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Surface Plasmon-Coupled Emission for Effective Collection and Transformation of Emission into Directional Radiation

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Abstract

The use of metallic particles to modify emission was accomplished by interaction of the excited dipoles of the fluorophore with oscillating electrons in a nearby metallic surface. We used the term "metal" to describe such surfaces. We described how a fluorophore near a metal can have a different radiative-decay rate. This is an unusual effect because this rate does not change substantially when a fluorophore is in different environments. In this study, we describe another phenomenon that occurs when a fluorophore is near a metal. Under certain circumstances a fluorophore can couple with a continuous metallic surface to create groups of oscillating electrons called surface plasmons. If the metal film is thin and on an appropriate substrate the plasmons radiate their energy into the substrate. We call this phenomenon surface plasmon coupled emission (SPCE). There are numerous potential applications for this phenomenon that efficiently collects the emission and transforms it into directional radiation.

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1. Introduction

Prior to describing the theory for SPCE it is informative to describe this phenomenon (Fig. 1). Suppose an excited fluorophore is positioned above a thin silver film, where the metal film is continuous and about 50 nm thick. Such films are visually opaque. Remarkably, the emission from the fluorophore is not reflected but is efficiently transferred through the film. The spatial distribution of fluorescence is isotropic or nearly isotropic. However, the emission seen through the film occurs only at a unique angle θ_F measured from the normal. Since the sample is symmetric about the normal *z*-axis the emission occurs as a cone around the axis. This cone is not due to selective transmission of emission through the film. A large fraction of the total emission appears in the cone. About half of the emission appears in the cone and about half is free-space emission away from the film. The emission in the cone has the same emission spectrum as the fluorophore.

The light from the excited fluorophore appearing in the cone is called surface plasmon-coupled emission (SPCE) [1]. This name reflects our current understanding of the phenomenon. We believe the excited fluorophore creates surface plasmons in the metal. These plasmons do not appear to be the result of RET to the surface because the distances over which SPCE occurs are too large for RET. SPCE occurs over distances up to 200 nm or 2000Å, which are much larger than Förster distances near 50Å. The plasmons radiate into the substrate at an angle determined by the optical properties of the metal and substrate. Since the wavelength distribution of SPCE is the same as the fluorophore emission it is tempting to assume it originates from the fluorophore. However, the emission is 100% p-polarized, even if the fluorophores are randomly oriented and excited with unpolarized light. See Chapter 2 for a definition of p-polarization. This polarization indicates the surface plasmons are radiating and not the fluorophores.

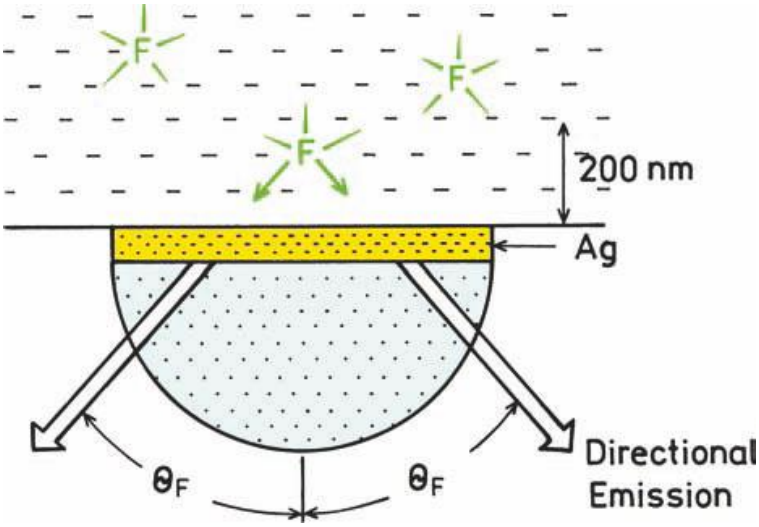

Fig. (1) Surface plasmon-coupled emission. F is a fluorophore.

The phenomenon of SPCE appears to be closely related to surface-plasmon resonance (SPR). SPR is now widely used in the biosciences and provides a generic approach to measurement of biomolecule interactions on surfaces [2-6]. A schematic description of SPR is shown in Fig. (2). The measurement is based on the interaction of light with thin metal films on a glass substrate. The film is typically made of gold 40–50 nm thick. The surface contains a capture biomolecule that has affinity for the analyte of interest. The capture biomolecule is typically covalently bound to the gold surface. This sample is optically coupled to a hemispherical or hemicylindrical prism by an index-matching fluid. Light impinges on the gold film through the prism, which is called the Kretschmann configuration. The instrument measures the reflectivity of the gold film at various angles of incidence (θ), with the same angle used for observation (θ).

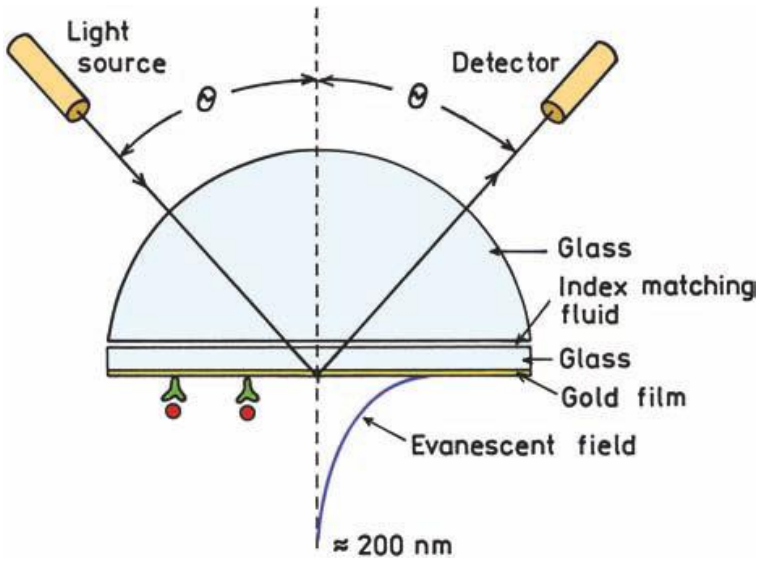

Fig. (2) Typical configuration for surface-plasmon resonance analysis. The incident beam is p-polarized

The usefulness of SPR is due to the dependence of the reflectivity of the gold film on the refractive index of the solution immediately above the gold film. The angle-dependent reflectivity of the gold surface is dependent on the refractive index of the solution because there is an evanescent field extending from the gold surface into the solution. Binding of macromolecules above the gold film causes small changes in the refractive index, which result in changes in reflectivity. Figure (3) shows typical SPR data: a plot of reflectivity versus the angle of incidence for a 47-nm gold film [7-9]. The reflectivity

minimum occurs at the SPR angle. The SPR angles change as the gold surface is coated with 11-mercaptoundecanoic acid (MU), then biotinylated polylysine (PL), and finally avidin. The changes in SPR angle are due to changes in the refractive index near the gold surface due to the adsorbed layers.

The decrease in reflectivity at the SPR angle (θ_{SP}) is due to absorption of the incident light at this particular angle of incidence. At this angle the incident light is absorbed and excites electron oscillations on the metal surface. The reflectivity is sensitive to the refractive index because of the evanescent field that penetrates approximately 200 nm into the solution (Fig. 2). The evanescent field appears whenever there is resonance between the incident beam and the gold surface. An evanescent field is not present when there is no plasmon resonance, that is, when the reflectivity is high.

The existence of an evanescent field is reminiscent of total internal reflectance (TIR), which occurs between a glass–water interface when the angle of incidence from the glass slide exceeds the critical angle [10]. There can be confusion about the relationship between the critical angle in TIR (θ_C) and the SPR angle (θ_{SP}). The physical origins of θ_C and θ_{SP} are similar, in that both are dependent on wavevector matching at the sample–glass or metal interface. However, these angles are different and not directly related. This difference between θ_C and θ_{SP} is illustrated in Fig. (4), which compares glass and silver–coated glass surfaces [11,12]. The silver-coated surface shows high reflectivity at all angles except around the plasmon angle near 30°. The reflectivity of a glass surface is quite different. The reflectivity is low below the critical angle θ_C, increases sharply to nearly 100% at θ_C, and remains high for all angles above θ_C. For the glass surface and angles above θ_C there exists an evanescent field from the totally internally reflected light. For the silver-coated glass there is no evanescent field in the aqueous phase unless the angle of incidence is near the SPR angle. The reflectivity of the silver film is high at angles significantly larger or smaller than θ_{SP}.

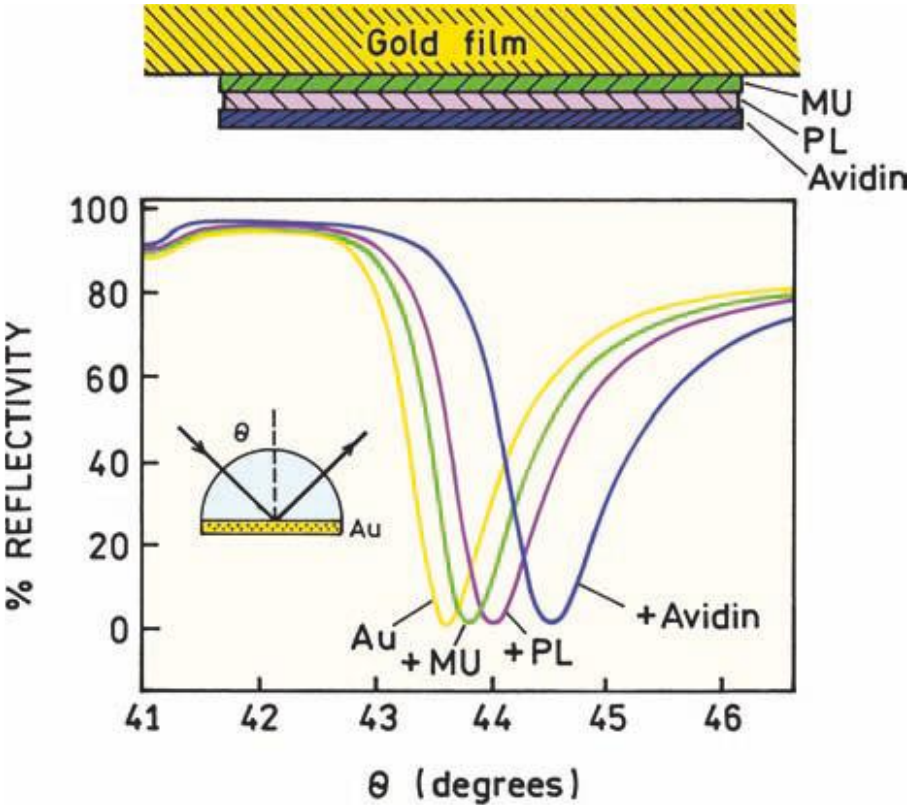

Fig. (3) SPR reflectivity curves for a 47-nm gold film on BK-7 glass. Illumination was at 633 nm. The gold film was progressively coated with 11-mercaptoundecanoic acid (MU), followed by biotinylated poly-lysine (PL), and then avidin [7–9]

The evanescent wave due to SPR is much more intense than that due to TIR [11-17]. The relative strengths of the fields can be measured by the fluorescence from fluorophores near the surface. For the sample shown in Fig. (4) fluorophores were localized within the evanescent field by coating with a polyvinyl alcohol (PVA) film that contained a fluorophore. The dependence of the emission on the incident angle indicates the relative intensity of the evanescent wave felt by the fluorophores. For the

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glass surface the emission intensity is low for $\theta < \theta_C$. This low value is essentially the same as seen in a typical fluorescence measurement where the fluorophore is excited in a glass or quartz cuvette. As the incident angle exceeds θ_C the intensity drops about twofold because the incident light undergoes TIR rather than passing into the sample. Above the critical angle the remaining intensity represents the amount of excitation due to the TIR evanescent wave. This result indicates that the field strength for TIR is roughly the same for the incident light and the evanescent wave.

Different results are seen for the labeled film on the silver surface. The emission intensity is near zero for angles above and below θ_C because of the high reflectivity of the metal film. In contrast to uncoated glass, the light does not penetrate the sample even though $\theta < \theta_C$. There is a dramatic increase in the emission intensity of the film near the plasmon angle: about 15-fold. This effect is due to a 10- to 40-fold increase in the intensity of the evanescent field above silver as compared to above glass with TIR [18-21]. This increase in field strength above a metal film is one origin of the increased sensitivity possible with plasmon-coupled emission.

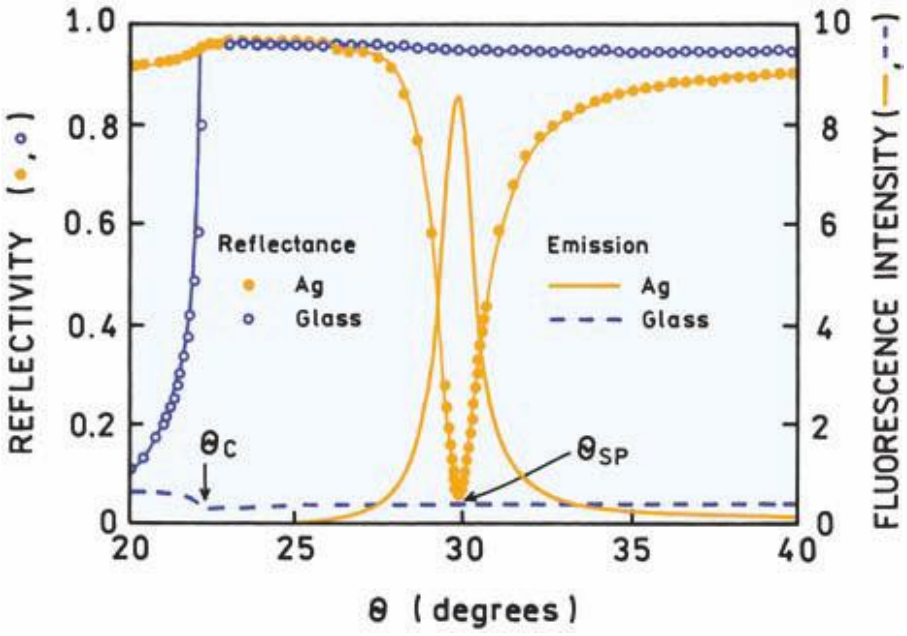

Fig. (4) Reflectivity curves for a bare glass and silver-coated glass, both spin coated with a fluorophore in polyvinyl alcohol. The prism is LaSFN9 glass, 633 nm. Also shown is the fluorescence from the labeled PVA film on the glass and silver surfaces [11]

An important characteristic of the SPR angles is that they are strongly dependent on wavelength. Figure (5) shows the reflectivity curves of a gold film for several wavelengths [22]. The surface plasmon angle decreases as the wavelength decreases. The dependence on wavelength can be understood in terms of the optical constants of the metals, which depend upon wavelength (frequency) and the dielectric constant of the adjacent prism. This dependence of θ_{SP} on wavelength is the origin of intrinsic spectral resolution when observing surface plasmon-coupled emission.

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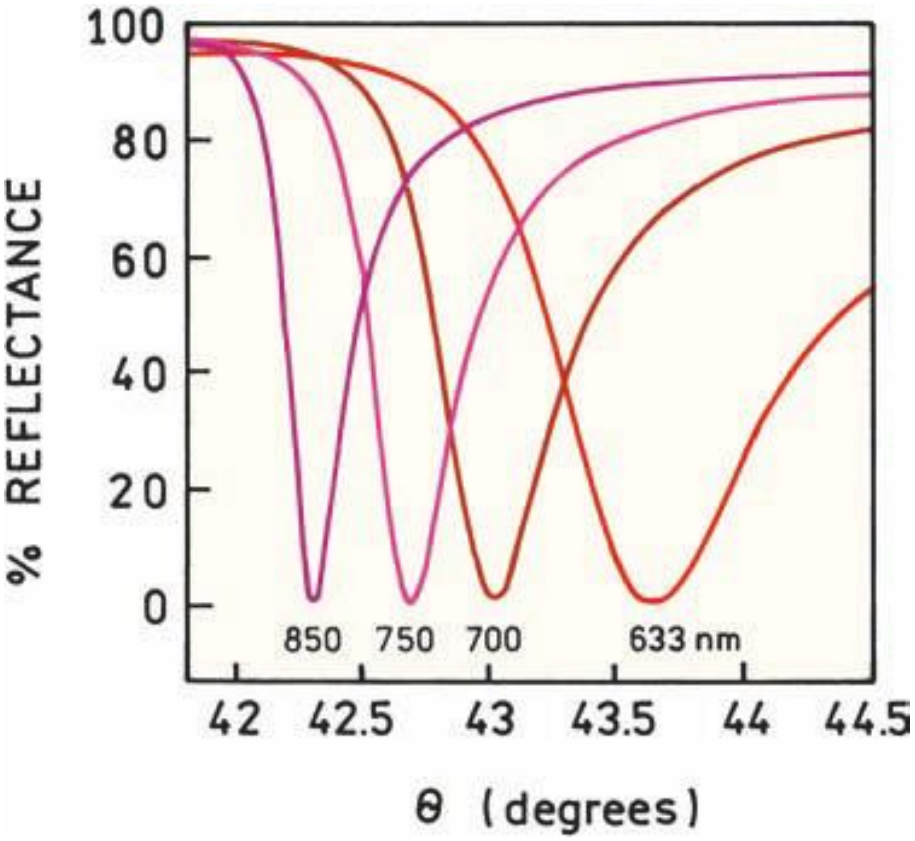

Fig. (5) Calculated wavelength-dependent reflectivity for a 47-nm-thick gold film [22]

4. Conclusion

In this study, we describe another phenomenon that occurs when a fluorophore is near a metal. Under certain circumstances a fluorophore can couple with a continuous metallic surface to create groups of oscillating electrons called surface plasmons. If the metal film is thin and on an appropriate substrate the plasmons radiate their energy into the substrate. We call this phenomenon surface plasmon coupled emission (SPCE). There are numerous potential applications for this phenomenon that efficiently collects the emission and transforms it into directional radiation.

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