

Highly Efficient Surface-enhanced Fluorescence on Ag Island Film of Large Pseudotabular Nanoparticles

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A highly reflective thick Ag island film, consisting of unique large pseudotabular nanoparticles, could be sputter-grown on mica. The film spin-coated with rhodamine B with a thin molecular spacer in between exhibited an unusually strong surface-enhanced fluorescence maximized at much shorter distance from the metallic surface than hitherto known.

The phenomenon that the fluorescent emission from dyes situated near the surfaces of metallic colloids and islands is significantly enhanced, known as surface-enhanced fluorescence (SEF), was established in its basic principle in early 1980s,^{1–3} but there have been some continued efforts to gain further optimization of the metal–molecule interactions for SEF,^{4–6} potentially useful in many applications such as biosensing and biomedical testing. SEF has one inherent problem associated with the dye-to-metal rapid radiationless energy transfer obeying d^{-3} law (d representing dye–metal spacing), which requires the dye fluorophores to be placed at certain significant distances, 30–100 Å or more, from the metal surface.^{7,8} In this letter, we introduce a remarkable short-ranged SEF capability of a highly reflective thick Ag island film (hereafter referred to as TAIF), suggesting that the problem can be greatly suppressed by using this novel system.

TAIF consists of large pseudotabular nanoparticles 60–200 nm across and 30–50 nm thick, as represented by the atomic force microscopy (AFM) image shown in Figure 1. This unique morphology could be grown on freshly cleaved natural mica by using a direct-current Ar⁺ ion sputtering method at a considerably high (200–300 °C) substrate temperature and low (1–2 nm/min) deposition rate. The big nanoislands are well separated from each other so that the film exhibits no electric conductance, but optically it is more like a continuous Ag film with a high specular reflectance in the visible region exceeding 50–60%.

To separate the dye fluorophores from the metallic surface for controlled distances (for up to ~250 Å), we used the self-assembled monolayers or multilayers of mercapto-substituted car-

boxylic acid compounds, such as 11-mercaptoundecanoic acid. A single monolayer was formed by sample immersion (for 10 min at room temperature) into 0.1-mM ethanolic solution of each compound. The formation of the multilayers followed the method of Evans and co-workers,⁹ i.e., via sequential adsorption of 11-mercaptoundecanoic acid and Cu²⁺ ions (from 1-mM ethanolic solution of Cu(ClO₄)₂). The variation of spacer thickness in the expected range was checked by X-ray photoelectron spectroscopy analysis (exponential attenuation of the Ag signal from TAIF underneath the spacer layer with its thickness).

The dye used in this work is rhodamine B (RhB), which is known to exhibit a high fluorescence quantum yield (greater than 0.6) in dilute solution,¹⁰ but to be subjected to strong self-quenching when deposited on solid surfaces depending on the dye coverage.¹¹ The deposition of RhB onto the sample surface was done by using the spin coating (at 3000 rpm) of 0.001–0.2 mM dye solution in ethanol. This method resulted in highly uniform and reproducible dye coverage proportional to the dye concentration of the spun solution. The total amount of the dye deposited per unit area was determined by an ethanolic extraction followed by the standard spectrophotometric quantification. The fluorescence measurement was done with a home-constructed system compatible with an angle-resolved fluorescence detection, with the excitation light (depolarized) of 10–50 mW/cm² in power density at normal incidence.

Figure 2 shows typical fluorescence spectra taken at two largely different levels (20:1) of dye coverage. The reference spectra without SEF were taken in the same conditions of excitation and detection (at the angle of 40° with respect to the sur-

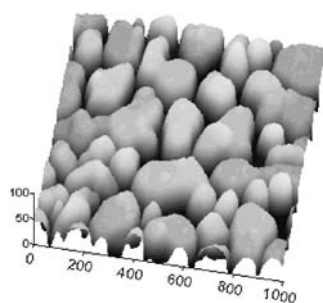


Figure 1. A typical AFM image of TAIF sputter-grown on mica. Scales are in nm.

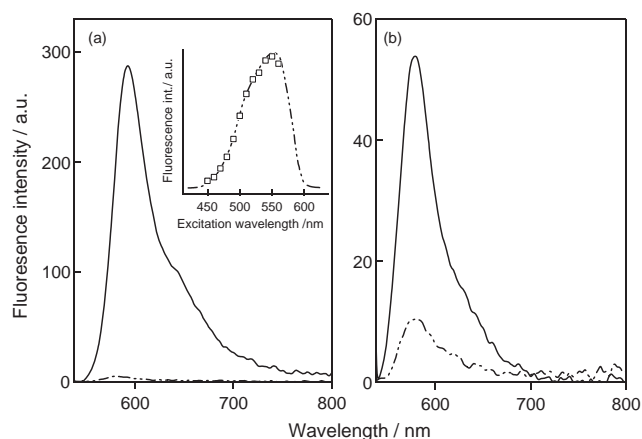


Figure 2. Comparison of fluorescence spectra between RhB-coated TAIF with ~14 Å thick spacer (solid line) and RhB-coated glass (dashed line) at the dye coverage of (a) 5×10^{13} and (b) 2.5×10^{12} molecules/cm². Excited at 532 nm. The inset shows an example of fluorescence excitation spectrum for dye-coated TAIF fitted by the net dye absorbance spectrum.

face normal) for dyes deposited directly on a glass surface.¹² The spacer separating TAIF and RhB is an only ~ 14 Å-thick monolayer. As compared to the solution spectra (not shown), the peak wavelength for the surface-bound RhBs exhibited a considerable red shift (from 568 nm) to 578 nm on glass and to 578–592 nm on TAIF more in the higher dye coverage; but the changes of the spectral shape were minor except for a noticeable broadening in the long-wavelength tail. Figure 2a shows a dramatic (by factor of ~ 40) fluorescence enhancement by TAIF at the higher coverage where the emission on glass was strongly self-quenched. At the much lower coverage (Figure 2b), the self-quenching became so small that a considerably more intense fluorescence signal was obtained on glass. However, a substantial fluorescence enhancement by TAIF by factor of ~ 5 is still evident at this low dye coverage.

Note that the comparison in Figure 2 is in terms of the apparent intensity at the same dye coverage. We found that the net light absorbance of dye-coated TAIF was a simple superposition of the contribution from TAIF and that from RhB, and that the latter agreed well with the fluorescence excitation spectrum as exemplified in the inset of Figure 2a. However, the evaluation of the exact fluorescence quantum yield is a difficult task particularly for such a heterogeneous system, requiring also a detailed analysis of the fluorescence angular distribution. We currently estimate a crude yield at the higher coverage (Figure 2a) to be ~ 0.01 on glass and more than 0.1 on TAIF, but these need to be further elaborated.

Here, we briefly address one impressive result relating to the fluorescence angular dependence. Namely, contrary to our initial expectation, the fluorescence intensity for dye-coated TAIF became stronger by $\sim 30\%$ or more in the backspace of TAIF/mica through the considerably thick Ag film. One possible interpretation is that the observed SEF may arise preferentially from dyes situated somewhere in the deep gap regions left between the large Ag islands (including their corners and side faces) where the local electromagnetic field may be so effectively concentrated. However, such a field enhancement effect, if any, should normally be much longer-ranged^{5,6} than associated with the present SEF (see below). Alternatively, the enhanced emission may come from a large induced emission dipole^{2,3} in TAIF rather than from the original dye emission dipole. The dyes effective for this coupling need not necessarily be located in the gap regions.

The important short-ranged nature of the present SEF is more explicitly shown in Figure 3, where we plotted the SEF emission intensity as a function of spacer thickness. There occurred a comparatively high efficiency even under direct contact between TAIF and RhB. With increasing spacer thickness the intensity sharply rose to the maximum at a quite short distance of ~ 10 Å. It then monotonically decreased and substantial SEF continued for only up to ~ 100 Å. We suggest that the initial sharp rise is probably caused by the suppression of a very short-ranged quenching due to a Dexter-type energy transfer involving electron tunneling.

At the distance of ~ 10 Å, the energy transfer obeying d^{-3} law takes over, but in usual cases it still strongly (almost completely in the case of smooth Ag film¹²) quenches the molecular fluorescence. However, the situation could be diametrically different if this energy transfer were coupled more strongly with the radiative modes of free electron motion confined in Ag is-

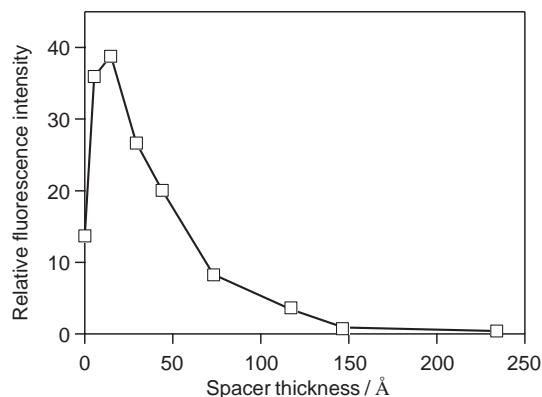


Figure 3. Dependence of relative fluorescence intensity of RhB-coated TAIF as a function of spacer thickness. Measured at the dye coverage of 5×10^{13} molecules/cm².

lands.^{2,3} Given that TAIF somehow satisfies this condition, then a strong enhanced emission may come out from TAIF in every direction. The spacer thickness of ~ 100 Å that mostly eliminated the present SEF also seems to be reasonable from this picture, since the required coupling to produce a large induced dipole should be likewise short-ranged.

At this moment, however, the relevance of the dyes more specifically associated with the deep gap regions (which are also characteristic of TAIF) is not excluded, and further study is necessary for better clarification of the underlying mechanism.

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- 11 Y. Liang, P. F. Moy, J. A. Poole, and A. M. P. Goncalves, *J. Phys. Chem.*, **88**, 2451 (1984).
- 12 The choice of such nonmetallic substrates as a reference without SEF is a common practice in the literature. On an atomically smooth Ag(111), we obtained no detectable fluorescence signals unless spacers thicker than ~ 30 Å were used, because of the extremely strong quenching by smooth metal surfaces.