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Observation of Surface Plasmon Coupled Emission using Thin Platinum Films

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Abstract

Surface plasmon-coupled emission (SPCE) is the directional radiation of light into a glass substrate due to excited fluorophores above a thin metal film. The sharp angular distribution of SPCE is a striking phenomenon and is in stark contrast with the isotropic fluorescence emission. In this paper, we show that SPCE can occur with thin platinum films at green and red wavelengths and was found to be mostly *p*-polarized. This SPCE emission is the result of near-field interactions of the excited fluorophores with the thin platinum film, and is not simply a reflective or transmissive phenomenon. Our preliminary observation suggests that platinum nanostructures can be part of several novel bio-analysis surfaces.

Keywords

Surface plasmon-coupled emission; rhodamine B; fluorescein; platinum

During the past several years there has been a growing interest in the interactions of fluorophores with metallic surfaces and particles [1–3]. Several laboratories have reported on favorable spectral changes such as increase intensity, photostability and [4–8] increased distances for fluorescence resonance energy transfer [9–10]. Excited state fluorophores can also resonantly interact with smooth thin metal attached to glass prisms that can lead to the generation of surface plasmons and the highly directional emission of the spectral properties of the excited fluorophores on the glass side [11–14]. This phenomenon is called surface plasmon-coupled emission (SPCE). Most of the previous reports showed SPCE and metal-enhanced fluorescence (MEF) with metallic silver surfaces and particles. It was also found that both SPCE and MEF could occur with both gold and aluminum, thereby, increasing the versatility of SPCE and MEF. Gold was found to be more useful at longer wavelengths [15–18] and aluminum found to be useful in the near-UV [19–20]

Because of our interest in SPCE and MEF we tested different metals such as silver, gold and aluminum. During the past several years of our research on metal-fluorophore interactions we found that SPCE generally occurs over longer distances than MEF [21–24]. For fluorophores near a smooth metal surface there appears to be three possible processes. The fluorophore can be quenched, can couple to surface plasmons or can emit into free-space. If the fluorophore is

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close to the surface (< 10 nm) there is a high rate for radiationless deactivation and the emission appears to be quenched. At distances between 10 to 100 nm the dominant decay rate is expected to be due to coupling to the surface plasmons. This is important for the applications of SPCE because coupling will occur over a significant volume in the sample allowing detection of lower overall analyte concentrations. At longer distances (> 100 nm) the reflected field interferes constructively or destructively, resulting in the oscillatory behavior reported for fluorophores in front of mirrors [25].

In the present report we show that SPCE can occur with thin platinum films at green and red wavelengths. The most convincing demonstration of SPCE can be obtained with reverse Kretschmann (RK) excitation where the incident light cannot induce surface plasmons. In RK configuration, the fluorophores are excited from the air side of the sample and the emission is observed on the distal glass/quartz side of the substrate. In this case, the incident light would not create surface plasmons and there is no evanescent field due to the incident light. An excited fluorophore near the metal film would not know how it was excited; that is, the emission should be the same whether the fluorophore is excited by evanescent field (Kretschmann configuration) or from a light source not coupled to the surface plasmon (RK configuration). In the RK geometry, the fluorophores are excited uniformly across the sample. However, only those fluorophores within a fractional wavelength distant from the metal will couple to the surface and result in SPCE. This allows the use of SPCE without the surface plasmon excitation, which can simplify the devices based on this phenomenon. Since fluorophores distant from the metal will not couple, autofluorescence from molecules not localized by the surface chemistry should be suppressed in the SPCE signal. We believe there will soon be a variety of metallic nanostructures for use in genomics, proteomics and medical testing. Our observation suggests that platinum nanostructures can be part of these novel bioanalysis surfaces.

Experimental Section

40 nm of platinum were deposited on quartz slides using an AJA sputtering system under high vacuum. The metal deposition step was followed by the deposition of 5 nm of silica via evaporation without breaking vacuum. This step served to protect the metal surface and also it adds a distance of 5 nm from the metal surface. The Pt-coated slides were spin coated with a solution of ~ 50 μ M fluorescein or rhodamine B in 0.5% PVA. The dye/PVA film is estimated to be approximately 15 nm in thickness. Figure 1 presents a schematic representation of the sample configuration.

The metal coated slides containing the samples were attached to a hemicylindrical prism made from quartz and the refractive index was matched using spectrophotometric grade glycerol between the back of the quartz slide (uncoated side) and the prism. This unit was then placed on a precise 360° rotatory stage. The rotatory stage allowed the collection of light at all angles around the sample chamber (shown in Figure 1). The excitation source used is a diode pumped solid state continuous-wave laser lasing at 532 nm. An Ocean Optics low OH 600 μ m diameter optical fiber with NA of 0.22 (Dunedin, FL) used for collecting the SPCE and free space signals was mounted on a holder that was screwed on to the base of the rotatory stage. SPCE and free space spectra were collected using a model SD 2000 Ocean Optics spectrometer connected to the optical fiber. The spectra were collected with an integration time of 1 second. Unpolarized, *p* and *s*-polarized signal information were collected for the SPCE signal (from $0 - 90^\circ$ and $270 - 360^\circ$ with respect to the front of the prism) and the Free-Space (FS) signal (from $90 - 270^\circ$ with respect to the front of the prism). Figure 1 presents a geometrical scheme for the measurement of angle-dependent emission. All data processing was performed using OriginPro 7. Time-resolved intensity decays were recorded using a PicoQuant Fluotime 100 time-correlated single-photon counting fluorescence lifetime spectrometer. The excitation source

was a pulsed laser diode (PicoQuant PDL800-B) with a 20 MHz repetition rate. The Instrument Response Function (IRF) is about 60 ps.

The fluorescence intensity decays were analyzed in terms of the multi-exponential model as the sum of individual single exponential decays:

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

In this expression τ_i are the decay times and α_i are the amplitudes. The fractional contribution of each component to the steady-state intensity is described by:

$$f_i = \frac{\alpha_i \tau_i}{\sum_j \alpha_j \tau_j} \quad (2)$$

The average lifetime is represented by:

$$\bar{\tau} = \sum_i f_i \tau_i \quad (3)$$

The values of α_i and τ_i were determined using the PicoQuant Fluofit 4.1 software with the deconvolution of instrument response function and nonlinear least squares fitting. The goodness-of-fit was determined by the χ^2 value.

Results and Discussion

We measured the emission intensities for all accessible angles around the z -axis in the plane of the Pt films. We used RK excitation since the incident light from this direction cannot excite surface plasmons. Fig. 2 shows polar intensity plots showing the SPCE and free space emission of PVA films containing fluorescein (top panel) and rhodamine B (bottom panel) respectively on 40-nm platinum films. The emission is sharply directed back into the hemicylinder and is distributed equally on both sides of the normal axis as shown in Figure 2. The emission was sharply distributed at 50° and 48° for fluorescein and rhodamine respectively. Figure 2 also shows the highly directional and predominantly p -polarized SPCE emission on Pt films, suggesting that the observed signal is due to surface plasmons. This is in stark contrast to the free-space emission which does not show any polarization or directional preference. It can be seen that the p -polarized signal intensity at the SPCE peak angle is lower in magnitude than the unpolarized signal. This occurs because the sheet polarizers used in the experiment have less than 100 % peak transmission efficiency for p - and s - polarizations. It is important to note that the angular distribution shown in Figure 2 is much sharper than those found for fluorophores on uncoated glass, and sharper than those due to reflections above a mirror.

We measured emission spectra of thin PVA films containing either fluorescein or rhodamine B on Pt films in both free-space and SPCE configuration to confirm the absence of scattered light. The emission spectra were recorded at the angle of maximum emission as shown in Figure 3. The emission spectra on the SPCE side are spectrally equivalent to the free-space emission spectra for both fluorescein and rhodamine B samples (Fig. 3a and 3b). We have also recorded the SPCE spectra through a polarizer as shown in Fig. 3c and 3d. The SPCE was almost completely polarized in the horizontal direction, which is p -polarized. The high polarization

value demonstrates that SPCE signal is due to plasmons which, because of the wavevector matching conditions are created by the excited-state fluorophores. Furthermore, the SPCE signal is *p*-polarized irrespective of the polarization of the incident light. The sharp angular distribution and *p*-polarization are characteristic of SPCE [11–14]. Our SPCE observations with reverse-Kretschmann (RK) configuration support that the surface plasmon coupling occurs in the excited state and that the SPCE is not directly created by the incident light. This suggests that the SPCE emission observed with thin Pt films is not due to direct transmission of fluorescence, but rather due to increased electromagnetic coupling efficiency between the excited state fluorophores and smooth Pt films.

Figure 4 shows intensity decays for the free-space emission and the SPCE emission for thin PVA films of fluorescein and rhodamine B on thin platinum films. We carefully considered possible artifacts and the effects of sample geometry, while recording the intensity decays. The most important conclusion from these intensity decay measurements is that the lifetimes of SPCE and the free space emission are essentially the same.

In summary, we have examined fluorescein and rhodamine B in thin polymer films on 40 nm thick Pt films on quartz substrates. We observed efficient SPCE through thin Pt films. This suggests that the energy effectively coupled through the Pt film into the quartz substrate at a sharply defined angle. A significant portion of the total emission appeared as SPCE. The SPCE emission was *p*-polarized with different wavelengths appearing at different angles. The high polarization indicates that the emission is probably due to surface plasmons which radiate into the prism. The emission lifetimes of fluorophores were mostly unchanged in the free-space and SPCE modes.

The phenomenon of SPCE has now been reported for four metals Al, Ag, Au and Pt. These metals are biologically benign and if needed can be coated with silica for which there is a great deal of surface chemistry available for linking biomolecules. Additionally, these metals are easily used in nanofabrication methods such as focused ion beam (FIB) and e-beam nanolithography (EBL). We expect SPCE to become widely used in devices for DNA and protein assays, and in diagnostic systems.

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Figure 1. Schematic representation for measurement of angle-dependent emission and sample configuration.

Figure 2. Angle-dependent intensities of (a) fluorescein and (b) rhodamine B containing PVA films on 40 nm thick platinum coated quartz slides.

Figure 3.

Top Panel: Free-space and surface plasmon-coupled emission spectra of (a) fluorescein and (b) rhodamine-B in PVA films. Bottom Panel: Polarized and unpolarized surface plasmon-coupled emission spectra of (c) fluorescein and (d) rhodamine-B in PVA films.

Figure 4. Intensity-time decays of (a) fluorescein and (b) rhodamine containing PVA films in the free space (blue) and SPCE (black) configuration. IRF is also included in the plots.