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Fluorescence Spectroscopy with Metal-Dielectric Waveguides

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Abstract

We describe a hybrid metal-dielectric waveguide structures (MDWs) with numerous potential applications in the biosciences. These structures consist of a thin metal film coated with a dielectric layer. Depending on the thickness of the dielectric layer, the modes can be localized near the metal, within the dielectric, or at the top surface of the dielectric. The optical modes in a metal-dielectric waveguide can have either S (TE) or P (TM) polarization. The dielectric spacer avoids the quenching, which usually occurs for fluorophores within about 5 nm from the metal. Additionally, the resonances display a sharp angular dependence and can exhibit several hundred-fold increases in intensity (E^2) at the silica-air interface relative to the incident intensity. Fluorophores placed on top of the silica layer couple efficiently with the metal, resulting in a sharp angular distribution of emission through the metal and down from the bottom of the structure. This coupling occurs over large distances to several hundred nm away from the metal and was found to be consistent with simulations of the reflectivity of the metal-dielectric waveguides. Remarkably, for some silica thicknesses, the emission is almost completely coupled through the structure with little free-space emission away from the metal-dielectric waveguide. The efficiency of fluorophore coupling is related to the quality of the resonant modes sustained by the metal-dielectric waveguide, resulting in coupling of most of the emission through the metal into the underlying

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ASSOCIATED CONTENT

Supporting Information. Figures S1-S4 data using RK illumination, and the simulation results on effect of probe distance dependence on the metal-dielectric waveguide coupled emission are included. This material is available free of charge via the Internet at <http://pubs.acs.org>

glass substrates. Metal-dielectric waveguides also provide a method to resolve the emission from surface-bound fluorophores from the bulk-phase fluorophores. Metal-dielectric waveguides are simple to fabricate for large surface areas, the resonance wavelength can be adjusted by the dielectric thickness, and the silica surface is suitable for coupling to biomolecules. Metal-dielectric waveguides can have numerous applications in diagnostics and high-throughput proteomics or DNA analysis.

Keywords

Plasmon coupled waveguide; Waveguide-coupled emission; Plasmon-controlled fluorescence; Surface plasmon-coupled emission; Surface plasmon-enhanced fluorescence; Total internal reflection

Introduction

During the past 15 years there has been a rapidly expanding interest in fluorophore-metal interactions.¹⁻³ This interest stems from a realization that excited state fluorophores can interact with plasmons on metal surfaces which can increase the radiative decay rate and result in a corresponding decrease in the excited state lifetime. These effects are useful because they can increase sensitivity and fluorophore photostability, and in the case of single molecule detection these effects can decrease blinking.^{4,5} A wide variety of metal-particle geometries have been tested including heterogeneous silver island films,^{6,7} well defined arrays of metal particles⁸⁻¹⁰ and clusters or aggregates of metal particles.^{11,12} This phenomenon is typically called metal-enhanced fluorescence (MEF). There have also been impressive advances using continuous metal films to modify the spatial distribution of fluorescence. This is possible because fluorophores can couple with and/or create surface plasmons on metal films under conditions when there would be only reflection with far-field incident light at the same frequency (wavelength). Stated differently, at near-field distances, fluorophores can create plasmons on the metal surface even when far-field light at the same wavelength is reflected. Importantly, the plasmons and/or fluorophore-plasmon system (plasmophore) then radiates from the bottom distal side of the metal film with a narrow angular distribution.¹³⁻¹⁵ This phenomena is called surface plasmon-coupled emission (SPCE). These observations demonstrate two important characteristics of metal-fluorophore interactions. First, fluorophores within near-field distances from a metal interact differently than freely propagating light at the same frequency. And secondly, the angular or spatial distribution of the emission is controlled by the geometric structure and/or optical properties of the metallic nanostructures. Realization of these principles opens the imagination to conceptualizing how nanostructures can be used to control emission, from its point of origin, rather than with optical components acting on the far-field propagating radiation. Additionally, these interactions can alter the radiative decay rates of the fluorophores and avoid the usual reliance on the intrinsic spectral properties of fluorophores. As one example, several laboratories have reported directional emission and/or beaming of fluorescence when the fluorophores are localized on or near the structures with nanoscale surface features.¹⁶⁻¹⁸ However, the cost and complexity of fabricating structures with nanoscale features,

particularly over large macroscopic (centimeter) dimensions, has limited their use in biological applications such as clinical assays and drug discovery.

To bypass the present limits of nanofabrication technology we have focused our efforts on multi-layer structures which can be made using simpler methods such as vapor deposition, spin-coating or self-assembly. The layers can be metals or dielectrics, typically with an individual thickness of less than a wavelength. For example, we have recently used multiple dielectric layers with different dielectric constants, which are typically called one-dimensional photonic crystals (1DPC) or Bragg gratings.¹⁹ These structures can display a photonic band gap (PBG) where a range of wavelengths cannot pass through the structures.^{20,21} With selected thickness these structures can also display Bloch surface wave (BSW) where the optical energy is trapped at the structure - air/sample interface. Although based on a different physics, BSWs are similar to surface plasmons (SP) except that there are less optical losses which allow higher local fields. We found that fluorophores on the surface of the 1DPC (not within) could couple with the BSW to result in Bloch wave-coupled emission (BWCE). We also found that fluorophores could couple with internal modes of the 1DPC where the mode density is almost completely in the structure. We refer to these phenomena as Bloch wave-coupled emission (BWCE) and internal mode coupled emission (IMCE), respectively.^{19,22} These results with 1DPCs, and the previous results for MEF and SPCE, suggest that novel and useful effects can be obtained by combining photonic and plasmonic structures.

In the present paper we described the interactions of fluorophores with a hybrid plasmonic-dielectric structure which we call a metal-dielectric waveguide (MDW). This structure consists of a thin metal film coated with a single dielectric layer of varying thicknesses. The term metal-dielectric waveguide is convenient but it should be noted that some of the metal-dielectric waveguide modes appear to have interactions with surface plasmons. The P-polarized modes are affected by the plasmonic properties of the metal film, especially P1 mode as shown with surface-plasmon coupled emission. The S-polarized modes are reflected by the metal but display little if any interactions with plasmons. When using the metal-dielectric waveguides the fluorophores are placed on top of the dielectric layer at the dielectric-air interface, which would be the location for surface-based assays. We found that fluorophores on this top surface can display efficient long range coupling with the metal film up to 500 nm away from the fluorophores. We refer to this phenomenon as waveguide-coupled emission (WGCE). For excitation fluorophores coupled to the evanescent fields at the dielectric-air interface created by the incident light. For emission the excited state fluorophores couple with the mode density at the dielectric-air interface. The metal-dielectric waveguides support both S- and P-polarized resonances, both of which can couple with the surface-localized fluorophores. The angular distribution of the emission can be controlled by the thickness of the dielectric film and different spectra can be observed at different observation angles. As compared to surface plasmons, the optical modes of the metal-dielectric waveguides show the less energy loss to the metal because both the modes and the fluorophores are distant from the metal film.

A variety of structures have been investigated for their effects on surface-localized fluorophores. To avoid confusion it is useful to compare our metal-dielectric waveguides

with structures which are used for SPR, SPCE and surface plasmon-enhanced fluorescence (SPEF). SPCE has been reported for dielectric-coated metal films.²³⁻²⁵ In all these cases the fluorophores were located throughout the dielectric layers where coupling could be expected. This location within the dielectric prevents the use of these structures for most applications because the fluorophores are in a solid phase and the samples do not penetrate into the dielectric. In the present paper the fluorophores are located on top of the metal-dielectric waveguide and directly accessible to the sample. To the best of our knowledge coupled emission from this location has not been reported. Thin metal films have also been used for surface plasmon-enhanced fluorescence (SPEF). SPEF use the enhanced plasmonic field on top of the metal for excitation but does not use the coupled emission, instead it uses free-space emission away from the top of the structure.²⁶⁻²⁷ SPEF has been extended to use with dielectric-coated metal films where the probes were located within hydrogels serving as the top layer.^{28,29} A variation of SPEF is to use a structure which supports long-range surface plasmons, but again only the free-space emission was used for detection.^{30,31} Surface plasmon resonance (SPR) also uses thin metal films and is widely used for label-free detection of binding to metal surfaces.^{32,33} Surface plasmon resonance has also been used with dielectric-coated structures which display narrow resonances because the mode is more localized in the dielectric.^{34,35} A variation of this approach was used for SPR by Mojahedi and co-workers who used the S- and P-modes to obtain different depths of the evanescent field and thus sample different regions in the sample.³⁶⁻³⁸ These methods are used to detect changes in refractive index above the metal film.

In the present paper the experimental results are presented first, followed by a description of the optical properties of the metal-dielectric waveguides. The optical properties are described in a progressive manner proceeding from transmission spectra to full dispersion diagrams. This progressive description is intended to enable chemists and biologists to use the metal-dielectric waveguides in their own research.

Experimental Methods

The methods used to prepare metal and dielectric films have been described in detail.^{39,40} Briefly, 50 nm films of Ag were deposited on clean glass slides by either thermal vapor deposition or sputtering vapor deposition. The Ag film is then coated with silica by sputtering. The thickness of the layers was determined from calibration curves of film thickness versus deposition time. These calibrations were confirmed by a K&N model 1200 spectroscope. For fluorescence measurements the structures were spin coated with polyvinyl alcohol (PVA) in water which contained Rhodamine B (RhB) to obtain a thickness of 25 nm. These structures will be called Ag-x-RhB where $\times$ refers to the silica thickness in nm.

The apparatus for measuring observation angle-dependent intensities and emission spectra was described previously in detail.^{15,23,24} The sample is illuminated at a known angle and polarization using a 532 nm CW laser and a 1 mm diameter optic fiber positioned 2 cm from the sample, with a 550 nm long-pass filter and a polarizer between the fiber and sample. Emission spectra are recorded using a model SD2000 Ocean Optic spectrometer with 1 nm resolution.

Simulations of transmission, reflectance and field intensities profiles of the metal-dielectric waveguides were performed using the C- method.⁴¹ Whilst the fluorescence intensities depend on the excitation field intensities at the top dielectric surface where the fluorophores are located. These effective intensities, relative to the incident light, were calculated two ways; the field intensity at the PVA-air interface, and the average intensity in the top 25 nm PVA layer. Depending on the polarization of the incident radiation, either S- or P-, the field intensity is calculated by taking the squared modulus of either the electric or the magnetic field, respectively. The calculated intensity is normalized to the intensity of the incident radiation, which allows a direct comparison between the S-polarized and P-polarized intensities. Where possible these simulations were confirmed using TFCalc from Software Spectra, Inc.

The optical configurations for the measurements are shown in Figure 1. The metal-dielectric waveguide structure is placed on a cylindrical prism and coupled with a refractive index matching fluid. The sample can be illuminated two ways. Light incident through the prism is called the Kretschmann (KR) illumination. Light incident from the free-space (sample) side is called reverse Kretschmann (RK) illumination. Emission away from the top of the sample will be called free-space emission (FS Em.). Emission out through the prism will be called coupled emission (CP Em.). P-polarization refers to an electric field oriented in the plane of incidence with a component perpendicular to the surface. S-polarization refers to an electric field across the plane of incidence and parallel to the surface. The angles of observation are relative to the surface normal, with 0° being directly below the sample and 180° being directly above the sample. Unless otherwise stated, the presented results were obtained with KR illumination through the structure. Similar results were obtained with RK illumination and are shown in the Supplemental Information. The S and P designations do not apply using reverse Kretschmann excitation. For S polarized incidence, the incident light electric vector was parallel to the S-polarized observation and similarly for the P polarized incidence it is parallel to P-polarized observation (Figure 1).

Results and Discussions

High Efficiency Coupling with Metal-Dielectric Waveguides

The interaction of fluorophores with metallic structures occurs over near-field distances. Maximum coupling of fluorophores with metallic nanoparticles occurs from 10 to 20 nm from their surfaces.^{42,43} Fluorophore coupling to continuous metal films occur at distances to 50 nm.⁴⁴ Hence we expect weak fluorophore-metal coupling for silica thickness larger than 50 nm when the fluorophore is located above the silica. Figure 2 compares the emission intensities when the fluorophore is directly on the metal surface (Ag-0-RhB) or separated from the metal by 130 nm of silica (Ag-130-RhB). For these distances the coupled emission was predominately P- or S-polarized, respectively. Surprisingly, we observed an over 115-fold higher CP emission intensity with the 130 nm spacer. This comparative difference was not completely due to quenching of RhB because the intensity did not increase substantially with silica spacers up to 75 nm (Figure 5, below). Comparable results were obtained with RK illumination (Figure S1). The intensity difference for RK illumination was smaller, about 8-fold, as compared to that with KR illumination.. This difference is due to a resonant

illumination condition obtained in KR configuration. In fact, when the laser wavelength, polarization and angle of incidence suitable for coupling with one of the modes sustained by the structure are reached, a rather intense field is produced at the structure surface. Such a field creation is not possible with RK configuration. This aspect is further detailed when discussing the optical properties of the metal-dielectric waveguide structures, below.

We anticipated that metal-dielectric waveguides will have potential applications in surface based bioassays. Currently, most of these studies are performed using regular microscope glass slides. Accordingly we also compared the fluorescence spectral features from metal-dielectric waveguides with that from glass slide. Figure 2 also shows such emission spectral comparison where we observed an over 180-fold higher coupled emission intensity with the metal-dielectric waveguide having 130 nm spacer as compared to it from glass. Once again the intensity difference for metal-dielectric waveguide versus glass using RK illumination was smaller (Figure S1), about 16-fold, as compared to that with KR illumination.

The coupled emission from Ag-130-RhB was found to be highly directional with KR (Figure 3) or RK illumination (Figure S2). The coupled emission with Ag-0-RhB is completely P-polarized and for Ag-130-RhB is completely S-polarized. In the case of Ag-0-RhB the intensity ratio between FS and CP is lower than that for Ag-130-RhB. This result indicates that RhB located 130 nm from the Ag film is efficiently coupled to the metal-dielectric waveguide. We also note that the emission angular distribution is wider for 0 nm silica as compared to 130 nm silica. This might be because of the higher losses due to the metal layer in Ag-0-RhB.

To investigate the distance-dependent coupling we prepared a series of samples, Ag-x-RhB, with silica thicknesses (x) ranging from 0 to 520 nm. Representative angular distributions are shown in Figure 4 for KR illumination. The peaks are numbered by their polarization and sequence of appearance with increasing silica thickness. For 80 nm silica, the emission is dominantly P-polarized with a modest distribution of emission angles. For 150 nm silica the emission is S-polarized with a very narrow angular distribution. For 260 nm silica both S- and P-polarized emission was observed. In this case the relative intensities of the S- and P-polarized emission were dependent upon the incident polarization. The same angular peaks were found for RK illumination with similar but not identical relative intensities (Figure S3). When the silica thickness increases to 260 nm, the relative intensity of coupled emission with respect free-space emission is decreasing as compared to the Ag-130-RhB sample (Figure 4).

We measured the effect of silica thickness on the coupled emission intensities (Figure 5). A precise comparison is difficult because each silica thickness requires a different incident angle and the apparatus needs to be aligned for each metal-dielectric waveguide structure. For silica thickness below 80 nm only P-polarized emission was observed (P1 in Figure 5). As expected the coupled emission intensity decreases with increasing the RhB distance from the metal. For a silica thickness above 100 nm there is a rapid increase in S1 intensity till it becomes over 115-fold more intense than P1 for 130 nm silica, which is consistent with the results shown in Figure 2. As the silica thickness increases the S1 intensity decreased. At about 200 nm silica the P2 resonance appears and above 400 nm silica weak emission at the

S2 resonance is observed. Similar trends were observed with RK illumination but the intensities were more variable (not shown).

The coupled emission with the metal-dielectric waveguide structures also provides spectral resolution by observation at different angles through the prism. For each resonance the apparent coupled emission spectra depend on small changes in the observation angles (Figure 6). The apparent emission maxima shift to shorter wavelengths at large observation angles. Similar results were found with RK excitation (Figure S4). The emission spectral shift occurs within each S- or P-resonance. Upon changing to another resonance a similar set of emission spectra are observed. That is, the emission maxima show similar angular dispersion around each metal-dielectric waveguide resonance. The spectral position of the emission maxima of the free-space spectra is not dependent on the observation angle. Only a decrease of the overall collected power is observed, as expected from a roughly isotropic angular distribution of the emission. This result demonstrates that the free-space emission is not affected by the metal-dielectric waveguide structure, but the emission which propagates through the structure, coupled to the optical modes of the metal-dielectric waveguide.

We examined the effect of incidence angle on the emission intensities of RhB with Ag-0-RhB and above Ag-100-RhB. These silica thicknesses were selected because P- or S-polarized emission could be observed from respective structures. We used the free-space emission for experimental simplicity. The emission intensities of RhB were strongly dependent on incident angles for both S- and P-polarized illuminations (Figure 7). The S-emission appears at a smaller angle than the P-emission, which is in agreement with the S1 and P1-coupled emission. The angle-dependent increases in emission intensity correspond with the decreases in reflectivity of the metal-dielectric waveguide for each polarization. The angular excitation resonance is wider for P1 than S1, which is a result of the plasmonic properties of the metal film. As will be shown below this wider resonance is due to the contribution of the plasmonic properties of these silver films.

It is well-known that fluorophores near metallic surfaces display decreased lifetimes, which is usually attributed to a high emission density of states (DOS) within near-field distances of metallic surfaces and/or the Purcell effect.⁴⁵⁻⁴⁷ Photonic crystals can also modify the local DOS and increase or decrease the radiative rate constant.^{48,49} We measured the intensity decays of RhB on two of the metal-dielectric waveguide structures. Both the free-space and coupled emission were measured for Ag-0-RhB and Ag-100-RhB. RhB on a plain glass slide displayed a decay time of 2.76 ns. The decay times of RhB were slightly reduced when placed on the metal-dielectric waveguides. For all measured conditions the decay times were only slightly reduced to values from 2.27 to 2.58 ns. We did not observe an initial short decay time as is frequently found with metallic nano-structures. These observed lifetimes are somewhat surprising and might need further understanding to interpret the plausible mechanisms involved. However, Ag-0-RhB data is consistent with the previous results on surface plasmon-coupled emission.^{15,23,24}

Optical Properties of the Metal-Dielectric Waveguides

The high efficiencies of WGCE and the simplicity of our metal-dielectric waveguides suggest they will find widespread applications in the biosciences. The design of the metal-

dielectric waveguides for specific applications is greatly facilitated by an understanding of their optical properties and mode locations within the structures. In the physics literature optical properties are often shown as dispersion diagrams of light frequency versus in-plane wavevector.^{19,20} An intuitive understanding of these dispersion diagrams can be difficult because the units of frequency and wavevector do not match the units used in the measurements. Additionally, these two-dimensional plots do not directly show the shapes of the resonances. For these reasons we first separately describe the dependence of reflectance on wavelength and incidence angle, and then incorporate these into the 2D dispersion diagrams. We simulated the wavelength-dependent reflectance spectra for several metal-dielectric waveguides with 45E, KR incidence (Figure 9). For Ag-0-RhB there is the well-known surface plasmon P-resonance near 800 nm. When the silica thickness is increased to 100 nm the previous P-resonance is no longer present. Instead there is an S-resonance at 520 nm and a weak P-resonance at about 320 nm. For Ag-250-RhB there are two S- and one P-polarized resonances. An alternative approach is to examine the angle-dependent reflectivity of the structures (Figure 10). Ag-0-RhB displays a single surface plasmon resonance (P1). With a 100-nm layer of silica the P1 resonance shifts to larger angles and the first S-polarized resonance (S1) appears at lower angles. As the silica thickness is increased (Ag-520-RhB) the P1 resonance disappears and additional S- and P-resonances appear at smaller angles.

A more general approach is to combine the wavelength and angle-dependent reflectivity into a single dispersion diagram (Figure 11). The dark bands indicate a decrease in reflectivity due to an optical mode in the structure. For RK illumination the structures display near complete reflection with minimal dependence on the incident angle (not shown). Resonances are found only with KR illumination. For Ag-0-RhB there is no S-polarized mode and only a single plasmon resonance P1 is observed (Figure 11, left panels). As the silica thickness is increased there is a progressive shift of the resonances to higher angles. As this shift occurs additional S- and P-polarization resonances appear as the previous resonances shift to higher angles. These plots also explain the different emission spectra observed at different observation angles (Figures 6 and S4). For a given thickness of silica the S and P resonances shift to longer wavelengths and the closely spaced S and P modes are responsible for the multiple peaks in some of the emission spectra.

The dispersion diagram in Figure 11 shows the reflectivity properties of the metal-dielectric waveguides. The reflectivities are not easily related to the local excitation intensities because they do not indicate the losses or quality of each mode. Additionally, the reflectivities do not directly show the emission intensities because the coupling efficiency for each resonance and silica thickness is not known. To understand these effects we simulated the field intensity (E^2) profiles for metal-dielectric waveguides with different silica thicknesses (Figure 12). These profiles were simulated using the incidence angles which correspond to the reflectance minima. The profiles are for the 580 nm emission wavelength, but will be similar for 530 nm, the modes involved being the same. For S-polarized incident light there is essentially no field for a silica thickness below 100 nm because there is no mode (Figure 11, top). An S-polarized mode appears above 100 nm thickness and the overall field can be enhanced to over 400-fold relative to the incident light. This is a surprising result because the fields with TIR are only enhanced to about 4-fold.^{50,51} The S-fields are located mostly

within the silica, but show intensity beyond the PVA layer for distances which depend on silica thickness. These local fields can excite fluorophores in the top PVA layer or in samples located above this layer, which could be the bulk phase of a sample.

Different field distributions were found for the P-polarized modes (Figure 12). At 0 nm silica there is the usual surface plasmon field which is enhanced about 200-fold. When the Ag is covered with 260 nm of silica the field at the interface increases to about 300-fold relative to the incident field. This increase is due to the distance of the mode from the metal and lower optical losses. The change in the field profile occurs when the silica thickness increases. The field intensity shifts to become localized at the PVA-air interface. At this location the P-polarized field is 2-fold higher than the usual surface plasmon field and 300-fold higher than the incident intensity.

For comparison with the measured intensities in Figure 5 we calculated field intensities at the PVA-air interface (Figure 13) for different values of the silica layer. This allows us to evaluate the best silica thickness for efficiently couple the emitted radiation into a desired mode at a representative emission wavelength $\lambda = 580$ nm. Similar results were obtained with averaging the field in the top 25 nm PVA layer (not shown). At each silica thickness the KR incidence angles were adjusted to obtain the minimum reflectance (i.e. mode coupling). These simulated field intensities approximately follow the measured WGCE intensities shown in Figure 5. The S1 mode is more intense than the P1 mode, and is comparable to P2. The appearance of the S1 mode is consistent with the high intensities observed for silica thickness from 100 to 200 nm. The nature of the S- and P-resonances in the metal-dielectric waveguide is revealed by the field intensities at the Ag-silica interface (Figure 14). In this location the P-resonances are more intense than the S-resonances.

The simulations in Figures 11-13 suggest a mechanism for the high WGCE intensities, in particular for the S1 intensity. To clarify this point we calculated the dispersion diagrams for 130 nm silica which showed the highest intensity (Figure 15). At the emission wavelength of 580 nm there is a single S1 mode. For this same thickness the P1 mode is beyond 80 deg for 580 nm, and the P2 mode is just starting to appear mostly at shorter wavelengths, so only the S1 mode is available for coupling and the energy is not distributed among multiple modes. This mode is confined by reflections by the metal and the dielectric-air interface and TIR. It seems likely that multiple reflections at this thin metal film results in leaking of most of the energy through the metal.

Conclusion

In conclusion, here we showed the concept of waveguide coupled emission and fabrication of the metal-dielectric waveguides and their optical properties dependence with the thickness of the dielectric silica layer. The experimental data is well supported with the numerical calculations and later guide the designing the structure of interest. In addition to the simple fabrication, the metal-dielectric waveguides have a number of properties which are favorable for surface-based assays. There is nothing that limits the metal-dielectric waveguide to silver, so Al and Au can also be used. The use of Al will extend the wavelength range to the ultraviolet⁵²⁻⁵⁴ and the use of Au will extend the response to the

NIR.⁵⁵ The fluorescence quenching due to gold will be minimized because the fluorophores will be outside the range for FRET, which is thought to be one of the quenching mechanisms.⁵⁶⁻⁵⁸ The structures can be optimized for a selected wavelength by simple modifications of the dielectric thickness. The top surface will be silica which can be activated for binding of biomolecules. Importantly, the metal-dielectric waveguides provide a new approach to the design of structures to control fluorescence.

The mode structure of the metal-dielectric waveguide can provide additional information about the surface-bound molecules. These structures display both S- and P-polarized modes. The evanescent fields can have different polarizations which can provide information about the orientation of the bound biomolecules. Dynamic changes in orientation may be obtained from the relative amounts of S- or P-polarized WGCE or by their time-dependent decays. The evanescent field depth is different for different modes. While the field depths are not completely adjustable, significant changes are available by selection of the dimensions, polarization and observation angle. This optical property of the metal-dielectric waveguide can be used to design structures with different surface sensitivities. The selectivity for surface-selective detection will be increased because of the large enhanced fields which can be obtained with KR illumination at specific angles.

The metal-dielectric waveguides can also be used with multiple optical geometries. For example, consider a high-throughput microwell plate. The metal-dielectric waveguides do not contain any nanoscale features besides the layers, and can thus be made with large areas at low cost. Fluorophore excitation can occur thin using either KR or RK illumination. In either case emission from fluorophores distant from the surface will not couple to the structure and will be reflected (Figure S5). The dielectric thickness can be varied at different locations to optimize detection for different wavelength. The S- and P-resonances in the metal-dielectric waveguides are narrower than the usual surface plasmon resonance, which can be used for multiple assays based on the angle of excitation and/or emission.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.
Schematic of the metal-dielectric waveguide structure and geometry of the measurements.

Figure 2.

Emission spectra of RhB in PVA on a metal-dielectric waveguide structure with 0 and 130 nm silica. P- (blue) and S-polarized (red) emission. KR excitation at the resonance angles for the P1 and S1 resonances were used as shown in the insets. The S-polarized emission for Ag-0-RhB and P-polarized emission from Ag-130-RhB are not significant.

Figure 3.

Angular distribution of RhB emission intensity at 580 nm. RhB is doped in PVA on the metal-dielectric waveguide structure with 0 (top) and 130 nm silica (bottom). KR excitation using 532 nm at resonance angles. Very weak signal was detected for the P-polarized emission at with 130 nm SiO₂ (not shown).

Figure 4.

Angular distribution of emission intensity at 580 nm from RhB in PVA on the metal-dielectric waveguide structures with various silica thicknesses. Intensity was measured with KR excitation using 532 nm; P – polarized (blue) and S – polarized (red).

Figure 5. Silica thickness-dependent coupled emission intensities for RhB in PVA on the metal-dielectric waveguide structures. Intensity measured at the angle for maximum intensity for KR illumination at 532 nm.

Figure 6.

Effect of observation angles on the emission from Ag-150-RhB for the FS (top) and CP emission (bottom). KR excitation using 532 nm.

Figure 7. Effect of the KR incidence angle and polarization on the FS emission intensities of Ag-0-RhB and Ag-100-RhB. Also shown are the simulated reflectivities.

Figure 8.
Intensity decays for RhB on the indicated metal-dielectric waveguides. IRF, instrument response function.

Figure 9.

Calculated reflectivity spectra of the metal-dielectric waveguides with KR incident light at 45 degrees. With RK incidence light spectra is over 90% for all wavelengths and angles.

Figure 10.

Angle-dependent reflectivity for 580 nm incident light on the metal-dielectric waveguides with silica thickness of 0, 100 and 520 nm.

Figure 11.

Wavelength and angle-dependent reflectivity for metal-dielectric waveguides with 0 (left), 100 (middle) and 520 nm (right) with KR illumination. The reflectivity with RK illumination at any angle shows complete reflection similar to 0 nm SiO₂ with S-polarized illumination (top left).

Figure 12.

Electric field intensities for S –polarized (top) and P –polarized incident light of 580 nm.

EFI were simulated at angles of minimum reflectance. Dotted lines show interface PVA/Air.

Figure 13. Simulated field intensity at the PVA-air interface, shown with a black arrow in the inset schematic.

Figure 14. Simulated field intensity at the Ag-Silica interface, shown with a black arrow in the inset schematic.

Figure 15.
Simulated reflectivity for Ag-130-RhB.