminescent materials. During the past decade, plasmon-enhanced luminescence has been reported in emissive layers, such as semiconductors, small organic molecules, polymer organic molecules, and rare-earth ions [2–4]. Many studies have dealt with the dynamics of spectral overlap between the localized surface plasmon (LSP) and the emission/excitation bands of the light emitter to achieve high luminescence [5]. For plasmon-enhanced luminescence, studies related to the area of influence are significant, as well as spectral overlap [6]. By adjusting the distance from the metal surface, plasmon resonance can be maximized and luminescence quenching can be prohibited [7,8]. Moreover, plasmon resonance is exponentially decayed in the near-field region. Motivated by this, we studied how plasmon resonance affects luminescence from Eu^{3+} ions as a function of distance and determined the optimum distance. Our initial work showed LSP-enhanced emission intensity from an Eu^{3+} -doped phosphor in close proximity to Ag nanoparticles [9]. This Letter shows this enhanced emission is effective within plasmonic resonance. We extend the results described in our earlier work related to plasmon-enhanced luminescence from Eu^{3+} ions [9]. Through the obtained results, we better understand how plasmon resonance can enhance the luminosity of a light emitter, and we can accordingly optimize the luminous enhancement.

In this Letter, we discuss how a localized surface plasmonic system can affect the luminescence enhancement of a light emitter as the distance increases. We evaporated an Ag source on indium-tin oxide (ITO) coated glass as a target substrate. The Ag source is deposited at a thickness of 0–3.5 nm by steps of 1 nm, and the thickness is monitored with a crystal oscillator. In this area of

thickness, the monitored thickness does not mean the actual thickness or the size of the Ag nanoparticles, since nanoscaled and isolated islands are formed, rather than a continuous film. Also, we evaporated magnesium oxide (MgO) at the interface between the light emitter and metal nanoparticles by means of electron-beam evaporation. The MgO layer was inserted to prevent luminescence quenching and examine the influence of the decay tail of plasmon resonance on luminescence enhancement [9]. As a light emitter, a 100 nm phosphor layer of Eu^{3+} -doped YVO_4 was evaporated on the MgO layer by means of an RF magnetron sputter. The Eu^{3+} ion is known for emitting red light with a narrow bandwidth. The LSP band of the Ag nanoparticles surrounded by the dielectric medium was confirmed by the extinction spectrum obtained using a Shimadzu UV-Vis spectrometer (UV2550, Japan) [10]. Also, the emission intensity of Eu^{3+} -doped YVO_4 was determined with a Hitachi spectrophotometer (F-7000, Japan). The size and morphologies of Ag nanoparticles were observed by a field emission scanning electron microscope (SEM) (Sirion, FEI Co., The Netherlands). To understand the plasmonic resonance driven by metal nanoparticles, we introduce a finite-difference time-domain (FDTD) calculation to obtain insight into the enhancement of the electromagnetic near-field distribution around the Ag nanoparticles. FDTD calculations were performed using the program FDTD Solutions [provided by Lumerical Solutions, Inc. (Vancouver, Canada)].

Figure 1(a) presents a schematic diagram of a plasmon-mediated sample structure on a luminescence system using rare-earth metal ions. To generate localized surface plasmons in the red emission region, we choose Ag nanoparticles and an MgO spacer with a high refractive index, as shown in Figs. 1(b) and 1(c). The fabricated Ag nanoparticles appear to be a polygon that closely approximates a spherical shape. The nanoparticles have a size distribution ranging from 5 to 35 nm. Distance-dependent plasmonic resonance was investigated by changing the thickness of the dielectric layer enveloping Ag nanoparticles. The MgO dielectric spacer was evaporated from 0 to 80 nm by steps of 20 nm. The thickness of

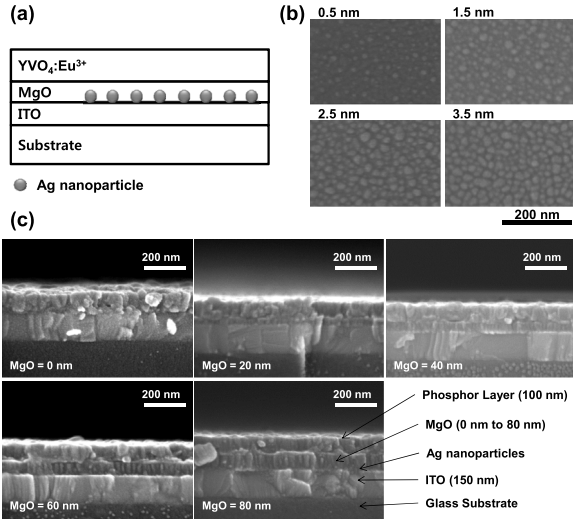


Fig. 1. (a) Graphical representation of the plasmon-mediated luminescence structure. (b) SEM images of Ag nanoparticles on ITO-coated glass substrates. (c) SEM images of cross section of structures on ITO.

the MgO layer is equivalent to the distance between the metal nanoparticles and the light emitter.

Figure 2(a) shows extinctions of Ag nanoparticles surrounded by ITO and MgO. Also, the emission spectrum of Eu^{3+} ions is plotted in Fig. 2(b). The extinction spectra of Ag nanoparticles deeply overlapped with the emission band of Eu^{3+} ions. By using MgO and ITO with a high refractive index, the extinction peaks under Ag nanoparticles of the same thickness are located at a longer wavelength. Therefore, the extinction of Ag nanoparticles extracted at 595 and 620 nm increased according to the evaporation thickness of Ag. The emission of Eu ion consists of 595 and 620 nm radiative transitions allowed by electric-dipole (ED) and magnetic-dipole (MD) transitions, respectively. Figures 2(c) and 2(d) illustrate the enhancement factors of MD-allowed transition and ED-allowed transition in terms of MgO thickness. The photoluminescence (PL) intensity is measured under

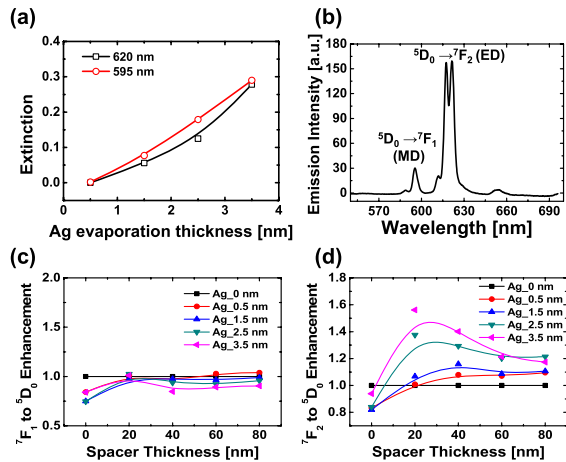


Fig. 2. (a) Extinction of Ag nanoparticles at major emission peaks. (b) Emission spectrum from the Eu^{3+} ion-doped phosphor. Enhancement factors on (c) MD-allowed emission spectra and (d) ED-allowed emission spectra.

irradiation by UV light with 254 nm. The enhancement was calculated by dividing the integrated intensity of Eu^{3+} ions with Ag nanoparticles by that of pure Eu^{3+} ions. In the case of Eu^{3+} ions with Ag nanoparticles, high luminescence intensity in only ED-allowed radiations was observed. However, the luminescence intensity decreased as the light emitter was located at a greater distance from the Ag nanoparticles. This trend is clearly observed in the sample with evaporation thickness of the 3.5 nm Ag. The enhancement factor of the luminescence became less than one unit due to luminescence quenching when the Eu^{3+} -doped phosphor layer was in direct contact with the metal surface. This PL enhancement is due to resonant coupling between ED transition of Eu^{3+} ions and LSPs owing to Ag nanoparticles [11,12]. LSPR can be detected through variation of the local field distribution, because the electric fields under the on-resonance condition are concentrated on the metal nanoparticles and constructively interfere with each other. To verify the local field enhancement, we have carried out theoretical calculations for the electric field distribution using the FDTD method [13].

Figure 3(a) shows a schematic representation of the numerical analysis using the FDTD method. This configuration follows the fabricated sample structure. Here, ED-allowed radiation of the Eu^{3+} ion was modeled as a 620 nm oscillating dipole source. Representatively, an Ag nanoparticle with an average diameter of 30 nm based on SEM images was applied. For approximation, Ag nanoparticles were assumed to be of spherical shape. The dipole source was perpendicularly oriented to the metal surface. The refractive indices of the background and materials are assumed to be from Palik and Ghosh's data [14]. The mesh size for the calculation of the electric field distribution was set from a minimum of 0.25 nm to a maximum of 3 nm. Also, the simulation time in all of the calculations is 400 fs. For clarity, all of the field

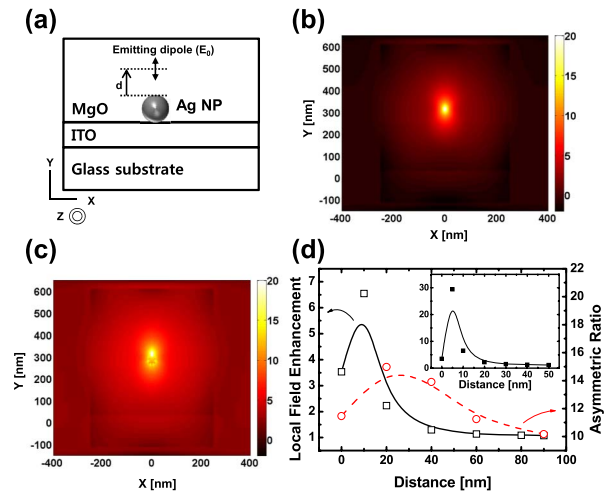


Fig. 3. (a) FDTD configuration for calculation of the electric field distribution owing to an Ag nanoparticle. (b) Electric field distribution shown for a 620 nm dipole source. (c) Electric field distribution around Ag nanoparticle with a diameter of 30 nm shown for a 620 nm dipole source. (d) Local field enhancement and asymmetric ratio in a 30 nm Ag nanoparticle as a function of distance from the metal nanoparticle. (Inset shows the details of local field enhancement.)

distributions were plotted on a logarithm graph. Figure 3(b) shows the electric field distribution of a 620 nm dipole source under the sample structure. Figure 3(c) shows the electric field distribution around a 30 nm Ag nanoparticle 5 nm away from a 620 nm dipole source. Figure 3(d) shows the distance-dependent electric field enhancement factor and asymmetric ratio for a 30 nm Ag nanoparticle illuminated with a 620 nm oscillating dipole source.

Here, the enhancement factor is plotted as a distance from the surface of the Ag nanoparticle. Also, the asymmetric ratio of the Eu^{3+} ion was calculated by the intensity ratio between ED and MD transitions in the PL spectrum [15]. The asymmetric ratio in the rare-earth metal ion is known to be modified by plasmon resonance [15]. The trend of PL enhancement of ED transition corresponds to the change in the asymmetric ratio of the Eu^{3+} ion. In addition, the change in the asymmetric ratio corresponds to the change in the average electric field enhancement around the Ag nanoparticle with a dipole source. The average electric field enhancement around the Ag nanoparticle decreased quickly as the distance became longer. This trend of the local field enhancement means that the plasmon resonance is exponentially decayed. The PL enhancement obtained in this work is in good agreement with the local field enhancement. The enhancement trend in the experimental condition of more than 20 nm corresponded to the simulation result. At less than 20 nm, the experimental results need to be carried out by applying a new evaporation method.

We have attempted to show why the plasmon-enhanced effect on PL decreases with distance. We believe the spectral overlap between the emission band of the Eu^{3+} ions and the LSP band owing to Ag nanoparticles leads to resonant coupling, contributing to enhanced luminosity. In experimental results, the luminescence intensity is maximized at 20 nm and decreased after 20 nm. This accounts for how the plasmon resonance owing to Ag nanoparticles exponentially decays along the normal axis. We believe that the plasmonic effect on luminous enhancement is more pronounced in the near-field region (<60 nm) than in the far-field region. The asymmetric ratio supported this distance-dependent effect of plasmon resonance. In the FDTD calculation, the local field enhancement decreases as the distance from the surface of the Ag nanoparticles increases. Therefore, we conclude that the luminous enhancement originates from plasmonic resonance, and accordingly the luminous enhancement decreases with the decay characteristics of plasmonic resonance.

Based on the numerical calculations, we predict the optimum distance to be less than 5 nm for high luminescence intensity of rare-earth metal ions.

In conclusion, we have elucidated the dependence of plasmon-enhanced luminescence on the distance from the metal surface to the light emitter by changing the thickness of the dielectric spacer. We observed that, although the radiative transition of Eu^{3+} ions overlapped with LSPR owing to Ag nanoparticles, the plasmon resonance cannot improve the luminescence intensity at a long distance. Numerical analysis using the FDTD method showed good agreement with the experimental results. The electric field intensity in the near-field region decreased exponentially, which indicated a decrease in luminous enhancement. We believe that further work is needed to clarify the optimal means of modifying an ultrathin dielectric spacer by applying the atomic layer deposition method.

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