

Voltage-Gated Metal-Enhanced Fluorescence

Yongxia Zhang · Kadir Aslan · Chris D. Geddes

Received: 1 December 2008 / Accepted: 23 January 2009 / Published online: 12 February 2009
© Springer Science + Business Media, LLC 2009

Abstract We demonstrate the influence of electrical current on the ability of surface plasmons to amplify fluorescence signatures. An applied direct current across Silver Island Films (SIFs) of low electrical resistance perturbs the fluorescence enhancement. For a given applied current, surface plasmons in just-continuous films are sparsely available for fluorophore dipole-coupling and hence the enhanced fluorescence is gated as a function of the applied current. For thicker, low resistance films, sufficient charge carriers are now present in the metal that metal-enhanced fluorescence (MEF) is perturbed to a lesser extent, induced surface plasmons readily formed on the surface by the close-proximity dipole.

Keywords Metal-enhanced fluorescence · Radiative decay engineering · Plasmon controlled fluorescence · Voltage gated metal-enhanced fluorescence

Abbreviations

MEF Metal-enhanced fluorescence
SIFs Silver Island Films
FITC Fluorescein isothiocyanate
SEM Scanning electron microscopy
AFM Atomic force microscope

Introduction

Since the earlier observations of the close-range interactions of metallic surfaces with luminescent species dating back to 1970s [1, 2] many laboratories have reported on the effects of fluorophores near-to plasmon resonant particles [3–5]. Our laboratory has also been working on both developing a fundamental understanding of the Metal-Enhanced Fluorescence (MEF) [6–8] phenomenon and secondly, applying the enhanced photophysical properties of fluorophores to biological applications [9]. In all of these reports, surface plasmons are induced in the near-field by close proximity fluorophore dipoles, the surface plasmons in turn radiating the coupled quanta, resulting in fluorescence amplification (Fig. 1—Top). The coupled fluorescence is for the most part very similar to the free-space fluorescence, observed in the absence of the metal, with the exceptions that the radiative lifetime is significantly shorter, which is thought to be underpinned by the plasmon decay [6–8] and the angular-dependent emission of the coupled emission [10]. In this paper, we further our understanding of the MEF phenomenon and show that we can significantly alter and indeed *turn off* MEF, by the passage of a direct current through Silver Island Films (SIFs) of low electrical resistance (Fig. 1—Bottom). Interestingly, non-continuous films with a high resistance show no effect with current, as expected, and thick continuous films with a low resistance, are simply not suitable for plasmon coupling as previously shown [11]. Subsequently, our findings suggest that *just-continuous films* with a low electrical resistance can therefore be used to gate MEF “on and off” and indeed at in between emission intensities. Given the recent interest in the uses of MEF, then we believe that our findings will be of very high significance for lab-on-a-chip based technologies, and in the development of new fluorescence

Y. Zhang · K. Aslan · C. D. Geddes (✉)
The Institute of Fluorescence,
University of Maryland Biotechnology Institute,
701 East Pratt St,
Baltimore, MD 21202, USA
e-mail: geddes@umbi.umd.edu

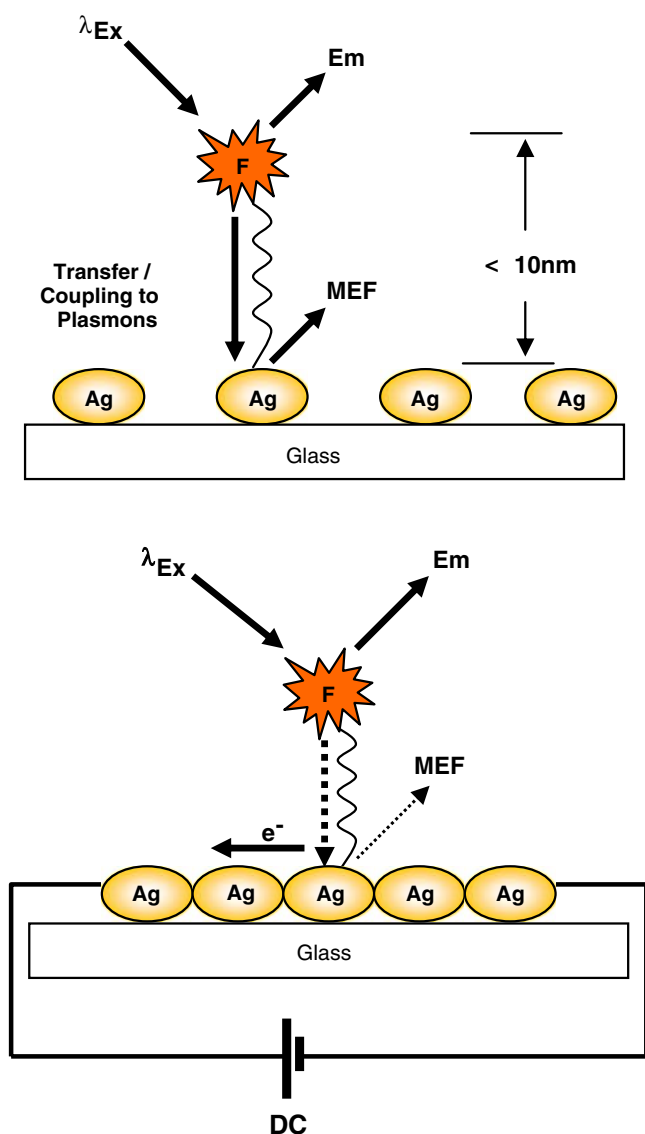


Fig. 1 Graphical representation of current interpretation of metal-enhanced fluorescence (*top*), Metal-enhanced fluorescence perturbed with applied voltage/current (*bottom*). *F* fluorophore, *MEF* metal-enhanced fluorescence, *Ag* silver nanoparticles

detectors, which directly measure coupled quanta/fluorescence [12].

Experimental

Materials

Silver nitrate (99.9%), sodium hydroxide (99.996%), ammonium hydroxide (30%), *D*-glucose and premium quality silane-prep™ glass slides (75×25 mm), Ethanol (HPLC/spectrophotometric grade), fluorescein isothiocyanate were

obtained from Sigma-Aldrich. All chemicals were used as received.

Methods

SIFs, which have previously been used for MEF [9, 13], were deposited on amine-coated glass slides, the procedure modified to allow the deposition of SIFs over a longer time-period to modify the electrical resistance of the surfaces. In a typical SIFs preparation, a solution of silver nitrate (0.5 g in 60 ml of deionized water) was prepared in a clean 100-mL glass beaker. 200 μL of freshly prepared 5% (*w/v*) sodium hydroxide solution and 2 ml of ammonium hydroxide were added to a continuously stirred silver nitrate solution at room temperature. The solution was subsequently cooled to 5 °C by placing the beaker in an ice bath, followed by soaking the Silane-prep™ glass slides in the solution and adding a fresh solution of *D*-glucose (0.72 g in 15 ml of water). The temperature of the mixture was then warmed to 30 °C. The beaker was removed from heat after 2 min and the slides were kept in solution for 1–30 min depending on the required resistance. Films deposited for >15 min were found to be completely conducting (Resistance <math>< 1 \Omega\text{-cm}^{-1}</math>), while films deposited for <math>< 6</math> min were non-conducting, (Resistance >math>> 10^6 \Omega\text{-cm}^{-1}</math>). Films deposited, between 5–10 min were “just” conductive, the films having resistances up to several hundred ohms. Scanning Electron Microscope (SEM) images of the surfaces show the particulate (high resistance) to continuous (low resistance) nature of the films, Figs. 2 and 4 inserts. The slides were then removed from the mixture, washed with water, dried under N_2 and the slides resistance measured with a GDT-11 voltmeter (GB Instruments™).

The preparation of dried samples on the surface was undertaken as follows: 300 μL fluorescein isothiocyanate (FITC, 2.5 mM) in ethanol solution was dropped on the surfaces of SIFs, which had different resistances. The solvent was evaporated and the samples were studied. For oxidation and dipole re-orientation studies (control samples), 100 μL FITC was dropped in 1 mL 0.25% (*w/v*) poly vinyl alcohol (PVA) in water, and spin-coated on the SIFs ($\approx 7 \Omega\text{-cm}^{-1}$). This procedure produced ≈ 37 nm thick films (measured using AFM, not shown here) which prevented both the diffusion of oxygen and the re-orientation of the fluorophore dipoles during current flow. Fluorescence measurements were collected at an angle of 90° to the surface, with 473 nm excitation light incident at 45° to the glass/silvered surface, using a Fiber Optic Spectrometer (HD2000) from Ocean Optics, Inc. Voltage gating experiments were carried out as follows: Direct current (Extech Instruments 382213) was applied to the SIFs with different resistances, Fig. 1—Bottom insert, and gated “on and off” during fluorescence measurements.

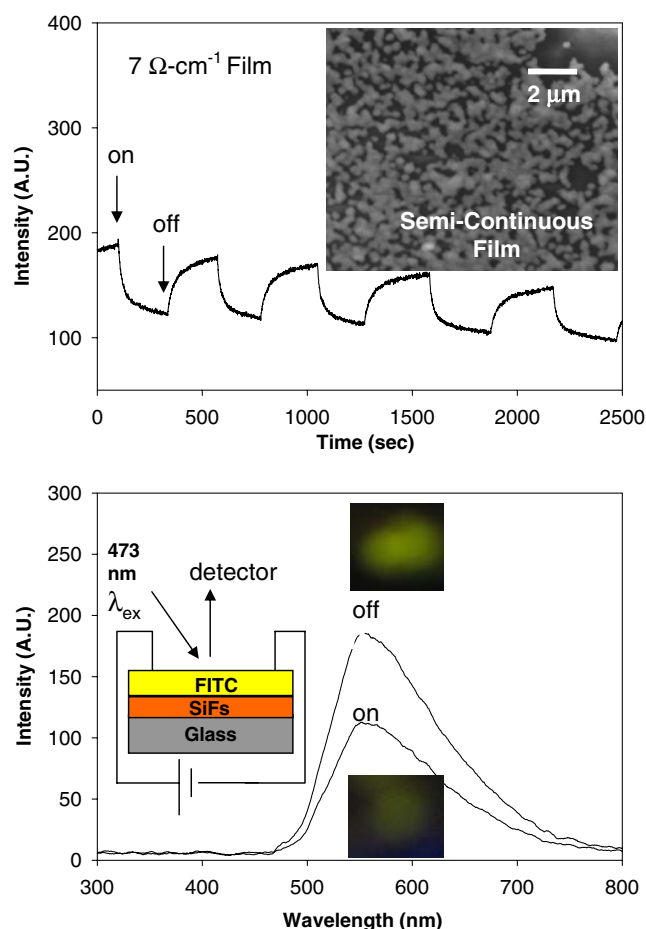


Fig. 2 *Top*—time-dependent fluorescence emission of FITC (measured at 544 nm) on semi-continuous SIFs with applied “on” and “off” voltage (2.1 V, 0.3 A). *Top-insert* shows the SEM image of semi-continuous SIFs film. *Bottom*—fluorescence spectra of FITC on SIFs with (2.1 V, 0.3 A) gated on and off. *Bottom-inserts* show the schematic representation of the experimental set-up and real-color photographs taken through a 473 nm notch filter

Results and discussions

Figure 2 shows the effects of an applied voltage on FITC coated on a semi-continuous (just-continuous) film ($7 \Omega\text{-cm}^{-1}$), the experimental set-up shown in Fig. 2—Bottom-Insert. Remarkably, as the voltage is gated on and off, the FITC fluorescence can be seen to both rise and fall respectively, a direct correlation with the applied current. The fluorescence emission spectra are otherwise spectrally identical during gating, only the magnitude of the intensity fluctuating. The color photographs of Fig. 2—Bottom-Insert, show the actual fluorescence during gating. In a series of detailed control experiments, silver background emission and changes in the plasmon absorption as a function of applied current/voltage were eliminated as the possible cause of the effect (not shown here). Interestingly, as the voltage and current were progressively changed, the

FITC emission was subsequently gated respectively, giving us a strong indication that our observations are a direct result of the applied current.

We also considered the possibility of surface oxidation and dipole re-orientation as a cause of the effect. However, in nitrogen purged thick 0.25% w/v PVA film ($\approx 37 \text{ nm}$), the fluorescence gating effect is still readily observed. It is interesting to consider the magnitude of the observed changes in the fluorescence signal. From Fig. 2—Top, we see an $\approx 50\%$ change in signal during voltage gating, however several factors are thought to account for the fluorescence signal not to change to an even further extent: (1) FITC molecules are coated both on and between the silver islands, hence a large population are likely to be unaffected by an applied current; (2) There is a temperature rise during voltage gating, which should result in an increase in FITC emission (11 °C and 28 °C for $7 \Omega\text{-cm}^{-1}$ (Fig. 3—Top) and $0.4 \Omega\text{-cm}^{-1}$ (thermal image not shown), respectively), offsetting the magnitude of the observed effect. In solution we observed an increase in FITC emission with temperature (Data not shown). Furthermore, the plasmon absorption of the SIFs is also shown to be unperturbed by an increased temperature; (3) The general decrease in fluorescence signal over time, both gated and

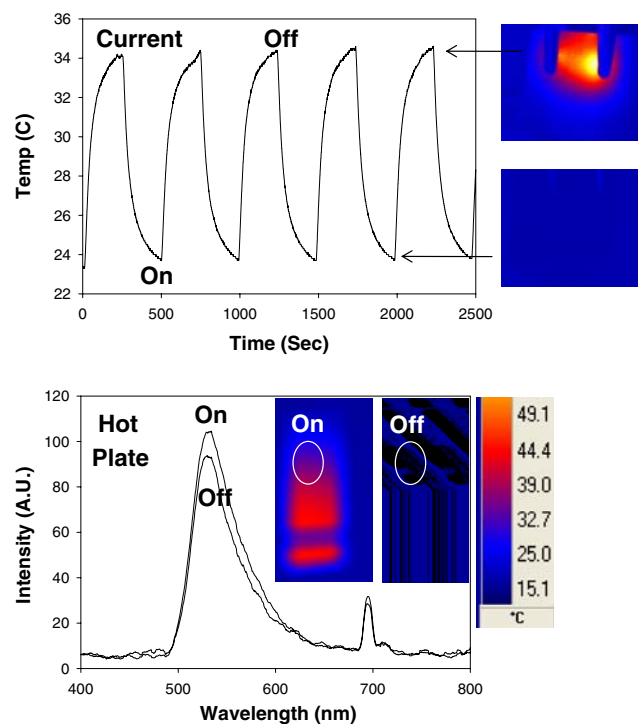


Fig. 3 Time-dependent temperature measurements of a $7 \Omega\text{-cm}^{-1}$ SIFs during voltage gating. Thermal images of SIFs were taken when the applied current was turned off” and “on” (*top*). Fluorescence emission of FITC from SIFs placed on a hot plate before the heat was turned “on” and after it was turned “off”. No current was applied in this experiment (*bottom*). *Circles* indicate the location, where the fluorescence emission spectrum of FITC was measured

not gated, is thought to be due to the photostability of FITC with 473 nm laser excitation.

It is equally informative to discuss the rate of change of emission. From Fig. 2, we can see an almost bi-exponential loss of fluorescence emission as the voltage is gated, eventually reaching a plateau over a few hundred seconds, i.e. <3 min. Interestingly, at the onset of an applied current, the fluorescence intensity drops very rapidly indeed, within a few seconds. At later times, the loss of emission is at a much slower rate. Our current interpretation of this rapid and then slow decay of fluorescence is thought to be underpinned by two competing processes. Initially, the fluorescence is *off-gated* by the passage of current, very rapidly due to the inability of the surface plasmons to both dipole-couple and therefore cause enhancement of fluorescence. At later times, the SIFs were observed to have warmed slightly, which we have shown in Fig. 3—Bottom results in an increased FITC emission. Subsequently, a rapid off-gating effect, followed by slow surface heating, due to the resistance of the films to current flow, is thought to account for the bi-exponential loss of fluorescence observed in Fig. 2 (Note: The slight increase in temperature does not account for the decreased gated fluorescence, it only offsets its magnitude).

We have also studied the effect of direct current on both very thick and thin films, i.e. low and high resistance respectively, Fig. 4. Interestingly, for thicker films, the magnitude of the MEF effect is notably lower (55 a.u. at time $t=0$) as compared to the low resistance films shown in Fig. 1, i.e. 190 a.u. This observation is completely consistent with our understanding and interpretations of MEF, [6–9, 13] where under the conditions employed here, continuous films cannot support the generation of surface plasmons and therefore MEF. Non-continuous films, with a very high electrical resistance (i.e. low current flow), show a greater initial MEF effect, i.e. ≈ 260 a.u., Fig. 4—Bottom, consistent with other reports of MEF from SIFs by our laboratory [6–9, 13]. Interestingly, both surfaces show a less pronounced fluorescence gating effect as the SIFs shown in Fig. 2, indicating the effect is more pronounced for *just continuous* films.

It is important to comment on the possible mechanism which results in the observed effects, shown in Figs. 2 and 4. It is widely thought that the plasmons themselves radiate the coupled quanta in MEF [8]. It is thought that the plasmons in the just-continuous films shown in Fig. 2, which have a low electrical resistance, are not available for dipole coupling and MEF when a current is applied, and hence the MEF effect is gated. For thick films, Fig. 4—Top, the films are sufficiently thick to allow current flow with the plasmons freely available for MEF, the net change in fluorescence observed during gating being much smaller. For non-continuous films, which are ideal substrates for

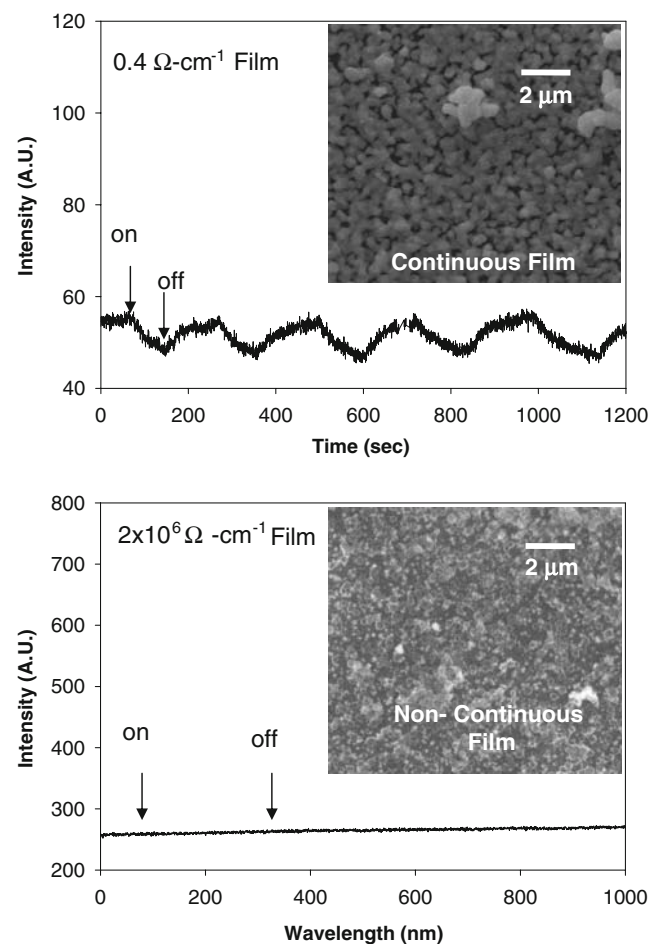


Fig. 4 Time-dependent fluorescence emission of FITC (measured at 544 nm), on (top) almost continuous SIFs with applied voltage/current gated “on” and “off”, and (bottom) non-continuous SIFs with applied voltage/current gated “on” and “off”. Inserts show the respective SEM images of SIFs

MEF, resistance to current flow is very high and hence no gating effect is observed, Fig. 4—Bottom. Figure 1—Bottom outlines our proposed mechanism for the voltage/current gated MEF effect.

Finally, to place our findings in context with recent publications we note several works of interest, where a scanning tunneling microscope is used to excite localized plasmon resonances in metallic nanoparticles [14, 15], due to the local field of the tip. Iwasaki et al. has subsequently shown that close-proximity luminophores to the nanoparticles are then subsequently excited resulting in molecular luminescence [15]. Our system here is macroscopic in nature and indeed almost the inverse mechanism. After optical excitation and induced surface plasmons, an additional applied current across the nanoparticles film decreases the extent of fluorophore dipole coupling, reducing the overall MEF effect (Fig. 1—Bottom). Interestingly, while these other reports are single nanoparticle based and not nanoparticle films [15], we have not been

able to similarly observe fluorescence without the need for additional optical excitation. We also note that similar to Iwasaki et al., our findings are not dependent on the polarity, identical results obtained by simply switching around the electrical leads (data not shown).

Conclusion

In this letter, we have shown the observation of gating MEF by the addition of an applied current across *just-continuous* silver films. Our findings suggest that for just-continuous films with an applied current, surface plasmons are not as readily available for near-field dipole coupling, the effect diminished as thicker metal is used, in essence increasing the number of charge carriers available for current flow and freeing up surface plasmons for dipole coupling (MEF).

Acknowledgment The authors acknowledge UMBI, MBC and the IoF for salary support.

References

- Drexhage KH (1970) Influence of a dielectric interface on fluorescence decay time. *J Luminesc* 1/2:693–701
- Persson BNJ (1978) Theory of damping of excited molecules located above a metal-surface. *J Phys C Solid State Phys* 11 (20):4251–4269 doi:10.1088/0022-3719/11/20/020
- Weitz DA, Garoff S, Hanson CD, Gramila TJ, Gersten JI (1981) Fluorescent lifetimes and yields of molecules adsorbed on Silver-Island Films. *J Lumin* 24–5:83–86 (Nov). doi:10.1016/0022-2313(81)90226-X
- Aroca R, Kovacs GJ, Jennings CA, Loutfy RO, Vincett PS (1988) Fluorescence enhancement from Langmuir–Blodgett monolayers on Silver Island Films. *Langmuir* 4(3):518–521 doi:10.1021/la00081a004
- Barnes WL (1998) Fluorescence near interfaces: the role of photonic mode density. *J Mod Opt* 45(4):661–699
- Geddes CD, Lakowicz JR (2002) Metal-enhanced fluorescence. *J Fluoresc* 12(2):121–129 doi:10.1023/A:1016875709579
- Aslan K, Gryczynski I, Malicka J, Matveeva E, Lakowicz JR, Geddes CD (2005) Metal-enhanced fluorescence: an emerging tool in biotechnology. *Curr Opin Biotechnol* 16(1):55–62 doi:10.1016/j.copbio.2005.01.001
- Zhang Y, Aslan K, Previte MJ, Geddes CD (2007) Low temperature metal-enhanced fluorescence. *J Fluoresc* 17(6):627–631 doi:10.1007/s10895-007-0235-8
- Aslan K, Geddes CD (2005) Microwave-accelerated metal-enhanced fluorescence: platform technology for ultrafast and ultrabright assays. *Anal Chem* 77(24):8057–8067 doi:10.1021/ac0516077
- Aslan K, Malyn SN, Geddes CD (2007) Angular-dependent metal-enhanced fluorescence from silver colloid-deposited films: opportunity for angular-ratiometric surface assays. *Analyst (Lond)* 132(11):1112–1121 doi:10.1039/b709170b
- Chowdhury MH, Aslan K, Malyn SN, Lakowicz JR, Geddes CD (2006) Metal-enhanced chemiluminescence: radiating plasmons generated from chemically induced electronic excited states. *Appl Phys Lett* 88:173104
- Boehm DA, Gottlieb PA, Hua SZ (2007) On-chip microfluidic biosensor for bacterial detection and identification. *Sens Actuators B Chem* 126(2):508–514 doi:10.1016/j.snb.2007.03.043
- Aslan K, Zhang Y, Hibbs S, Baillie L, Previte MJ, Geddes CD (2007) Microwave-accelerated metal-enhanced fluorescence: application to detection of genomic and exosporium anthrax DNA in <30 seconds. *Analyst (Lond)* 132(11):1130–1138 doi:10.1039/b707876e
- Makinen AJ, Foos EE, Wilkinson J, Long JP (2007) STM-induced light emission from substrate-tethered quantum dots. *J Phys Chem C* 111(23):8188–8194 doi:10.1021/jp0712396
- Liu HW, Ie Y, Nishitani R, Aso Y, Iwasaki H (2007) Bias dependence of tunneling-electron-induced molecular fluorescence from porphyrin films on noble-metal substrates. *Phys Rev B* 75 (11). doi:10.1103/PhysRevB.75.115429