Highly directional fluorescence emission from dye molecules embedded in a dielectric layer adjacent to a silver film

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Abstract. We report measurements on the angular radiation patterns from dye molecules embedded in a polymethyl methacrylate thin film spin-coated on a thin silver film. We systematically studied the influence of the thickness of the silver films and the thickness of the dielectric layers on the radiation pattern. We present the detailed radiation patterns over a large angular range showing highly polarized fluorescence emission coupled into the surface plasmon modes or waveguide modes. We also studied the influence of the polarization of the excitation beam on the radiation patterns. The experimental data are compared with numerical simulations using an asymptotic approach based on the Lorentz reciprocity theorem.

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1. Introduction

Light emission through thin silver films has attracted much interest for several decades [1]. The scattered light from bare rough silver films associated with surface plasmon excitation was observed to form a bright backscattered light cone [2]–[5]. In many experiments, the silver surface is covered with a dielectric film. Coating the silver surface with a thin dielectric film that does not support any waveguide modes modifies the power flow for the surface plasmon mode [6]. On the other hand, waveguide modes can be excited when the silver surface is coated with a thick dielectric film [7]. The thin silver film in this case replaces the buffer layer in a conventional dielectric resonant mirror [8].

The problem becomes more interesting when dye molecules are involved. The fluorescence emission can then excite the surface plasmon mode or waveguide modes, and be coupled out directionally [9]–[12]. The directional nature of the emissions is relevant to fluorescence microscopy, fluorescence-based biosensors [13, 14], etc. Understanding the angular and polarization dependence of fluorescence emission can have a strong influence on the light gathering efficiency and can help to interpret experimental data from those applications.

The theory of dipole radiation (where we use electric dipoles to simulate dye molecules) in a multilayer system has also been studied [15]–[18].

Here, we report detailed measurements of the angular and polarization dependence of fluorescence emission from rhodamine B dye molecules embedded in a polymethyl methacrylate (PMMA) layer on top of a thin silver film. The radiation pattern is compared with an asymptotic simulation based on the Lorentz reciprocity theorem where we treat fluorescent molecules as electric dipoles that radiate incoherently.

2. Sample preparation

Figure 1 illustrates the sample geometry. Silver films were deposited onto BK7 (*n* = 1.5171 @ 580 nm) glass substrates by dc magnetron sputtering. The thickness of the silver films was controlled by the deposition time and was measured with a profilometer. The thickness so determined, along with the complex dielectric constant of the silver, were subsequently refined by fitting the attenuated total internal reflection (ATR) data [19]. ATR curves were measured...
at 532 nm (Nd: YAG laser, Spectra-Physics Millennia V) and 632.8 nm (He–Ne laser). We then assumed that the real and imaginary parts of the silver dielectric constant behave linearly between these wavelengths. The real part of the silver dielectric constant at 580 nm, which is the center of rhodamine B fluorescence emission (figure 2), is found to vary in the range from $-14.85$ to $-13.59$, and the imaginary part in the range $0.61$–$0.97$. This is reasonable since it is difficult to produce identical silver films and the dielectric constant does vary with film thickness.

Since the dye molecules tend to quench if they aggregate, we embedded the dye molecules in a PMMA film. PMMA films were spin-coated on top of the silver films. To make thick PMMA/dye films (that can support waveguide modes), we dissolved 8.40 milligrams (mg) of rhodamine B dye (Sigma–Aldrich [81-88-9]) into a mixture of 10 ml PMMA (Microlithography Chemical Corp. NANO™ 495 PMMA A4, 4% in anisole) and 4 ml ethyl alcohol. The final weight percentage of dye in the PMMA is about 2.1. The ethyl alcohol was added to increase the solubility of the rhodamine B. The PMMA/dye film thickness was controlled by the spinning

Figure 1. Schematic of the sample and the associated hemispherical prism.

Figure 2. Fluorescence emission spectrum of rhodamine B molecules embedded in PMMA when excited at 532 nm. Data are smoothed from the measured curve.
speed. The spinning speed was set at 1500 and 3000 revolutions per minute (rpm), respectively. To make very thin PMMA/dye films that do not support a waveguide mode, the above solution is further diluted with 30 ml anisole (Acros Organics [100-66-3]). The diluted solution was then spin-coated at 3000 rpm. A BK7 substrate that is about 0.56 mm thick was then stuck to a BK7 hemispherical lens using index matching fluid (Cargille Laboratories).

The thickness of the PMMA/dye film was first measured with the profilometer. The refractive index and the thickness of the PMMA/dye films were then refined by fitting the reflectivity curves. The refractive index of our PMMA/dye films at 580 nm is approximately 1.51.

3. Experimental setup

The experimental setup for measuring the fluorescence emission pattern is similar to the one used in our previous work [20]. The dye molecules are excited by the Nd: YAG laser, which outputs a 532 nm continuous wave. The fluorescence emission is observed to center on 580 nm when pumped at 532 nm. The full width at half maximum (FWHM) of the peak is around 50 nm (figure 2). The laser light is first modulated by a chopper operating at a frequency of 360 Hz, and then focused onto the center of the hemispherical lens using a focusing lens (\( f = 500.0 \text{ mm} \)). The focused spot size is several hundred microns and the energy arriving at the film is about 200 \( \mu \text{W} \). The laser beam is incident from the air side, normal to the flat surface of the hemispherical lens. Part of the laser beam is extracted by a beam splitter and falls on a photodiode, the output of which serves as the reference signal for the lock-in amplifier. The signal collection system for the fluorescence emission from the dye molecules is mounted on an arm that is fastened to a stepping-motor-driven precision rotator; the hemispherical lens is independently mounted such that its center lies on the rotational axis. The signal collection system consists of a Semrock edge filter, which blocks the 532 nm excitation beam and passes longer wavelengths; a polarizer; an iris with about a 1 mm opening; an OG550 filter; a 30.0 mm focusing lens; and a photomultiplier tube (PMT). The distance between the iris and the center of the hemispherical lens is about 190 mm. The whole collection system can rotate more than the required 180° around the symmetry axis of the hemispherical lens. The output of the PMT is fed into a lock-in amplifier. The output signal from the lock-in amplifier is read by an SR245 computer interface (Stanford Research Systems). A program was written in LabVIEW to automatically control the stepping motor and read the data from the computer interface. The scanning step was set at 0.5° for all scans.

4. Simulation methods

We used a theory based on the Lorentz reciprocity theorem to carry out our simulations for this four-layer system, which consists of air, PMMA/dye, silver and BK7 [17, 21]. This method allows us to calculate the power \( P^{\alpha \beta}(\theta, \varphi) \) radiated in the direction \((\theta, \varphi)\) in the differential solid angle \( d\Omega = \sin \theta \, d\theta \, d\varphi \), associated with a dipole oriented at the angle \((\alpha, \varphi_0)\). The azimuth angles are \( \varphi \) and \( \varphi_0 \) from the positive x-axis, and \( \theta \) and \( \alpha \) are the zenith angles from the negative and positive z-axis, respectively (figure 3). The superscripts stand for the polarization of the emissions. The power \( P^{\alpha \beta}(\theta, \varphi) \) is normalized by the total integrated power of a dipole radiating in the vacuum. In order to obtain \( P^{\alpha \beta}(\theta, \varphi) \), we require three basic quantities, \( P^{\parallel}(\theta), P^{\perp}(\theta) \), and \( P^{\alpha \beta}(\theta, \varphi) \).
and $P^p_{\perp}(\theta)$. The subscripts stand for the dipole orientation, either parallel or perpendicular to the interface. Here, $P^p_{\perp}(\theta)$ corresponds to the signal emitted by a dipole oriented perpendicular to the interface; i.e. $\alpha = 0$, $\varphi_0$ is arbitrary, whereas $P^p_{\parallel}(\theta)$ and $P^s_{\parallel}(\theta)$ correspond to the p- and s-polarized signals emitted in the $\varphi = 0$ and $\varphi = \pi/2$ planes, respectively, by a dipole oriented parallel to the interface at $\varphi_0 = 0$, i.e. $\alpha = \pi/2$, $\varphi_0 = 0$. The power $P^{p,s}(\theta, \varphi)$ is given by

\[ P^p(\theta, \varphi) = \cos^2 \alpha P^p_{\perp}(\theta) + \sin^2 \alpha \cos^2(\varphi - \varphi_0) P^p_{\parallel}(\theta), \]

\[ P^s(\theta, \varphi) = \sin^2 \alpha \sin^2(\varphi - \varphi_0) P^s_{\parallel}(\theta). \]

(1)

Considering an incoming wave propagating from infinity in the opposite direction, as is done when using the Lorentz reciprocity approach, the three basic quantities, $P^p_{\parallel}(\theta)$, $P^s_{\parallel}(\theta)$ and $P^p_{\perp}(\theta)$, are proportional to the square of the absolute amplitude of the ratios between the resultant electric fields at the dipole position and the incoming electric field. The electric field at the dipole position,

\[ E_\lambda(z_0) = \begin{bmatrix} E^{(-)}_\lambda(z_0) \\ E^{(+)}_\lambda(z_0) \end{bmatrix}, \]

(2)

can be calculated from the Fresnel reflection and transmission coefficients using the transfer matrix formalism [22], where (+) and (−) stand for the forward and backward propagating electric fields, and $\lambda$ stands for the s- and p-polarized waves. The transfer matrix is

\[ M^\lambda_{i,i+1} = \frac{1}{t^\lambda_{i,i+1}} \begin{bmatrix} 1 & r^\lambda_{i,i+1} \\ r^\lambda_{i,i+1} & 1 \end{bmatrix}, \]

(2)

and the propagation matrix is

\[ \Phi_i(z) = \begin{bmatrix} \exp(ik_i z) & 0 \\ 0 & \exp(-ik_i z) \end{bmatrix}, \]

(3)

\[ \text{Figure 3. Illustration of dipole orientation and fluorescence emission direction.} \]
where \( i \) and \( i + 1 \) are the layer indices. Setting the incoming electric field \(|E_{\text{in}}| = 1\), for the air-side incoming wave \((0 < \theta < \pi)\), we then have

\[
\begin{bmatrix}
T_{14} \\
0
\end{bmatrix} = M_{43} \Phi_3 M_{32} \Phi_2 M_{21} \begin{bmatrix}
1 \\
R_{14}
\end{bmatrix},
\]

\[
\begin{bmatrix}
E_\lambda^{(+)}(z_0) \\
E_\lambda^{(-)}(z_0)
\end{bmatrix} = \Phi_2(z_0) M_{21} \begin{bmatrix}
1 \\
R_{14}
\end{bmatrix}.
\]

For the hemispherical-lens-side incoming wave \((\pi < \theta < 2\pi)\), we have

\[
\begin{bmatrix}
T_{41} \\
0
\end{bmatrix} = M_{12} \Phi_2 M_{23} \Phi_3 M_{34} \begin{bmatrix}
1 \\
R_{41}
\end{bmatrix},
\]

\[
\begin{bmatrix}
E_\lambda^{(+)}(z_0) \\
E_\lambda^{(-)}(z_0)
\end{bmatrix} = \Phi_2(z_0) M_{23} \Phi_3 M_{34} \begin{bmatrix}
1 \\
R_{41}
\end{bmatrix}.
\]

The indices 1–4 in the above equations stand for the air, PMMA/dye, silver and BK7, respectively. The three basic quantities are then given by

\[
P_s(\parallel)(\theta) = \frac{3}{8\pi} n(\theta) \left| E_\lambda^{(+)}(z_0) + E_\lambda^{(-)}(z_0) \right|^2,
\]

\[
P_p(\parallel)(\theta) = \frac{3}{8\pi} n(\theta) \left| E_\lambda^{(+)}(z_0) - E_\lambda^{(-)}(z_0) \right|^2 |\cos \theta_2|^2,
\]

\[
P_\perp(\theta) = \frac{3}{8\pi} n(\theta) \left| E_\lambda^{(+)}(z_0) + E_\lambda^{(-)}(z_0) \right|^2 |\sin \theta_2|^2,
\]

where \( n(\theta) = n_1 \) and \( n_4 \) for the air side and the glass side, respectively, and \( \theta_2 \) is the refraction angle in the PMMA/dye layer.

We use the expressions for a radiating dipole to simulate the fluorescence emission. We assume that an ensemble of dipoles spaced an average of 1 nm (for the thin PMMA/dye case) or 5 nm (for the thick PMMA/dye case) along the normal of the interface are radiating incoherently. Here, we use dipoles with fixed strength (the standing wave effects on the excitation beam caused by the reflection of the silver film can be taken care of by modifying the strength of the dipole accordingly, which minimally affects the simulations). All the simulations are carried out for a wavelength of 580 nm.

### 5. Angular fluorescence emission pattern

Figure 4 shows that the p- (also called transverse magnetic (TM)) and s- (also called transverse electric (TE)) polarized radiation patterns (fluorescence emission intensity versus angle \( \theta \)) are different in the intensity when excited by a TM- or TE-polarized laser for a 20 nm PMMA/dye layer with (Ag : 52 nm) and without a silver film on a BK7 substrate. The same phenomenon occurs for all the patterns we measured. This phenomenon implies that the fluorescent molecules do not ‘forget’ the state of the excitation completely.

Figure 5 shows the radiation pattern from rhodamine B molecules embedded in a thin PMMA layer adjacent to a silver layer with various thicknesses. Figure 6 shows the radiation pattern from rhodamine B molecules embedded in a thick PMMA layer adjacent to a 53 nm thick silver films. All the experimental data presented are modified from the measured data to account for the following: (i) the hemispherical-lens-side data were scaled by the normal-incident
Figure 4. Radiation patterns demonstrating a dependence on the polarization of the excitation beam for a 20 nm PMMA/dye layer with/without underlying silver film: (a) without silver, excited by TM mode; (b) without silver, excited by TE mode; (c) with 52 nm silver, excited by TM mode and (d) with 52 nm silver, excited by TE mode.

reflection coefficient between the BK7 and air \( ((1.5171 - 1)/(1.5171 + 1))^2 = 0.0422 \), since we were using uncoated BK7 lenses; (ii) the finite thickness of BK7 substrate offsets the source from the center of hemispherical lens, which caused up to 3° difference between the measured angle and the theoretical angle; and (iii) we used both horizontally and vertically polarized laser light to excite the fluorescent molecules and summed the data from these two cases by weighing the excitation intensity in order to eliminate any influence of laser polarization on the fluorescence emission patterns. The intensities of the simulations are also scaled to fit the experimental data.

5.1. Thin PMMA/dye layer

When the PMMA/dye layer is very thin, which is around 20 nm in the present case, most of the fluorescence emission will be coupled into the surface plasmon mode, which is TM.
Figure 5. Angular radiation pattern for a 20 nm thin PMMA/dye layer over silver films with various thicknesses. The excitation laser power and PMT voltage were kept constant for all the measurements.
Figure 6. Angular radiation pattern for a thick PMMA/dye layer over a 53 nm silver film together with the simulation for two different combinations of the dielectric constants at 580 nm (a) $\varepsilon_{\text{Ag}} = -13.78 + 0.79i$, $n_{\text{PMMA/dye}} = 1.51 + 0.007i$ and (b) $\varepsilon_{\text{Ag}} = -13.64 + 0.88i$, $n_{\text{PMMA/dye}} = 1.51 + 0.005i$.

Figure 7. Intensity and FWHM of the peak emission versus the silver film thicknesses (derived from the experimental data).

The peak intensity and line width vary with the silver film thickness, which results from (i) coupling into the surface plasmon mode, (ii) enhancement of the electric field, and (iii) absorption [12]. Figure 7 shows the intensity and FWHM of the peak emission versus the silver film thicknesses derived from the experimental data. The fluorescence emission from a PMMA/dye layer in the absence of a silver film is used to determine the anisotropy of the dipole orientation (around 12% off the normal for the 20 nm PMMA/dye film\(^5\)). The imaginary

\[ P^p(\theta, \varphi) = a \times P^\perp_0(\theta) + b \times P^\parallel_0(\theta) \]
\[ P^n(\theta, \varphi) = b \times P^\parallel_1(\theta) \]

is a straightforward integration with respect to the dipole orientation ($\alpha$, $\phi_0$) from equation (1) and $a = b = 1/3$. For the very thin PMMA/dye film case, we have to use $a = 1/3 - 0.04$ and $b = 1/3 + 0.04$ (0.04/(1/3) = 12%).

\(^5\) If the dipole is randomly oriented, we have $P^p(\theta, \varphi) = a \times P^\perp_0(\theta) + b \times P^\parallel_0(\theta) + c \times P^\parallel_1(\theta)$, which is a straightforward integration with respect to the dipole orientation ($\alpha$, $\phi_0$) from equation (1) and $a = b = 1/3$. For the very thin PMMA/dye film case, we have to use $a = 1/3 - 0.04$ and $b = 1/3 + 0.04$ (0.04/(1/3) = 12%).
Figure 8. Simulated reflectivity and dipole radiation curves: the silver film is 53 nm thick and $\varepsilon_{\text{Ag}} = -13.64 + 0.88i$; the PMMA/dye film is 225 nm thick and $n_{\text{PMMA/dye}} = 1.51 + 0.005i$.

part of PMMA/dye refractive index is set to be around 0.07 to fit the experimental data. The measured emission peak is broader compared with simulation, which is caused by the finite spectral width of the fluorescence.

5.2. Thick PMMA/dye layer

When the PMMA/dye layer is thick enough to support waveguide modes, most of the emission is coupled into these modes, which can be both TM and TE. The imaginary part of the PMMA/dye refractive index is set to be 0.007 and 0.005 to fit the experimental data. These values are smaller than we used for thin PMMA/dye films, and may be explained in terms of a larger roughness in the thinner films. The emission simulation is smoothed (convoluted) by averaging neighboring points in order to account for the finite detection area (the iris); this is essential when the FWHM is small.

Figure 8 shows the simulated reflectivity and dipole radiation patterns for the sample with the thicker PMMA/dye layer. The coincidence of the dip and peak verifies that the peaks of the fluorescence emission on the hemispherical lens side do originate from the waveguide modes.

6. Summary

We have measured the angular fluorescence radiation pattern from dye molecules embedded in a PMMA layer adjacent to a silver film. For thin PMMA/dye layers that do not support a waveguide mode, the fluorescence radiation is coupled into the surface plasmon mode. The peak intensity and line width vary with the silver film thickness. The scattering on the hemispherical-lens-side is highly directional and is TM polarized. For a thick PMMA/dye layer supporting one or more waveguide modes, the fluorescence radiation is coupled into these modes. The back scattering is highly directional and can be either TM or TE polarized. All of the measured results are in good agreement with our simulations. By confining most of the fluorescence emission into guided modes, it allows us to collect signal only in the desired small angular range and block all light outside this range. This helps to improve signal-to-noise ratio.
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