Distance dependence of surface plasmon-coupled emission observed using Langmuir-Blodgett films

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Surface plasmon-coupled emission (SPCE) is a phenomenon in which fluorophores in the excited state couple with metallic structures resulting in surface plasmons that radiate into the substrate. The authors examined the dependence of SPCE on the distance and orientation of a fluorophore in the nanometric range of the Ag surface. The distance of the fluorophore from the Ag surface was controlled from 2 to 52 nm using Langmuir-Blodgett films. For a horizontally oriented cyanine dye, the experimental intensity and lifetime measurements are in excellent agreement with the detailed theoretical analysis of SPCE. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2751125]

At present the vast majority of fluorescence experiments utilized emission from fluorophores into the far field. The fluorophores are usually in transparent dielectric media so that the molecules radiate into free space. However, there is now a growing interest in the near-field interaction of fluorophores with metallic nanostructures. These interactions are of interest because they offer an opportunity to modify and control the excited state deactivation pathways and spatial distribution of the emission.[1,2] One example of such interactions is the phenomenon of surface plasmon-coupled emission (SPCE). In SPCE an excited state fluorophore undergoes near-field interactions with a thin metal film. This interaction results in creation of surface plasmons which radiate into the substrate at a well-defined angle.[3,4] Thus the interactions of the fluorophores with the metal film result into directional emission. This control of the optical energy from fluorophores will result in a generation of devices for fluorescence sensing.

The effective use of SPCE will depend on an understanding of how the fluorophore-metal coupling depends on fluorophore distance and orientation relative to the metal surface. In fact, theoretical studies of SPCE have recently appeared.[5,6] While there have been several experimental studies of SPCE (Refs. 7–9), we are not aware of an experimental study of the dependence of SPCE on distance and orientation. In this letter, we studied these effects using Langmuir-Blodgett (LB) films to place fluorophores at well-defined distances from a 43-nm-thick Ag surface. This distance-dependent study of SPCE for a well-defined oriented probe is important for applications of SPCE toward a potentially powerful tool for highly sensitive fluorescence detection. These studies are also of interest because experimental results can be compared with analytical theory. We have particularly chosen the probe DiI, a long chain amphiphilic cyanine dye, to obtain a transition dipole orientation parallel to the metal film.[10] We measured the angular distribution of the emission and the distance-dependent intensity decays of the DiI molecules organized on the Ag film at varying distances. Since the orientation and distance of the

fluorophore relative to the Ag surface were well controlled by LB technique, a quantitative theoretical calculation of horizontally oriented transition dipole moment of DiI molecules relative to the metal surface could be achieved. The theoretical treatment in this letter is based on a semiclassical approach described in detail elsewhere,[5] accounting for all the parameters employed in this experimental geometry.

A silver film with thickness of 43 nm and 2 nm of SiO_2 were deposited on silanized glass slides via thermal evaporation under high vacuum ($\sim 3 \times 10^{-7}$ Torr). These 43 nm smooth Ag film and 2 nm SiO_2 on glass slides are the substrates for our present SPCE experiments. Depositions of LB films on the substrate were accomplished using a computer controlled KSV 5000 LB trough. We first deposited DiI-stearic acid (SA) (in 1:10 molar ratios) monolayer directly on the surface to obtain a probe layer with 0 nm distance from the surface (i.e., distance of 2 nm from the Ag surface due to the SiO_2 layer). Subsequently, to obtain the probes with defined distances from the surface, we deposited required number (i.e., 0, 2, 4, 6, 10, or 20) of SA layers followed by the probe layer. The use of 0, 2, 4, 6, 10, and 20 layers of SA results in total DiI probe distances (*d*) of 2, 7, 12, 17, 27, and 52 nm, respectively, from the Ag surface. In all of the samples, the top layer consisted of a single layer of DiI and SA, the alkyl chains were pointed away from the substrate. At a molar ratio of DiI:SA of 1:10, the absorption and emission spectra indicated that DiI was in a monomeric state and not aggregated.

The spectroscopic measurements were performed on a home built setup as described earlier.[7] The sample was attached with index-matching fluid to a hemicylindrical prism and positioned on a precise rotary stage. The stage was equipped for fiber optic detection, which allowed observation at any angle relative to the incident angle. The incident light ($\lambda_{ex} \sim 532$ nm) was normal to the sample interface. The output of the fiber was directed to the spectrofluorimeter (Ocean Optics SD2000) for steady-state spectroscopic measurements. For measurements of intensity decays, we have used the same geometrical configuration with fiber optic coupled with the 10 GHz frequency-domain (FD) fluorometer.[7] An excitation of 514.5 nm was from a pulsed mode-locked argon ion laser (76 MHz repetition rate). The FD intensity decays were analyzed in terms of the multiex-

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ponential model $I(t) = \sum_{i=1}^{n} \alpha_i \exp(-t/\tau_i)$, where τ_i are the decay times and α_i are the amplitudes and $(\sum_i \alpha_i = 1.0)$. It was found that intensity decays of DiI were heterogeneous, and three-exponential model was used to yield a sufficiently good fit of the experimental frequency-domain data. For each sample, the amplitude weighted lifetime $(\langle\tau\rangle = \alpha_i\tau_i/\sum_i\alpha_i\tau_i)$ was calculated. The detailed studies of complex intensity decays of DiI dye were reported even in homogeneous lipid membranes and were suggested not to assign any physical significance to the individual exponential components but rather to treat them as empirical parameters.[11,12] For comparative studies of our experimental intensity decay data with the theoretical calculations, an average lifetime of DiI in the monolayer assembly was used.

The theoretical treatment is based on a semiclassical approach, which considers a fluorescing molecule as an ideal dipole emitter. A detailed theoretical background of SPCE has been reported earlier.[5] A core quantity required for calculating the optical detection properties of interest is the angular distribution of radiation (ADR), representing the power emitted by the fluorophore (DiI in the present study) into a given solid angle. For horizontal dipole orientation, the dependence of ADR in the LB film half-space (S_f) and the ADR in the glass half-space (S_g) could be deduced as

$$S_{f,g}(\theta,\phi,z) = S_{f,g}^{\parallel}(\theta,z)\cos^2\phi + S_{f,g}^{\parallel}(\theta,z)\sin^2\phi, \quad (1)$$

where θ is the angle between the direction of emission and surface normal, and ϕ is the angle around the surface normal, and z is the fluorophore's distance from the metal surface. The total energy emitted into glass is given by

$$I_g^{\parallel}(z) = 2\pi\int_0^{\pi/2} d\theta\,\sin\theta\frac{S_g^{\parallel}(\theta,\phi,z)Q_0}{(1-Q_0)S_0 + Q_0 S_{\text{total}}^{\parallel}(z)}, \quad (2)$$

where S_0 is the total electromagnetic emission power of a molecule far away from the surface, Q_0 is its intrinsic quantum yield of fluorescence, and S_{total} is the changed total emission power near the surface. The lifetime of a molecule at a distance z away from the surface is given by

$$\frac{\tau}{\tau_0} = \frac{S_0}{(1-Q_0)S_0 + Q_0 S_{\text{total}}^{\parallel}(z)}. \quad (3)$$

It should be noted that, when calculating the total emission $S_{\text{total}}^{\parallel}(z)$, one has not only to take into account the emission into the glass and the LB film half-space but also the energy absorbed by the metal film.

Angle-dependent fluorescence intensities are shown in Fig. 1 (left panel). The emission seen through the prism displays a very sharp angular distribution. The angular distribution is most narrow for the 2 nm distance, just 1.2°, and appears to become somewhat larger as the distance from the Ag is increased. The origin of the increasing angular width with distance from the Ag film could be described as the linkage between the intrinsic optical properties of metallic structures and fluorescence. These results suggest that the angle-dependent emission intensities and the width of the peaks reflect the plasmon resonance properties of the Ag films, and not due to a distance-dependent change in the mechanism of fluorophore-metal interactions. Calculated polar plots of angular distribution of radiation using Eq. (1) presented in the Fig. 1 (right panel) agree well with the experimental results. The differences in the intensities of radiation into the free space of the theoretical and experimental
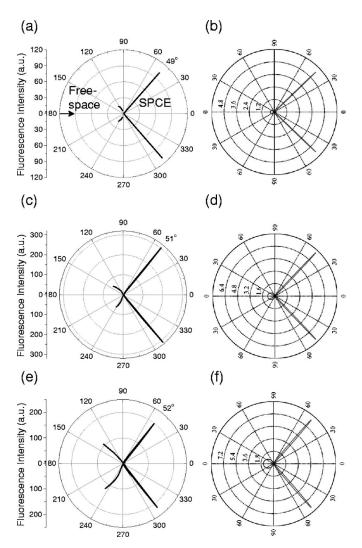

FIG. 1. Angle-dependent intensities of DiI at distances of (a) 2, (c) 17, and (e) 27 nm from the Ag surface. Calculated angular distribution of radiation from monolayer of DiI-SA at distances of (a) 2, (b) 17, and (c) 27 nm from the Ag surface.

curves (as shown in Fig. 1) could result from the surface roughness of the metal substrate. However, it should be emphasized that the theoretical results presented here were calculated for the ideal case of perfectly planar substrates.[5]

It is of interest to examine the emission intensity of the probe near the Ag films. The emission intensity consists of at least two components, the fraction of the emission coupled to plasmons and seen through the prism and the free-space emission propagating into the air side of the sample. Figure 2(a) shows an example of these components, which were recorded using the same instrumental conditions. When DiI is close to the Ag, most of the emission appears as SPCE and the free-space emission is weak. The emission spectra of DiI remain the same independent of distance and direction of observation, demonstrating that dispersion effects are negligible across the emission spectrum of the dye. An important property of SPCE is complete p polarization. We measured the polarization of the free-space and plasmon-coupled emission. The SPCE was found to be near 100% p polarized for all the samples. In contrast to the SPCE, the free-space emission was less strongly polarized. These results demonstrate that the emission seen throughout the prism is, in fact, due to radiating plasmons.
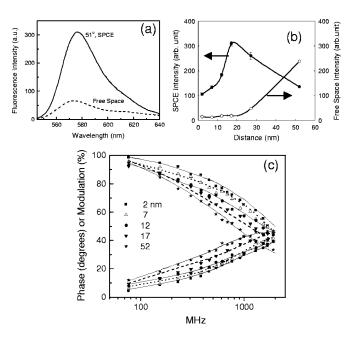
FIG. 2. (a) Free-space and SPCE spectra of DiI-SA LB film at 17 nm distance from the Ag surface. (b) Peak SPCE and free-space intensities (at a particular angle) of DiI-SA LB film as a function of distance from the Ag surface (c) Distance-dependent intensity decays of DiI-SA monolayer into SPCE mode.
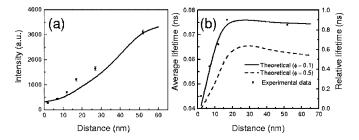

FIG. 3. (a) Total intensity of emission into SPCE mode as a function of distance from the Ag surface [the scattered plot is the experimental data and the solid line is the theoretical calculation generated by Eq. (2)]. (b) Distance-dependent average lifetime of DiI in the monolayer assembly (scattered plot); the solid and dashed lines are the calculated lifetimes of a monoexponential decaying dye as a function of distance from the Ag surface assuming fluorescence quantum yields of 0.1 and 0.5, respectively.

We used the SPCE and free-space intensities to estimate the distance dependence of the coupling efficiency of DiI to the Ag film. Figure 2(b) summarizes the distance-dependent maximum SPCE and free-space intensities. The free-space emission intensities of DiI at varied distances from the Ag film [Fig. 2(b)] were measured at a particular angle (145°) for all of the samples. In addition to the SPCE and free-space emission, we expect some portion of the energy to be lost in the Ag film due to quenching by the metal. It is observed from our measurements that the fractional amount of directional SPCE peak intensity is maximized when the probe is about 20 nm from the surface. This is a fortunate distance because many biological assays are based on surfaces coated with one or more layers of protein. Such layers are about 10–20 nm thick. Our results show a larger amount of quenching as the fluorophore approaches the metal.

If the excited fluorophores are being deactivated by interactions with the surface plasmons, it is intuitive to expect a decrease in lifetime due to this coupling. We measured the FD intensity decays of SPCE of DiI at several distances from the metal surface [Fig. 2(c)]. The fast intensity decays of DiI required to use FD instrument equipped with microchannel photomultiplier tube allowing to acquire data up to 2 GHz. Shorter fluorescence lifetimes (FD responses shifted toward higher frequencies) were observed for fluorophore close to Ag surface indicating strong and fast coupling of energy into the plasmons. The SPCE intensity decays were fit with a three-exponential model, and amplitude weighted lifetimes were calculated with values from about 50 ps for a distance of 2 nm to about 110 ps for a distance of 52 nm.

Figure 3(a) shows the total measured and numerically calculated intensity of emission from the DiI molecules into the SPCE mode at varying distances from the metal. Figure 3(b) presents the distance-dependent average lifetime of the DiI into the SPCE mode. For comparison the numerically simulated lifetimes of an emitting molecule with quantum

yields of 0.1 and 0.5 as a function of distance from the metal surface are included in the same plot. There is a very good agreement between calculated (assuming single exponential decay with quantum yield of 0.1) and the experimental lifetime data which are based on heterogeneous intensity decays. Figure 3 demonstrates strong coupling of energy for fluorescence to the surface plasmons. At very short distances both intensity and lifetime are significantly decreased which indicates that strong energy coupling does not result in efficient SPCE. The presence of the Ag film increases the radiative transition rate for fluorophores near the surface as can be deduced from decrease of lifetime at shorter distances of fluorophore from metal surface.[5]

In this letter we studied the effect of fluorophore-metal interaction on SPCE. We observed a sharp angular distribution from the fluorophore-induced plasmons and that the angular distribution was dependent on the distance. For these studies we selected a well-defined geometry of distance and orientation to allow comparison with theory. Our numerical calculations are in excellent agreement with our experimental results. For a horizontally oriented cyanine dye, the peak fluorescence intensity in the SPCE mode was observed when the fluorophore was ~20 nm from the metal surface. The SPCE emission from the monolayer of parallel oriented transition dipole moments of fluorophores is always *p* polarized, irrespective of the polarization of the incident light. As the efficiency of SPCE coupling is distance dependent, this property could be exploited for background suppression for biological samples that would be useful in a variety of analytical and medical sensing applications.

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