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Coupling of Fluorophores in Single Nanoapertures to Tamm Plasmon Structures

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Abstract

Metal nanostructures (such as plasmonic antennas) have been widely demonstrated to be excellent devices for beaming and sorting the fluorescence emission. These effects rely on the constructive scattering or diffraction from different elements (such as metal corrugations or nanorings) of the nanostructures. However, subwavelength-size nanoholes, without nearby nanoscale features, results in an angularly dispersed emission from the distal surface. Herein, we demonstrate for the first time the emission redirection capabilities of a single isolated nanoaperture milled in a thick silver film deposited on a dielectric multilayer. Specifically, we show that a dye dissolved in ethanol filling in the nanoaperture can couple to Tamm Plasmon Polariton (TPP) modes of the structure. Due to the small in-plane wavevectors of the TPPs, the fluorescence from Tamm-coupled dyes within the nanoaperture is emitted normally to the sample surface, with a minimum angular width of about 12.54°. This kind of fluorescence manipulation has proven to be effective with various nanoaperture shapes, such as circles, squares, and triangles. Our work is also the first experimental demonstration of lateral coupling of fluorophores with TPPs in nanoholes, with potential applications in bioanalysis and biosciences.

TOC Graphic

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Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:XXX Schematic of the experimental setup, angle-dependent reflectivity curves calculated from the structure in without a nanoaperture in the metal film, electric field intensity (E^2) distributions within the Tamm Plasmon structure, without nanoapertures in the metal film, with incident angles fixed at the resonant angle of TPPs, angularly and spectrally-resolved reflectivity maps for the metallic-dielectric multilayer structure here considered, SEM images, FFP and BFP fluorescence images from the single nanoaperture with various diameters, are all included in the support information.

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INTRODUCTION

Fluorescence-based techniques have been widely used in optics, chemistry, material science, super-resolution optical microscopy, molecular biology, medical sciences, drug screening and DNA sequencing¹⁻⁷. Many fluorophores show high quantum yields with omnidirectional emission i.e. emission occurs in all directions and it is difficult to capture a significant fraction of the total emission. High Numerical aperture (N.A.) objectives and/or closely located lenses with multi-cm diameters are used to increase the detection efficiencies. These requirements result from the far-field radiation distribution being due to the usually random orientations of the dipoles. In recent years, an alternative concept has emerged, which exploits a near-field coupling of fluorophores with nearby nano-structures to control or modify the angular distribution of the emission. When metallic nano-structures sustaining plasmonic resonances are used, we refer to plasmon- controlled fluorescence⁸. This kind of near-field effects has been used to develop plasmonic nanoantennas⁹⁻¹⁴. Examples include large single-molecule fluorescence enhancements produced by a bowtie nano-antenna made of two closely placed triangle gold nanoparticles¹⁵, and the optical Yagi-Uda antennas that are analogous to a traveling wave phase array antenna and can induce strong directionality of the coupled fluorescence emission¹⁶. A nanoaperture surrounded by a periodic set of shallow grooves in a gold film has also been proposed for beaming and sorting the fluorescence emission. For each fluorescence wavelength, the direction of the emitted power is oriented along a specific direction with a given angular width, thus enabling a micrometer-size dispersive antenna¹⁷⁻²¹. Periodic plasmonic structures (such as finite-sized hexagonal arrays of nanoaperture milled in gold film) have also been exploited to enable directional emission from single fluorescent molecules in the central aperture²². The total emission intensity, integrated over the whole solid angle, is often enhanced many-fold as compared to the corresponding total emission from a free-space dipole. This effect is thought to be due to several factors, such as an increased excitation rate due to high light-induced fields in the structures, an increased quantum yield due to increased radiative rates and a decreased photo bleaching²³⁻²⁴. The directional emission is achieved by the coherent near-field coupling between scattering metal nano-scale features working as the building blocks of these plasmonic structures. The coherent scattering (or constructive interference) enhance the interaction strength of each scattering building block²⁵⁻²⁷. Fluorescence emission

enhancement and controlled directionality by means of plasmonic elements requires often complicated metal nanostructures, and to the best of our knowledge these effects were not reported with an isolated metal nanoaperture^{22, 28}. Herein, for the first time, we demonstrate directional control of fluorescence from a single nanoaperture in a metal film. This effect is obtained by fabricating the nano-aperture on a metallic film deposited on a multilayered dielectric structure exhibiting a photonic band gap (PBG). Such a metallic-dielectric structure supports Tamm Plasmon-Polaritons (TPPs)^{29, 30}, which are electromagnetic modes that can be formed in a multilayered dielectric structures (e.g. a Bragg mirror) coated with a thick metallic film. TPPs are characterized by an electromagnetic energy distribution that is highly localized at the interface between the metallic film and the multilayer, (see Supplementary Figure S3). Differently from Surface Plasmons on planar films, TPPs are spectrally dispersed according to curve laying within the light cone of the both the substrate and the outer medium, as shown in Supplementary Figure S4. As a result, TPP can have close-to-zero in-plane wavevector components (k_x , k_y) at certain wavelengths and a corresponding electric field oriented substantially parallel to the multilayer interfaces. In a previous work, we exploited this feature to obtain coupled fluorescence directed along the surface-normal z-axis³¹⁻³². However, as the TPP maximum amplitude is located beneath the metallic film, an efficient coupled fluorescence is obtained only from emitters that are sandwiched between the top dielectric layer and the metal coating.

In an attempt to overcome this geometrical constraint, we present here a novel approach based on nano-apertures in the metal film. We questioned if the TPPs can continue to exist under a metal-free nanoaperture and if fluorophores within the aperture can couple to the TPPs. This configuration can greatly reduce the fabrication requirements and complexity for metal nanostructures, and can provide a new structure for highly multiplexed genetic or diagnostic assays.

METHODS

Nanoapertures were fabricated by focused ion beam (FIB) milling in silver films. Figure 1 presents our experimental configuration (a) together with scanning electron microscope (SEM) view of our sample (b). The silver film is about 200 nm thick, which essentially eliminates transmission through the structure and confines the observation volume to the isolated aperture. The diameter (D) of the aperture is about 620 nm. We also used varied diameter (D) of the aperture in the subsequent experiments. The silver film is deposited on a dielectric multilayer consisting of alternative SiO₂ (low refractive index, $n = 1.46$, 105 nm thick) and Si₃N₄ (high refractive index, $n = 2.13$, 55 nm thick) layers which were fabricated by the Plasma-enhanced chemical vapor deposition (PECVD). The top Si₃N₄ layer that is in contact with the silver film is of about 53 nm thick, which enables the Tamm Plasmon Resonant (TPR) wavelength for 580 nm light with near normal incidence (Figure 1c). An ethanol solution containing fluorescent molecules (Rhodamine B, RhB) with 10⁻⁴ M concentration was spotted on top of the sample to fill the aperture. The excitation laser light is focused from the bottom of the sample (glass substrate) by means of a 1.35 N.A. oil immersion objective (Figure S1). The illumination wavelength is set at 532 nm and the polarization is linear. In order to analyze the angular fluorescence emission, we collected the fluorescence intensity distribution by means of back focal plane (BFP, or so-called Fourier

plane) imaging onto a scientific camera (Andor, Neo sCMOS). In BFP images, the fluorescence intensity is distributed according to the emission direction. More specifically, the radial coordinate scales as $n \sin \theta$, where n is the refractive index of the external medium^{33, 34} and θ is the polar emission angle with respect to the optical z-axis. In our setup, an oil-immersion objective is used, therefore $n = 1.515$ (refractive index of the oil matched the glass substrate) and the polar angle θ is the fluorescence emission angle in the oil medium. Upon averaging over the azimuthal angle, fluorescence radiation patterns can be calculated as a function of the polar angle θ . Another CCD (Lumenera's INFINITY2-1M digital CCD camera) is used for front focal plane (FFP, or direct space) imaging.

In our measurements, Rhodamine B (RhB) dyes are used. The fluorescence spectrum (Figure 1d) collected by means of a spectrometer (iHR 550, HORIBA Scientific) shows the broad spectrum typical for the RhB emission. In order to collect a spectrally-resolved fluorescence images from the TPP structure, three band pass filters are used, with center wavelengths at 560 ± 2 nm, 580 ± 2 nm, and 600 ± 2 nm (full width half maximum, FWHM = 10 ± 2 nm).

RESULTS AND DISCUSSION

Experimental FFP and BFP images with a single nanoaperture ($D=620$ nm) at three selected fluorescence wavelengths are presented in Figure 2. The FFP images clearly show that the fluorescence is only emitted from the nano-aperture location, thus demonstrating that silver film is thick enough to block the fluorescence from emitters outside the aperture. The BFP images display remarkable differences with the three selected emission wavelengths. At a 580 nm wavelength, a beam surrounded by a ring at a larger angle is observed. At 560 nm, the central beam expands to a ring, while at 600 nm, no central beam is found. In order to better evaluate the differences in the radiation patterns, we reconstructed a polar plot (Figure 2g) of radiated flux per solid angle (θ) by averaging the radiated power over the azimuthal angle (ϕ). In the data processing, the fluorescence intensity on the positions of the same polar angle (θ) but with different azimuthal angle (ϕ , ranging from 0° to 360°) will be summed, then this sum represent the fluorescence intensity at this selected polar angle (θ) as shown in Fig. 2g.

A narrow beam with an angular width of about 19.48° (half-width at half-maximum, HWHM) appears in the direction normal to the glass for emission wavelength at 580 nm. The observed angular width is consistent with other observations of directional emission from Rhodamine 6G molecules coupled to plasmonic antennas (such as a metal nanoaperture surrounded with metallic grooves)¹⁸. At 560 nm emission wavelength, the fluorescence is directed at a polar angle $\theta=17.63^\circ$, with an intensity minimum along the direction normal to the sample surface. Based on our previous work^{31, 32}, emission peaks at 0° ($\lambda=580$ nm) and 17.63° ($\lambda=560$ nm) correspond to the Tamm plasmon coupled emissions (TPCE)^{31, 32}, where TPPs are confined between the metal film and the dielectric multilayers. The emission peaks at 32.60° (for $\lambda=580$ nm) and 38.82° (for $\lambda=560$ nm) are associated to fluorescence coupled to internal modes of the dielectric multilayer (referred to as internal mode coupled emission, IMCE)^{31, 32}. The IMCE emission angles are determined by the mode in-plane wavevector components at the corresponding wavelengths. Similarly,

due to the small in-plane wavevector components of TPPs, the observed TPCE is directed almost normally to the sample. In fact, at $\lambda = 580$ nm, the dominant Tamm Plasmon Resonant Angle (TPRA) is nearly at 0° . The TPRA increases as the fluorescence wavelength decreases. For example, at $\lambda = 560$ nm the observed TPRA is about 17.63° ³⁵. On the other hand, if the fluorescence wavelength increases, for example at $\lambda = 600$ nm (Figure 2f, 2g), the corresponding TPP coupled emission disappears, as no Tamm plasmons are available at this wavelength. The changes of TPRA with the wavelength are consistent with the calculated angle-dependent reflectivity curves (Figure S2), where the TPRA is 17.36° (for P-polarization) or 18.16° (for S-polarization) for 560 nm wavelength, and 0° for 580 nm wavelength. The structure does not support Tamm plasmons at 600 nm and a resonant dip does not appear at 600 nm. The difference between experimental IMCE angle and calculated internal mode resonant angle is probably due to the broad angular width of these coupled emissions. The optical field of internal modes is mainly confined inside the dielectric multilayers (Figure S3b, S3d), with evanescent tails leaking out in the outer medium. However, a weak coupling of fluorophores to the internal modes is still observed. Our experimental results demonstrate that the interplay of a single aperture in a metallic film with a dielectric multilayer may result in a directional sorting of the fluorescence emitted by dyes within the aperture itself, whereas no significant directional feature is observed for nanoapertures on metal-coated glass substrate^{22, 28}. More importantly, the results shown in Figure 2 indicate that emitters can still couple to Tamm plasmons without being necessarily located underneath the metal film.

Experimental results are well supported by rigorous calculations. The near-field interaction emitter-structure is investigated by means of a three-dimensional Finite Difference Time Domain (FDTD) model (Lumerical Inc.). Single dipoles are placed at the bottom of a 600 nm diameter aperture, in a central position, with dipole momentum oriented either perpendicular (vertical) or parallel (horizontal) to the sample surface. Upon calculation of the near-field energy distribution in a close volume surrounding the sources, a far-field projection is performed in order to get the free-space emitted power in the glass half-space. Results are shown in Figure 3.

When dealing with horizontally-oriented dipoles, the radiation patterns presented in Figures 3a-c are calculated by averaging the emitted power from multiple dipoles having momentum laying on the sample surface with a varying azimuthal orientation over a 2π range. In this way, we eliminate the axial symmetry about the dipole momentum of the emitters and obtain azimuthally homogeneous intensity distributions that provide a closer picture to the experimental observations. FDTD calculations have been performed by considering emitters with a well-defined orientation and position with respect to the nano-aperture in order to illustrate the coupling mechanism to photonic and plasmonic modes of the structure. Worth to recall, however, that the experimental observations are related to RhB molecules in ethanol, which are continuously moving and rotating at random, in time.

At $\lambda = 560$ nm (Figures 3a, d), both horizontal and vertical dipoles are shown to contribute to TPCE, at leakage angles according to the Tamm plasmon dispersion curve for s- and p-polarizations (see Figure S4). At $\lambda = 580$ nm, Tamm plasmons have small in-plane wavevector components and an electric field oriented mainly parallel to the multilayer

surface. Therefore, horizontally-oriented dipoles will preferentially contribute to TPCE (Figure 3b), which is angularly distributed within a narrow beam about the surface normal. Vertically-oriented dipoles are substantially polarization-mismatched with TPPs, thus resulting in a weak TPCE (Figure 3d). At $\lambda = 600$ nm, no Tamm plasmons are available (see Figure S4) and all dipoles weakly couple to internal modes of the multilayer, depending on their polarization orientation (Figure 3c, e).

In the following experiment, four isolated apertures with diameters $D = 200, 400, 800$, and 1000 nm are investigated to show the effect of the aperture diameter on the directional coupled-emission. Nano-aperture SEM micrographs, FFP and corresponding BFP fluorescence images are shown in Figure S5. Figure 4 shows the emission radiation patterns from single apertures as observed on the BFP. For aperture having $D = 200$ nm, the IMCE is suppressed relative to the TPCE at $\lambda = 560$ nm and $\lambda = 580$ nm, and only one emission peak (TPCE) is dominant in the radiation pattern (Figure 4a). With an increasing aperture diameter, IMCE becomes stronger and finally approaches the intensity of TPCE in the case of $D = 1000$ nm (Figure 4d).

This effect can be explained by assuming the coupling to TPPs to occur preferentially in proximity of the bottom aperture boundaries, close to the lateral metallic walls. Instead, all dipoles filling the inner area of the aperture will preferentially couple to the multilayer internal modes or directly to the free-space, as TPPs is not available anymore. As a result, for an increasing aperture diameter, the TPCE intensity is expected to increase proportionally, but the relative TCPE intensity over the total emission intensity follows an opposite trend. Apart from a change of the intensity ratio between TPCE and IMCE, the TPCE angular width at 580 nm wavelength is also increased gradually with the increasing diameter. The minimum angular width is about 12.54° observed at $D = 200$ nm (Figure 4a). Differently from previous reports on plasmonic antennas that can direct the fluorescence beam along a specific direction for each emission wavelength, in this case fluorescence is directed along two specific directions (TPCE and IMCE). The influence of the aperture size on the directional sorting of fluorescence emission provides a means to control the intensity ratio of fluorescence beams along the two specific directions by tuning the relative weights of TPCE and IMCE.

Finally, we demonstrate that triangular and squared apertures can control the fluorescence emission. One of the advantages of single nanoaperture for manipulating the fluorescence emission is that single apertures can be fabricated with low cost over large scale for high throughput sensing. Each aperture can work as a single antenna to manipulate the fluorescence emission and the aperture array can be seen as a set of parallel antennas. The advantage of this arrangement is investigated by considering two arrays of 5×5 triangular and square nano-apertures, as shown in Figures 5a and 5e. The side length is 804 nm for the triangular and 532 nm for the square aperture, which results in nearly equal area for both types. The period of the aperture arrays is $1.5 \mu\text{m}$, which is much larger than the fluorescence wavelength. The excitation laser beam was focused onto the central aperture of the two arrays (Figures 5b, and 5f). FFP fluorescence images show that the maximum of fluorescence intensity is associated to the central aperture. The BFP images at two selected fluorescence wavelengths (560 nm (Figures 5c and 5g) and 580 nm (Figures 5d and 5h)) are

similar to Figures 2d and 2e. Despite a different shape, TPCE is beamed normally to the sample (at 0°) for 580 nm and at about 20.01° for 560 nm emission (Figures 5i and 5j). This observation suggests that the angular dispersion of the coupled emission is independent on the aperture shape, as far as dye molecules can be near-field coupled to the Tamm plasmon confined beneath the silver coating. In our experiment, if we focus the laser beam into other apertures of the array, the radiation pattern does not change, meaning that each aperture can work independently as an individual antenna. If the distance between each aperture is furtherly increased, to several micrometers, the eventual coupling between apertures can be totally ignored. Since the angular distributions are the same for a single aperture and the 5×5 aperture arrays, the overall TPP resonance was not significantly affected by the selective removal of metal corresponding to each aperture. This is a favorable result for use of these structures in DNA sequencing or other highly multiplexed assays.

The present results significantly extend the scope of previous observations concerning fluorophores coupled to Tamm Plasmon structures³⁵⁻³⁸. In that work, the fluorophores were located under a continuous metal film. Embedding molecules below the metal film is not favorable for applications in fluorescence sensing or imaging, especially for liquid samples. To the best of our knowledge, the present study demonstrates for the first time that coupling can also occur when fluorophore is located within apertures in the metal film of a Tamm structure, regardless of the aperture shape. In this configuration, fluorescent probes can be located inside the metal aperture without necessarily being buried below the metal film. The aperture can also be filled with probes at different emission wavelengths, in order to implement a high throughput sensing.

CONCLUSIONS

In conclusion, we have demonstrated a new class of structures, which can be used to obtain surface-normal or angularly directed emission. The Tamm plasmon structure is highly versatile for several reasons. Incident light can couple into and out of the sample in either direction, away from the top metal film or down through the dielectric layers. Both S- and P-polarized light can couple to the Tamm plasmon modes. In contrast to surface plasmons on a metal-coated glass slide the wavelengths and coupling angles can be adjusted over a wide range by adjusting the thicknesses of the dielectric layers. The top metal film can also be Al or Au, which allows this structure to be used from deep UV to NIR wavelengths. Thus a wide range of wavelengths and fluorophores can be used for multiplex assays. Since the Tamm plasmon coupled emission occurs at angles below the critical angle a coupling prism is not required, which allows these structures to be immediately useful with the microwell plates and printed array images which are widely used in biomedical research.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

(a) Schematic of the Tamm Plasmon Structure. Thicknesses of the Si_3N_4 and SiO_2 layers are 55 and 105 nm respectively. The top Si_3N_4 layer is of about 53 nm thickness. (b) SEM image of the metal aperture milled in a silver film 210 nm thick. The diameter (D) of the aperture is about 620 nm. (c) Reflection spectrum from the sample shows a dip located at 577 nm wavelength. (d) Fluorescence spectrum of the RhB molecules dissolved in the ethanol solution. The solution is spotted on the sample surface. The peak wavelength is located at 580 nm. Three narrow bandpass filters with center wavelengths at 560, 580, and 600 nm were used to select the fluorescence wavelength. The filters spectral width is 10 nm.

Figure 2.

FFP fluorescence images from the sample at three selected wavelengths, 560 nm (a), 580 nm (b), and 600 nm (c). (d), (e) and (f) are corresponding BFP images. The green circles on (a, b, c) label the focused spot of the excitation laser beam (532 nm wavelength). The white dashed circles on (d) represent the largest collection angle ($\theta=63^\circ$) determined by the N.A. of the objective (1.35). The short red dashes represent TPCE and the long red dashes IMCE. The polar angles (θ) of TPCE and IMCE are 17.63° and 38.82° (d), 0° and 32.60° (e). For the wavelength at 600 nm, only IMCE appears at 27.70° . (g) Angular radiation patterns in

the polar angle (θ), as derived from BFP images (d, e, f). The arrows (a, d) show the polarization of the incident laser beam (vertical direction for FFP images and horizontal direction for BFP images).

Figure 3.

Angularly-resolved (normalized) power emitted at 560 nm, 580 nm and 600 nm wavelength in the glass substrate from horizontally-oriented dipoles (a-c) and vertically-oriented dipoles (d-f) placed within a 600 nm diameter aperture.

Figure 4.

Angular radiation patterns in the polar angle (θ) from single nanoaperture with diameter D of about 200 nm (a), 400 nm (b), 800 nm (c) and 1000 nm (d). The plots are deduced from the BFP images in Figure S5. The emission wavelengths center at 560 and 580 nm

Figure 5.

SEM images (a, e), FFP (b, f) and BFP (c, d, g, h) fluorescence images from the samples with 5×5 apertures array. The apertures are filled with ethanol solution of Rhodamine B. The nanoapertures have a triangular shape with side length 804 nm (a, b, c), and a squared shape with side length 532 nm (d, e, f). (i) and (j) are the radiation patterns derived from corresponding BFP images. The arrows (b, c) show the polarization of the incident laser beam (vertical direction for FFP images and horizontal direction for BFP images).