Long Range Enhancement of Molecular Fluorescence by Closely Packed Submicro-scale Ag Islands

Tomohiro Fukuura and Mitsuo Kawasaki‡
Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Katsura, Kyoto 615-8510, Japan
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We found that closely packed submicro-scale Ag islands (each ~370 nm across and ~90 nm in height on the average) produced not only extremely short-range fluorescence enhancement for rhodamine dye (RhB) placed only ~1 nm away from the metal surface, but also a novel, long-range enhancement for the same dye for the metal–molecule distance up to ~50 nm. The net enhancement factor for the spin-coated RhB, with a fluorescence quantum yield of ~2 % in the absence of Ag islands, was as high as ~20-folds at the metal–molecule distance of ~30 nm. We propose that strong interparticle surface plasmon interactions involving such large Ag islands play crucial roles for the long-range fluorescence enhancement. [DOI: 10.1380/ejssnt.2009.653]

Keywords: Photoluminescence; Plasmons; Sputtering; Silver; Nano-Films

I. INTRODUCTION

The fluorescence of dye molecules situated near the surface of metal nanostructures or colloidal particles can be significantly enhanced. The mechanism of this impressive phenomenon, referred to as surface enhanced fluorescence (SEF) or metal-enhanced fluorescence (MEF), has extensively been studied from early 1980s [1–7]. A simple qualitative account for SEF is that the enhanced emission originates from the radiative part of the surface plasmon excitation, as induced by the nearby molecular-emission dipoles; whereas the nonradiative part (nonradiative coupling) represents quenching [8]. Early studies suggested that SEF was optimized when the fluorophores were placed 3–10 nm away from the metal surface, below which the quenching dominated [7–17]. However, we have recently shown that a relatively thick Ag island film consisting of considerably large pseudotabular particles (~200 nm across) allowed an extremely short-range SEF for rhodamine dyes that was maximized at metal–molecule distance of only ~1 nm [18]. This result suggests that by controlling the shape and size of metal nanostructures, the optimal metal–molecule distance for SEF may be shortened substantially.

From the viewpoint of wider application of SEF, however, it seems more desirable to control SEF so that the effective metal–molecule distance is expanded also in the opposite direction for much longer range of tens of nm at least. Such a long-range SEF then would open a way to application of SEF to e.g., thin film light emitting devices that involve a luminescent layer tens of nm in thickness. To achieve this aim, however, changing just the shape and size of metal nanostructures is probably not very promising. Indeed, for various other potential applications of surface plasmons, the recent interest of many groups seems to be directed more to the surface plasmon interactions between adjacent metal nanostructures than to the behavior of a single particle. These include a ‘hot spot’ issue for two interacting metal nanoparticles [19], the effect of interactions between metal nanorods in a subwavelength plasmonic image transfer device [20], emergence of surface plasmon polariton with longer propagation length by interaction between two surface plasmons propagating along the opposite surfaces of a thin (~15 nm) Ag film [21], and so forth [22–26].

In this paper, we address one notable effect of such plasmon–plasmon interactions between adjacent metal particles in the context of SEF that indeed allowed us to observe a novel long-range SEF expanding the effective metal–molecule distance for up to ~50 nm. Specifically, we examined even larger submicro-scale Ag islands (up to ~400 nm in diameter) than those employed in our previous study [18]. We thereby found that the long-range SEF was activated only when the Ag islands exceeds ~300 nm in diameter and are packed sufficiently close to each other. We propose that some strong plasmon–plasmon interactions involving such large Ag islands in close proximity is most probably relevant for the novel long-range SEF established in the present work.

II. EXPERIMENTAL

A. Materials and Sample Preparation

Ag island films were grown primarily on freshly cleaved natural mica (purchased from The Nilaco Corporation) by the direct-current Ar⁺-ion sputtering method in the same apparatus as used elsewhere for preparation of atomically flat Ag(111) and Au(111) films [27, 28]. In the present experiment, we chose a considerably high substrate temperature of 250–350°C and a very small deposition rate of 1–2 nm/min to make as large discrete Ag islands as possible. The Ag island films prepared by this method are characterized by the highest possible packing density of islands for discontinuous Ag films and by a pseudotabular island morphology with a small height/diameter ratio of ~0.25.

The pseudotabular island morphology and the high packing density associated with the sputtered Ag films could be largely modified, however, by high-temperature (up to ~600°C) post-deposition thermal annealing of the sputtered film in the ambient atmosphere; thereby we could obtain much less closely packed and hemispherical Ag islands.

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†Corresponding author: kawasaki@ap6.mbox.media.kyoto-u.ac.jp
Another useful method for preparation of Ag island films is to utilize stabilizer-free Ag nanoparticles (10–20 nm in diameter) dispersed in acetone with a typical concentration of ≈0.2 wt%. They can be produced easily by the laser-induced fragmentative decomposition of acetone-suspended Ag₂O micropowders, as reported in detail elsewhere [29]. By spin-coating of this stable acentonic solution of Ag nanoparticles, preferably on glass, followed by high-temperature (250–600°C) thermal annealing in the ambient atmosphere, some large Ag islands, comparable to those prepared by the sputtering method, could be obtained with considerably smaller packing densities. In some cases, we used repeated cycles of spin-coating of additional Ag nanoparticles and subsequent thermal annealing to gain control over the island size and packing density in a wider rage.

It should be also noted that, by X-ray photoelectron spectroscopy (XPS) analysis with an ESCA-750 spectrometer (Shimazu Corp), we confirmed that the high-temperature thermal annealing of the Ag surface in air, as used in the above-noted procedures, developed a minor surface oxide layer if any, ≈1 nm in thickness at most.

As for the spacer layers to separate the dye molecules from the metal surface for controlled distances, we employed commercial spin-on-glass (SOG, type 111 from Honeywell) solution for convenience, diluted with ethanol by 10–1000 times in volume. Each solution of selected concentration was either spin-coated (at 3000 rpm) or simply spread by casting (for 10 µL) onto the sample typically ≈15×15 mm² in area and dried at room temperature. The resulting film then was cured at ≈200 °C in air for 10–20 min. A series of XPS analysis of the spacer-induced attenuation of the Ag₃d signal allowed us to verify that the Ag islands were successfully covered by a spacer with the average thickness proportional to the concentration of the given SOG solution, for at least up to ≈10 nm. We then used the linear extrapolation of this relationship to higher SOG concentrations to obtain the nominal thickness for thicker (>10 nm) spacers. It was comparable to (only ≈30% smaller than) that measured directly by step height measurement with a VN-8000M atomic force microscope (Keyence Co) for an equivalent film coated on a flat substrate.

The sample preparation for the fluorescence measurement (see below) was completed by spin-coating (at 3000 rpm) of 0.15 mM ethanolic solution of RhB (chloride, obtained from Exciton Inc.). This yielded a molecularly thin layer of RhB with a net surface coverage of ≈5×10¹³ molecules/cm². The measured absolute fluorescence quantum yield (in the absence of Ag islands) at this dye coverage (subjected to some strong self-quenching) was ≈2%.

B. Spectroscopic Measurements

The specular transmission and reflection spectra (at normal incidence) of all kinds of samples were acquired by using a home-assembled microscopic spectrometer system comprising a Nikon microscope, a multichannel analyzer (Hamamatsu Photonics, PMA-11), and two independent halogen lamps for transmission and reflection measurements.

The fluorescence measurement was done by using the same apparatus as described in detail elsewhere [18] that allows quantitative measurement of angle-resolved fluorescence as well as scattering. A simplified experimental geometry for the fluorescence measurement is shown in Fig. 1. A 150-W Xe lamp combined with a monochromator allowed us to select any wavelength in the visible region for fluorescence excitation at normal incidence. The fluorescence signal was detected both in the front space at the angle of 40° and in the back space (behind the substrate) at the angle of 140° with respect to the excitation light.

The angle-resolved scattering spectra measured by using the above apparatus were combined with the specular transmission and reflection data to determine the total absorptivity of arbitrary samples. From the difference in total absorptivity between samples with and without the RhB layer, we could have a reliable estimate of the net light absorptivity of the RhB layer placed atop, as influenced by the Ag islands underneath.

III. RESULTS AND DISCUSSION

A. Preliminary System Characterization

Figure 2 shows a typical deposition-time series of AFM images (5000×5000 nm²) taken of the Ag island films sputter-grown on mica in the very slow deposition conditions as specified above. It can be seen that the average island diameter increased dramatically with deposition time, up to ≈400 nm across (at 120 min), while preserving the highest possible packing density for discrete (discontinuous) island films. Thus the maximum island size available for the present study was approximately doubled as compared to ≈200 nm achieved in the considerably (by 3–4 times) faster deposition condition employed in the previous study. More specifically, Figure 3 shows how the average island diameter and the aspect ratio (defined by height/diameter ratio) changed with deposition time for films imaged in Fig. 2. Despite the large change in the average island diameter, the aspect ratio was maintained approximately constant at ≈0.25 inde-
FIG. 2: A deposition-time series of height-mapped AFM images (5000×5000 nm²) of Ag island films sputter-grown on mica in a very slow deposition conditions as specified in the text; (a) 20, (b) 35, (c) 50, (d) 70, (e) 90, (f) 120 min.

FIG. 3: The average island diameter (left axis) and height/diameter ratio (aspect ratio, right axis) as functions of deposition time for films imaged in Fig. 2.

Independently of deposition time. This relatively low aspect ratio, associated with what we refer to as ‘pseudotabular’ Ag islands, is characteristic of the sputtered Ag island films grown on mica.

Figure 4 shows a collection of three-dimensional AFM images (1000×1000 nm²) for comparison of several different forms of Ag islands made available in this study, in terms of the island morphology and the packing density. In all images here, the island diameter is roughly similar to be in the 140–200 nm range. Figure 4(a) represents a sputtered Ag film that is identical with that already shown Fig. 2(b) (by 35 min deposition). The film imaged in Fig. 4(b) is one of those prepared from spin-coated Ag nanoparticles on glass, and likewise exhibits a pseudotabular morphology though with a considerably smaller packing density. Figure 4(c) exemplifies hemispherical Ag islands with a low packing density that were derived by high-temperature thermal annealing of a sputtered Ag film.

In the present study, we have chosen SOG for the spacer material, instead of the self-assembled molecular multilayers (covalently linked) on the Ag surface used in the previous study [18]. The latter method allows more precise control of the spacer thickness, but making spacers with tens of nm in overall thickness by this method is extremely times taking. A problem with the SOG spacer (either spin-coated or simply cast) is in that it does not necessarily cover uniformly the Ag island film with some substantial corrugation in height. Thus, even though we carefully checked the average spacer thickness by XPS and AFM (see experimental), there still remains some uncertainty about the real thickness of the spacer covering respective Ag islands. From this viewpoint, we examined how closely the SOG spacer could reproduce the previous result of exclusively short-range SEF by pseudotabular Ag islands that are typically ~200 nm across and ~50 nm in height, corresponding to the films imaged in Fig. 4(a) and Fig. 4(b). Besides, we also examined the metal–molecule distance (spacer thickness) dependence of SEF for the hemispherical islands as imaged in Fig. 4(c), for which we expected to reproduce a common optimal distance for SEF, 3–10 nm, as addressed in earlier reports [7–17]. Overall, the results were sufficient to give us confidence that the SOG spacer allows proper control of the metal–molecule distance.

B. Occurrence of Long-Range SEF

Figure 5 demonstrates how largely the metal–molecule distance dependence for SEF was altered from the previously known behaviors by using the sputtered Ag film consisting of largest Ag islands that we could make; ~370
FIG. 4: Comparison of three-dimensional AFM images (1000×1000 nm²) of several different forms of Ag islands (140–200 nm in diameter) prepared in this work, in terms of island morphology and packing density. See text for more detail.

nm across and ~90 nm in height on the average. Here, the excitation wavelength was set at 490 nm. The filled squares represent fluorescence intensity measured in the front space (θ=40°) and the open squares in the back space (θ=140°). The result clearly manifests not only the short-range SEF sharply peaked at d~1 nm, but a striking long-range enhancement broadly peaked at d~20 nm. As a result, some substantial enhancement persisted for up to d~50 nm. With the control fluorescence signal taken without the Ag island film as the reference (corresponding to the estimated fluorescence quantum yield of ~2%), the apparent enhancement factor here measured as ~80-folds and ~40-folds at the short-range and the long-range enhancement peaks, respectively.

In Fig. 5, it should be also noted that the spacer-thickness dependence is very similar for both signals measured in the front and back space, and that a large part of the enhanced fluorescence was emitted also into the back space behind the closely packed big Ag islands. These features, common to both short- and long-range SEF, can be rationalized based on the concept of plasmon-coupled enhanced emission, where the enhanced signals detected in both front and back spaces come from the radiative part of the surface plasmon as induced by the molecular-emission dipoles of photoexcited RhBs (i.e., following rapid dye-to-metal energy transfer). The enhancement occurs because the radiative yield of the thus induced plasmon dipole can be significantly higher than the original fluorescence quantum yield of RhBs in the absence of Ag islands [18]. The relative magnitudes of the front-space and back-space signals, then, are determined by the angle dependence of the plasmon emission characteristic of the given Ag islands. The spacer thickness simply controls the efficiency (rate) with which the excited dye energy is transferred to the radiative plasmon mode, so that the spacer-thickness dependence becomes similar for both signals. According to this mechanism, the long-range SEF observed in Fig. 5 suggests that the closely packed large submicro-scale Ag islands offer some new channel of coupling for dye-to-metal energy transfer in that long range. This point will be discussed further in the following section.

Here, we address another important result that further testifies to the above-noted mechanism of SEF, regarding the role of molecular-emission dipoles. Figure 6 shows a typical fluorescence excitation spectrum taken for the novel long-range SEF (for d~30 nm). It should be noted that the presence of the submicro-scale Ag islands causes strong light absorption and scattering by surface plasmon excitation that dominates the extinction spectrum of the present system (see Fig. 9 discussed later). Nevertheless, the excitation spectrum (measured point by point) in Fig. 6 simply and closely followed the dye absorption spectrum in the reference system (spin-coated RhB on SOG-coated plain substrate). A similar result was obtained also for the short-range SEF sharply peaked at d~1 nm in Fig. 5. This not only suggests that the net absorption spectrum of RhB on SOG-coated Ag islands is identical with that in the reference system, but also proves that both short- and long-range SEF indeed involve (be initiated with) the molecular-emission dipoles of photoexcited RhBs. They can be strongly coupled, however, with the radiative part of the surface plasmon as noted above, which the enhanced emission finally comes from.

It should be noted, however, that the absolute magnitude of the light absorptivity of RhB on SOG-coated Ag islands may be more-or-less enhanced as a whole due ei-
ther to the enhanced near field or to the scattering effect by the Ag islands underneath. We estimated carefully the net light absorptivity of RhB in the presence of Ag islands according to our standard method (total reflectivity measurements; see experimental). We then found that the corresponding absorption spectrum was indeed indistinguishable from that in the reference system within our experimental error, but was subjected to overall \( \approx 4 \) times and \( \approx 2 \) times absorption enhancement at \( d \approx 1 \) nm and \( d \approx 30 \) nm, respectively. Therefore, the net enhancement factor, representing the real fluorescence enhancement corrected for this relatively minor absorption enhancement, turns out to be \( \approx 20 \)-folds both for the short-range and for the long-range enhancement peaks in Fig. 5.

C. Origin of Long-Range SEF

Considering that films consisting of relatively small Ag islands, up to \( \approx 200 \) nm in diameter (as those imaged in Fig. 4), only exhibited either short-range (peaked at \( d \approx 1 \) nm) or relatively short-range (peaked at \( d \approx 3–10 \) nm) SEF irrespective of the island morphology and packing density, the large submicro-scale Ag islands well exceeding \( \approx 300 \) nm in diameter, characteristic of the film used in Fig. 5, may at least in part be the key to the occurrence of such a long-range enhancement as demonstrated above. However, the film relevant for this novel phenomenon also distinguishes itself by the large packing density of such big islands. To clarify the relative importance of these two factors, we compared several Ag films that commonly consist of sufficiently large Ag islands but with considerably different packing densities. Figure 7(a) and Figure 7(b) show typical AFM images of such large (some exceeding even \( \sim 500 \) nm in diameter) Ag islands with more-or-less decreased packing densities. These large islands still exhibited a pseudotabular morphology with an even smaller aspect ratio of \( \approx 0.2 \) than that (\( \approx 0.25 \)) typically associated with the sputtered Ag films (cf. Fig. 3). For reference, we reproduced in Fig. 7 the image (Fig. 7(c)) of the closely packed Ag islands for which we were able to clearly observe the long-range enhancement in Fig. 5.

Figure 8 compares the SEF capabilities of these three kinds of Ag island films in terms of the metal–molecule distance dependence for SEF (measured in the front space). It can be seen that the least closely packed Ag islands (Fig. 8(a)) essentially lost the SEF capability both for the short-range and for the long-range enhancement. By contrast, the increased packing density (Fig. 8(b)), while producing still minor short-range enhancement peak, now gave rise to a considerably strong long-range enhancement signal, comparable to that for the closely packed Ag islands (Fig. 8(c)). The result thus strongly suggests that the long-range SEF is not attributed simply to the increased island size, but shows up when submicro-scale large Ag islands are so closely packed together as to allow some substantial interparticle surface plasmon interactions.

The important role of the interparticle surface plasmon interactions for the long-range SEF, as suggested above, is further supported by the series of extinction spectra presented in Fig. 9 for the three kinds of Ag island films. First of all, the difference in packing density for these
films is clearly reflected in the difference in the maximum film absorbance. More importantly, Figure 9 illuminates a systematic peak shift caused by the increasing packing density, as intimately correlated with the emergence of the long-range enhancement signal in Fig. 8. In the spectrum (a) for the least closely packed Ag island films, there are two plasmon peaks at ~400 nm and ~630 nm. In particular, the latter long-wavelength peak is common to Ag islands more than 100 nm in diameter according to the Mie theory [30–33]. A broad long-wavelength plasmon peak is also the common observation for agglomerated Ag nanoparticles. Then, what is remarkable in Fig. 9 is that the increased packing density of the large Ag islands rather caused a distinct blue shift of the long-wavelength plasmon peak. As a result, the spectrum (c) for the most closely packed Ag islands was unusually sharpened for submicro-scale Ag particles. This is difficult to rationalize without some strong interparticle plasmon interactions.

It thus follows that for the long-range SEF focused on in this paper to be activated, two conditions have to be met; i.e., the large island size exceeding ~300 nm in diameter and sufficient interparticle plasmon interactions to give rise to a largely modified extinction spectrum. Precise estimate of the interparticle spacing necessary for such interactions is difficult in the present stage. However, judging from the series of AFM images shown Fig. 8 (within the limited lateral resolution of AFM), it seems that the relevant Ag islands need to come so close to each other that they leave interparticle gaps with probably less than tens of nm at most.

Here, care should be taken in that the spectral shape and intensity (absorbance) associated with such extinction spectra of Ag island films represent the direct optical interactions between the Ag islands and the incoming light. They thus provide useful information about the interparticle plasmon interactions as noted above, but yet have no direct relevance for the efficiency of SEF or for the corresponding enhancement factor. As emphasized already, the fluorescence excitation spectra, for both short- and long-range SEF, agreed well with the RhB absorption spectrum, thereby supporting the concept of plasmon-coupled emission. Although the presence of the Ag islands more-or-less increased the net light absorbivity of RhB, this contribution to the apparent fluorescence enhancement was of relatively minor significance. What mainly determine the efficiency of SEF are how efficiently the molecular emission dipole can induce (couple with) the radiative mode of the surface plasmon and how efficiently the thus induced plasmon dipole can radiate (i.e., radiative yield). As suggested already, the role of the interparticle plasmon interactions is probably to provide some new channel for the longer-range coupling between the surface plasmon and the molecular emission dipoles.

Finally, it is not yet clear how the island shape (morphology) can influence the interparticle plasmon interactions. Although the films for which we observed the long-range SEF are presently limited to those consisting of pseudotabular islands, there is a possibility that even hemispherical Ag islands, for example, might also lead to a similar long-range SEF if they were made sufficiently large and packed closely enough. However, we have not yet been successful in making such comparative films to address this remaining issue.

IV. CONCLUSION

By modifying the DC sputtering condition for making Ag island films on natural mica (choosing a very small deposition rate less than 1 nm/min at higher temperature of ~300 °C), we could expand the available range of island diameter for up to ~400 nm, while preserving the largest possible packing density for discrete islands as well as the pseudotabular island morphology with a small (~0.25) height/diameter ratio. This offered us the opportunity to observe for the first time a novel long-range SEF that largely enhanced the molecular fluorescence of a test dye, RhB, placed 20–50 nm apart from the metal surface. We experimentally confirmed that for the long-range SEF by Ag islands to be activated, they need to exceed ~300 nm in diameter and, at the same time, they have to be so closely packed that some substantial interparticle plasmon interactions become feasible.

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