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Use of aluminum films as substrates for enhanced fluorescence in the ultraviolet-blue spectral region

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Abstract

Thermal evaporation was used to deposit particulate aluminum films of varied thicknesses on quartz substrates. These substrates were characterized by scanning electron microscopy (SEM), which reveal that with an increase in aluminum thickness, the films progress from particulate towards smooth surfaces. Until now, metal-enhanced fluorescence (MEF) has primarily been observed in the visible-NIR wavelength region using silver or gold island films and roughened surfaces. We now report that fluorescence can also be enhanced in the ultraviolet-blue region of the spectrum using nano-structured aluminum films. We used two probes, one in the ultraviolet (a DNA base analogue 2-aminopurine: 2-AP) and another one in blue spectral region (a coumarin derivative: 7-HC) for the present study. We observed increased emission, decrease in fluorescence lifetime and increase in photostability of the dyes in a 10 nm spin-casted polyvinyl alcohol film on the Al nanostructured surfaces. We observe that the fluorescence enhancement factor depends on the thickness of the Al films because the size of the nanostructures formed varies with Al thickness. These studies indicate that Al nano-structured substrates can potentially find widespread use in MEF applications particularly in the UV – blue spectral regime. Finite-Difference Time-Domain (FDTD) calculations were performed that revealed enhanced near-fields induced around aluminum nanoparticles by a radiating fluorophore emitting at the emission wavelength of 2-AP. The effect of such enhanced fields on the fluorescence enhancement observed is also discussed.

Keywords

Surface plasmons; plasmonics; metal enhanced fluorescence; fluorescence; aluminum; 2-aminopurine; coumarin; plasmon controlled fluorescence

1. INTRODUCTION

Fluorescence detection is the basis of a myriad of measurements in biological research and medical diagnostics. The principles and applications of fluorescence have undergone extensive development since its introduction to biochemistry in the 1950's. Fluorescence provides numerous measurement opportunities including studies of biological macromolecules, cell imaging and DNA sequencing. Exotic phenomena such as multi-

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photon excitation¹ and time-resolved microscopy¹ are now routinely performed in many laboratories for cellular imaging. While fluorescence is a sensitive method, there is a continuing need for increased sensitivity, which is evident in the use of amplification methods such as ELISA^{2,3} and PCR^{4,5}. This is because the detection limits and sensitivity of fluorescence based techniques is limited by the fluorescence quantum yield and photostability of the probes. Additionally for biological applications, autofluorescence from the background of the sample poses significant obstacles. In our opinion, fluorescence technology has reached a plateau in which the fundamental principles are mostly developed. We believe that fluorescence is poised for a paradigm shift which will dramatically expand its experimental capabilities.

During the past several years there has been a growing interest in the use of colloidal metal particles or roughened metal surfaces for enhanced fluorescence^{6–9}, in particular metal colloids and metal island films. We use the term metal to describe conducting metallic surfaces and particles, not metal ions. In recent years we have reported on the effects of silver nanoparticles deposited randomly on glass substrates (primarily in the form of silver island films - SiFs) for increasing the emission intensities (quantum yields), reducing fluorescence lifetimes and increasing the photostability of fluorophores with excitation and emission wavelengths in the visible regime. A large number of reports have demonstrated that fluorescence intensities can be increased 10-fold or more when the fluorophores are in close proximity to the silver particles.^{7–9} The mechanism of this enhancement is, at least in part, due to an increased rate of radiative decay near the particles. Fluorophores in the excited state undergo near-field interactions with the metal particles to create plasmons. While the mechanism of metal-enhanced fluorescence (MEF) is not completely understood, an important factor is the ability of the plasmons to radiate away from the metal particle.⁹ Since this interaction is of an electromagnetic nature, rather than a chemical one, it is reasonable to question whether aluminum can cause MEF.

Initially it was not obvious to us that aluminum would be suitable for MEF as it was reported that aluminum quenches fluorescence.¹⁰ However, it has been shown that excited fluorophores over smooth aluminum films could create surface plasmons which eventually radiate into the substrate.¹¹ The spectral properties of the radiation were found to be essentially identical to that of the fluorophore, except for a highly *p*-polarized emission. The angular dependence of the radiation, as well as the *p*-polarization, is consistent with radiating surface plasmons. According to the radiating plasmon (RP) model for MEF⁹, the scattering component of the extinction of a metal particle contributes to MEF and the absorption component contributes to quenching. Thus far, MEF has largely been reported for silver and gold surfaces. These metals however, restrict the selection of fluorophores to those absorbing and emitting at visible or the near infrared. However, many widely used fluorophores absorb or emit at ultraviolet wavelengths. In this regard, aluminum nano-structured substrates can potentially find widespread use in MEF applications particularly in the UV – blue spectral regime. Aluminum is also less expensive than gold or silver. Another added advantage is that aluminum nano-structured substrates are very stable in buffers that contain chloride salts compared to usual silver based substrates that are traditionally used in

MEF, thus furthering the usefulness of these substrates in many biological assays where high concentration of salts are commonplace.

In this report, we present the observation of MEF displayed by fluorophores in close proximity to particulate aluminum films. The particulate Al surfaces were obtained by thermal evaporation followed by depositing a layer of SiO₂. The silica layer was used as a spacer layer to avoid direct contact of the fluorophore with the aluminum surfaces. It is reported that the extent of MEF depends on the size of the particles and the distance between the metal and the fluorophore.^{6,8,9} Hence we investigated the variation in the size of the aluminum nanostructures to identify the optimum conditions for MEF in the ultra-violet and blue spectral region. We also used numerical Finite-Difference Time-Domain (FDTD) calculations to understand our experimental results. FDTD is an implementation of Maxwell's time-dependent curl equations for solving the temporal variation of electromagnetic waves within a finite space that contains a target of arbitrary shape, and has recently become the state-of-the-art method for solving Maxwell's equations for complex geometries.^{12–17} A major advantage of FDTD is that it is a direct time and space solution, and hence offers the user a unique insight into a myriad of problems in photonics. Our calculations show that fluorophores in the near-field of an aluminum nanoparticle induces enhancements of the near-fields around the particle, which we believe play a role in our observation of MEF from aluminum surfaces.

2. MATERIALS AND METHODS

Aluminum slugs, silicon monoxide, and 2-aminopurine (2-AP) were purchased from Sigma-Aldrich and used as received. 7-hydroxycoumarin-3-carboxylic acid, succinimidyl ester (7-HC) was obtained from Invitrogen Molecular Probes. Distilled water (with a resistivity of 18.2 MΩ-cm) purified using Millipore Milli-Q gradient system was used for sample preparation. Aluminum of varying thicknesses was deposited on quartz slides using an Edwards Auto 306 Vacuum Evaporation chamber under high vacuum ($<5 \times 10^{-7}$ Torr). In each case, the metal deposition step was followed by the deposition of 5 nm of silica via evaporation without breaking vacuum. The silica deposition step served to protect the metal surface as well as it adds a spacer layer between the metal surface and fluorophore. The deposition rate was adjusted by the varying the current in the heating filament and the thickness of the film was measured with a quartz crystal microbalance. The fluorescence probes were deposited on the surface of the substrate by spin coating (Specialty coating system Inc., Speedline Technologies, IN) 0.25 wt % aqueous solution of low molecular weight poly(vinyl alcohol) (PVA, MW. 13 000-23 000; Aldrich) at 3000 rpm. This composition of PVA forms ~10nm thick film. The schematic of the proposed sample structure is shown in Figure 1.18

Extinction spectra of the various samples were collected using a Hewlett-Packard 8453 spectrophotometer. Fluorescence spectra of the probes on the aluminum substrates were recorded using a Varian Cary Eclipse Fluorescence Spectrophotometer. Both the steady-state and time-domain lifetime measurements were carried out using front face illumination. Time-domain lifetime measurements were obtained on a PicoQuant lifetime fluorescence spectrophotometer (Fluotime 100). The excitation source used for the lifetime measurements

was a pulsed laser diode (PicoQuant PDL800-B) with a 20 MHz repetition rate. The Instrument Response Function (IRF) is about 60 ps. The excitation wavelengths are 285 and 405 nm for 2-AP and 7-HC respectively. Intensity decays were measured through appropriate bandpass interference filters. Emission lifetimes were measured with vertically polarized excitation, and the magic angle observation was used in the emission path for the time-domain measurements. This optical configuration reduced scattered light of the excitation wavelength without significant distortion of the spectra or lifetimes.

A small portion of the aluminum substrates were cut and mounted on an Al stub with conductive tape, and then imaged using a Hitachi SU-70 scanning electron microscope (SEM) directly, i.e., without any further treatment of the sample. Due to the nonconductive substrate (SiO_2), ultra-low voltage was employed for high resolution shallow surface observation and imaging using beam deceleration technology. The samples were surveyed at low magnifications to see the general features and the homogeneity. Representative areas with interesting features were selected for higher magnification investigation.

FDTD calculations were performed using the program FDTD Solutions (Version 5.0) obtained from Lumerical Solutions, Inc., (Vancouver, Canada). The calculations were performed with the parallel FDTD option on a Dell Precision PWS690 Workstation with the following components: Dual Quad-Core Intel Xeon E5320 processors at 1.86 GHz, and 8 GB RAM. All post-processing of FDTD data were performed using MATLAB (version 7.0) purchased from Mathworks (Natick, MA). A time-windowed dipole source, radiating at a fixed wavelength of 375 nm, was used to mimic the emission of 2-AP. This is a soft source, i.e. it allows backscattered radiation to pass through it.¹⁹ All of the calculations were performed with a background relative refractive index of 1.0 (i.e. air/vacuum). The auxiliary differential equations method¹² was used to implement a realistic, frequency-dependent and lossy dielectric model for the aluminum nanoparticle. In order to maintain the accuracy and stability of the FDTD calculations, the smallest grid size to accurately model the system without being computationally prohibitive was obtained in an iterative fashion (convergence testing). In our implementation of FDTD, convergence testing was done by starting the first calculation with a grid size of $\lambda_0/20$, where λ_0 is the smallest wavelength expected in the simulation, and then reducing the grid size by half in sequential simulations and comparing the results of the calculations. Reduction of the grid size was ceased when a grid size () was approached where results closely match with the set of results that are obtained from half that particular grid size (/2).¹⁹ As a result of convergence testing, we proceeded to use a grid size of 2.5 nm for our calculations. In FDTD Solutions, the time step of the simulation is determined by the values of the spatial grid to ensure numerical stability of the time stepping algorithm and the user has the flexibility to set the total time of the simulation in femtoseconds (fs).¹⁶ Our simulations ranged around 400 fs. This leads to all of our simulations having an excess of 85,000 time steps. Our FDTD software has frequency domain monitors that perform discrete Fourier transforms of the time domain fields while the simulation is running, which is how continuous wave (CW) information is obtained at any pre-specified wavelengths for the various field components (E_x , E_y , E_z , H_x , H_y and H_z). Additionally, the time domain monitors can provide time-domain information of the various field components within the FDTD simulation region over the entire course of the

simulation. At the end of the simulation, the various field components are checked to see if they decay to zero, thus indicating that the simulation has run for a sufficiently long time for the CW information obtained by Fourier transformations to be valid.¹⁶

3. RESULTS AND DISCUSSION

A slow thermal evaporation rate was used to create rough Al surfaces on the quartz substrates. This is because surface roughness is known to provide a pathway for the coupling of incident light (plane waves) to surface plasmons and the creation of far-field radiation from plasmons.²⁰ The surface morphology was manipulated by the Al film thickness from 2 to 80 nm. The change of surface morphology with the thickness of Al film is characterized by SEM. The 2-nm film was found to be composed of individual particles. With an increasing thickness of the metal film, it was shown that the particle size became larger. As the Al film thickness is further increased to 40 nm and above, the metal film became more and more continuous. Representative SEM images of the 5nm, 10nm and 80nm Al film are shown in Figure 2(a–c).

The optical density (as measured by the extinction spectra) of the Al film increased with increasing thicknesses of the Al layer. Interestingly, there was no clear sharp plasmon absorbance bands observed in any of the evaporated aluminum samples. Figure 3 shows the extinction spectra of the 5 nm and 10 nm thick Al film.

The emission spectra of spin coated 10 nm PVA film containing 2-AP on 10 nm and 80 nm thick aluminum films and quartz substrates is shown in Figure 4. We found a significant change in the fluorescence intensity when the fluorophores are in proximity to the particulate Al surface. The emission spectra of 2-AP shows approximately an 8.5-fold increase in fluorescence intensity from the 10 nm thick particulate aluminum films compared to the control sample (quartz). A 4-fold enhanced emission was noticed for 80 nm thick aluminum film compared to the quartz control. The enhancement factor is defined as the ratio of the integrated fluorescence intensity of 2-AP in the 325–500 nm spectral region on the aluminum substrates to the quartz substrate. This increase in emission intensity of 2-AP is similar to our reports on the MEF phenomenon primarily observed on the silver island film substrates.^{8–9} We have previously reported that the normalized emission spectra of 2-AP on the Al substrates and quartz are almost identical in shape, thus confirming that the emission spectral properties of 2-AP are preserved on both Al films (data not shown).¹⁸

The emission spectra of 10 nm PVA film containing 7-HC on quartz, 10 nm and 80 nm thick aluminum films are shown in Figure 5. The intensity of 7-HC is increased approximately 6- and 2- fold on 10nm and 80 nm aluminum films respectively as compared with the control quartz substrate. We have previously reported that the normalized emission spectra of 7-HC on the Al substrates and quartz are almost identical in shape, thus confirming that the emission spectral properties of 7-HC are preserved on both Al films (data not shown).¹⁸

Figure 6 presents the change in the fluorescence enhancement factor of a PVA film containing 2-AP and 7-HC respectively as a function of the thicknesses of the aluminum film. The highest enhancement of approximately 8.5 fold for 2-AP and about 6 fold for 7-HC was observed on the 10nm thick aluminum films. For 2-AP and 7-HC, the enhancement

was about only 1.5 fold and 2.1 fold on the 2 nm thick aluminum films respectively. This could be because of the highly particulate nature of the 2 nm thick Al film, there still remains a large area of uncoated quartz, and a major portion of the dyes are still on quartz surface. The enhancement factor for 2-AP is consistently around 4-fold for films of 20 nm Al thickness or more. However for 7-HC, the enhancement factor is decreasing monotonically above 10nm thick aluminum film.

The enhanced fluorescence observed from the probes on particulate aluminum films cannot be attributed simply to conventional far-field reflection. Reflection is thought to occur when a 'metal' is extended over several wavelengths in size. The majority of the deposited aluminum particles are smaller than or on the order of the wavelength of light, so these aluminum surfaces essentially behave like particles. Since the fluorophores are approximately within 5–15 nm away from the metal surface, i.e. essentially in the near-field of metal, it is thought that the excited state molecules couple to the plasmons on the surface of the aluminum and the combined excited fluorophore-metal complex acts as a unified system, which radiates. We believe that the observed emission occurs from this metal-fluorophore complex. Figure 3 also reveals that the extinction spectra of the Al coated slides do not show a sharp plasmon resonance for the Al coated films, but is rather broadband (the extinction spectra is essentially a far-field property of the Al surface and does not show any distinct spectral overlap with the absorbance and emission spectra of 2-AP and 7-HC.). However, our fluorescence measurements show consistent enhancements with these films. This is another indication that it is the near-field interaction between the excited state molecules of the dye with the surface plasmons of the Al particles that causes the observed enhancement.

We also examined using FDTD, the electromagnetic near-field distributions around an aluminum particle in the near-field of an excited fluorophore.¹⁸ Figure 7(a) is a schematic illustration of the system studied. A spherical, aluminum nanoparticle with a diameter of 500 nm is placed at the origin. The SEM images of the 10 nm thick aluminum film in Fig. 2(b) (which gave the maximum enhancements) revealed average particle sizes of approximately 500 nm, and hence we choose this dimension for our calculations. The main objective of the calculations is to investigate whether an excited fluorophore in the near-field of an aluminum nanoparticle can cause field enhancements around the particle. We believe that any near-field enhancements induced by a fluorophore around the aluminum nanoparticle plays a significant role in creating the MEF effect that we observe experimentally. In our calculations, the fluorophore is placed 10 nm from the surface of the aluminum along the negative x -axis. It is assumed the excitation stage of fluorescence has occurred and the fluorophore is now emitting radiation. We model this radiating fluorophore as an oscillating, point dipole. The fluorophore is oriented with its dipole moment along the x -axis which is normal to the metal surface.

Figure 7(b) is an image of the near-field enhancement in the x - y plane around the 500 nm aluminum nanoparticle separated 10 nm from the fluorophore that is generated by dividing the intensity of the fields around the fluorophore-nanoparticle complex by the intensity of the fields around the isolated fluorophore. All the images are displayed in the logarithmic scale (base 10) for clarity of presentation. The grayscale used in Figure 7(b) has been set

from 0 to 3.2 to focus on regions which show enhancement. The areas in Figure 7(b) which correspond in the grayscale map to values greater than 'zero' are areas where we see enhancements in the near-field around the aluminum particle. The regions of maximum enhancements are the 'light gray' to 'white' areas. It is interesting to observe that the near-field is not enhanced between the particle and the fluorophore, but is distributed around the nanoparticle with the maximum enhancements on the side of the nanoparticle distal to the fluorophore. Such spatial variations in the near-field enhancements are not easily inferred from experimental observations and thus provide additional insight into the nature of metal enhanced fluorescence.

In metal-enhanced fluorescence, one observes a reduction in lifetime of the emission system occurring simultaneously with increase in emission intensity. We have recorded the fluorescence intensity decays of 2-AP and 7-HC on quartz and various thicknesses of aluminum substrates. The intensity-decay data were fit to the multi-exponential model where the intensity decay is given by: 1

$$I(t) = \sum_{i=1}^n \alpha_i \exp(-t/\tau_i) \quad (1)$$

where α_i are amplitude factors associated with each decay time τ_i . The sum of α_i values are normalized to unity, $\sum_i \alpha_i = 1.0$. The amplitude-weighted lifetime is given by: 1

$$\langle \tau \rangle = \sum_i \alpha_i \tau_i \quad (2)$$

This value represents the area under the decay curve. The values of α_i and τ_i were determined with the deconvolution of the instrument response function and nonlinear least squares fitting. The goodness-of-fit was determined by the reduced χ^2 value.

The fluorescence intensity decay curves of 2-AP on quartz and 10 nm thick aluminum films are shown in Figure 8. Also shown in the figure is the instrument response function (IRF). The solid lines indicate the best fit to the experimental decay curves. Figure 8 reveals that the intensity decay of 2-AP on the aluminum nano-structured surface is faster than observed on quartz substrate (control). The amplitude weighted lifetime of 2-AP was found to decrease from 1.7 ns on the control quartz substrate to 0.45 ns on the 10nm thick particulate aluminum substrate, a reduction of about 4-fold. This shortening of lifetime on aluminum nano-structured substrate strongly supports that the increase in observed fluorescence intensity is due to the radiation from the plasmon-fluorophore complex that results when the aluminum nanoparticles interact with the excited fluorophores in the near-field.

Figure 9 shows the fluorescence intensity decays of 7-HC on quartz and 10nm thick aluminum film substrates. We observed a faster decay of 7-HC on the aluminum surface compared to that on the quartz surface. The amplitude weighted lifetime on quartz and 10nm thick aluminum film is about 1.1 ns and 0.5 ns respectively. These reductions of fluorescence lifetimes are in accordance with our previously reported findings and could be

well described by radiating plasmon model.⁹ According to our understanding, since the dyes are within the near-field of the aluminum nanostructures, they couple very efficiently with the particulate aluminum surface. This coupling interaction leads to inducing radiating plasmons in the aluminum particles. This faster (and hence more efficient) emission from the excited fluorophore-metal complex is the reason behind the observed shortened lifetime.

Figure 10 shows the dependence of the ratio of amplitude weighted lifetimes of 2-AP on the Al films to that on quartz as a function of the thickness of Al films. The most important point to note is that the largest reduction of emission lifetime was observed on the 10nm thick Al film. As mentioned earlier, we have also observed the largest enhancement in the emission intensity of both the fluorophores, 2-AP and 7-HC, on the 10nm thick particulate aluminum substrates. We believe the shorter lifetimes of both probes observed on the aluminum nano-structured surface are due to an increase in the radiative decay rate, but we cannot rule out quenching of some portion of the population.

In most fluorescence based sensing applications, it is fluorophore detectability that governs the utility and sensitivity of the sensing approach. Hence we believe it will be worthwhile to comment on the total detectability of fluorophores in presence of the metal nano-structures/ particles. While a maximum of 8–9 fold increase in fluorescence intensity is clearly beneficial, a reduced fluorescence lifetime of probes also enables the system to be cycled faster, as the lifetime of a species determines its cyclic rate. Hence, 8-fold increase in intensity coupled with a 4-fold reduction in lifetime of the probes in proximity to the aluminum nano-structured surfaces provides a significant increase in detectability. In addition, a reduced lifetime also affords for increased fluorophore photostability as there is less time for excited state photodestructive processes to occur. We have previously reported a comparison of the photostability of the two probes on quartz and Al substrates, where both the probes show higher photostability on the Al substrates.¹⁸ In total, it appears that the detectability of UV-blue fluorophores can be increased significantly near aluminum particles considering the cooperative effects of enhanced fluorescence intensity, reduced lifetime and increased photostability on particulate aluminum substrates.

4. CONCLUSION

This study introduces particulate aluminum films as potential substrates for MEF in the ultraviolet-blue spectral region. We investigated the variation in the size of the aluminum nanostructures to identify the optimum conditions for MEF in the ultra-violet-blue spectral region. A maximum of ~9-fold increase in emission intensity and a 4-fold reduction in fluorescence lifetime from a DNA base analogue 2-aminopurine (2-AP) was observed in proximity to the aluminum nano-structured surfaces which provides increased detectability when compared to the quartz control. A maximum of ~6-fold increase in fluorescence intensity and about 2-fold decrease in lifetime was also observed for the probe 7-HC on particulate aluminum films. The results indicate that the observed emission arises due to the near-field metal-fluorophore complex. The observation of MEF on particulate aluminum films suggests the use of these stable nanostructures in surface-localized bioassays. These robust particulate aluminum substrates could be useful in many fluorescence based bioassays such as DNA arrays as these substrates are very stable in the buffers containing

chloride salts, which is a key component of biological buffers. UV fluorophores such as diphenylhexatriene, pyrenes, dansyl, and anilinonaphthalene-type fluorophores are routinely used to label proteins and membranes. Based on our results, such fluorophores should also display MEF on Al substrates. Our results on MEF with particulate aluminum surfaces indicate that the range of wavelengths can be extended down to the ultraviolet. This will provide a wide range of wavelengths for development of multi-analyte assays using different color fluorophores. The combination of fluorescence with plasmonics can also result in a paradigm shift for both technologies. Fluorescence instrumentation, devices and sensors can potentially begin to use plasmons for the creation of excited states and manipulation of the emission energy. The field of plasmonics can expand to include studies of the factors which govern fluorophore-metal interactions and how to optimize the desired effects. These new approaches to fluorescence and plasmonics will definitely be facilitated by the rapid growth of nanofabrication methods, resulting in new approaches to high throughput biology, diagnostics and molecular imaging.

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References

1. Lakowicz, JR. Principles of Fluorescence Spectroscopy. 3. Springer; New York: 2006.
2. van Dyke, K. Luminescence immunoassay and molecular applications. CRC Press; Boca Raton: 1990.
3. Hemmila, A. Application of fluorescence in immunoassays. John Wiley & Sons; New York: 1992.
4. Walker NJ. A technique whose time has come. Science. 2002; 296:557–559. [PubMed: 11964485]
5. Livak KJ, Flood SJ, Marmaro J, Giusti W, Deetz K. Oligonucleotides with fluorescent dyes at opposite ends provide a quenched probe system useful for detecting PCR product and nucleic acid hybridization. PCR Methods Appl. 1995; 4:357–362. [PubMed: 7580930]
6. Lakowicz JR. Radiative decay engineering: Biophysical and biomedical applications. Anal Biochem. 2001; 298:1–24. [PubMed: 11673890]
7. Geddes CD, Cao H, Gryczynski I, Gryczynski Z, Fang JY, Lakowicz JR. Metal-enhanced fluorescence (MEF) due to silver colloids on a planar surface: Potential applications of indocyanine green to in vivo imaging. Phys Chem A. 2003; 107:3443–3449.
8. Ray K, Badugu R, Lakowicz JR. Distance-Dependent Metal-Enhanced Fluorescence from Langmuir-Blodgett Monolayers of Alkyl-NBD Derivatives on Silver Island Films. Langmuir. 2006; 22:8374–8378. [PubMed: 16981751]
9. Lakowicz JR. Radiative Decay Engineering 5: Metal-Enhanced Fluorescence and Plasmon Emission. Anal Biochem. 2005; 337:171–194. [PubMed: 15691498]
10. Weitz DA, Garoff S, Gersten JI, Nitzan A. The Enhancement of Raman Scattering, Resonance Raman Scattering and Fluorescence from Molecules Adsorbed on a Rough Silver Surface. J Chem Phys. 1983; 78:5324–5338.
11. Gryczynski I, Malicka J, Gryczynski Z, Nowaczyk K, Lakowicz JR. Ultraviolet surface plasmon-coupled emission using thin aluminium films. Anal Chem. 2004; 76:4076–4081. [PubMed: 15253645]
12. Taflov, A.; Hagness, SC. Computational Electrodynamics: The Finite-Difference Time-Domain Method. Artech House; Boston: 2000.
13. Sullivan, DM. Electromagnetic simulation using the FDTD method. IEEE Press; New York: 2000.

14. Yang P, Liou NK. Finite-difference time domain method for light scattering by small ice crystals in three-dimensional space. *J Opt Soc Am A*. 1996; 13:2072–2085.
15. Gray SK, Kupka T. The propagation of light in metallic nanowire arrays: Finite-difference time-domain studies of silver cylinders. *Phy Rev B*. 2003; 68:045415.
16. Reference Guide for FDTD Solutions™ Release 5.0. 2007<http://www.lumerical.com/fdtd>
17. Chowdhury MH, Gray SK, Pond J, Geddes CD, Aslan K, Lakowicz JR. Computational study of fluorescence scattering by silver nanoparticles. *J Opt Soc Am B*. 2007; 24(9):2259–2267. [PubMed: 19777118]
18. Ray K, Chowdhury MH, Lakowicz JR. Aluminum Nano-structured Films as Substrates for Enhanced Fluorescence in the Ultraviolet - Blue Spectral Region. *Anal Chem*. 2007; 79(17):6480–6487. [PubMed: 17685553]
19. Taflove A, Brodwin ME. Numerical solution of steady-state electromagnetic scattering problems using the time-dependent Maxwell's equations. *IEEE Trans Microwave Theory and Techniques*. 1975; 23:623–630.
20. Shadowitz, A. *The Electromagnetic Field*. Dover; New York: 1988.

Figure 1.
Schematic of the sample geometry.

Figure 2.
SEM images of: a) 5 nm; b) 10 nm; c) 80 nm thick thermally evaporated Al films on quartz substrates.

Figure 3.
Extinction spectra of 5 nm and 10 nm thick aluminum films deposited on quartz.

Figure 4. Fluorescence spectra of spin coated 10 nm PVA film containing 2-AP on 10 nm and 80 nm thick aluminum films and quartz. Inset shows the chemical structure of 2-AP.

Figure 5. Fluorescence spectra of spin coated 10 nm PVA film containing 7-HC on 10 nm and 80 nm thick aluminum films and quartz. Inset shows the chemical structure of 7-HC.

Figure 6. Dependence of fluorescence Intensity enhancement factor of 2-AP and 7-HC on the thicknesses of aluminum films.

Figure 7.

(a) Schematic diagram of the model radiating fluorophore/metal nanoparticle system studied using FDTD; (b) Enhancement of near-fields around a 500 nm aluminum nanoparticle that is induced by an excited fluorophore radiating at 375 nm, separated 10 nm from the particle surface and oriented along the x-axis. Note the image is displayed in the log scale.

Figure 8.
Intensity-time decays of 2-AP on quartz and 10 nm thick aluminum films.

Figure 9.
Intensity-time decays of 7-HC on quartz and 10 nm thick aluminum films.

Figure 10.

Ratio of average lifetime of 2-AP on quartz and Al substrates as a function of Al thickness.