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Radiative decay engineering 7: Tamm state-coupled emission using a hybrid plasmonic–photonic structure

Ramachandram Badugu [a], Emiliano Descrovi [b], Joseph R. Lakowicz [a,*]

[a] Center for Fluorescence Spectroscopy, Department of Biochemistry and Molecular Biology, University of Maryland School of Medicine, Baltimore, MD 21201, USA
[b] Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, Torino 10129, Italy

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ABSTRACT

There is a continuing need to increase the brightness and photostability of fluorophores for use in biotechnology, medical diagnostics, and cell imaging. One approach developed during the past decade is to use metallic surfaces and nanostructures. It is now known that excited state fluorophores display interactions with surface plasmons, which can increase the radiative decay rates, modify the spatial distribution of emission, and result in directional emission. One important example is surface plasmon-coupled emission (SPCE). In this phenomenon, the fluorophores at close distances from a thin metal film, typically silver, display emission over a small range of angles into the substrate. A disadvantage of SPCE is that the emission occurs at large angles relative to the surface normal and at angles that are larger than the critical angle for the glass substrate. The large angles make it difficult to collect all of the coupled emission and have prevented the use of SPCE with high-throughput and/or array applications. In the current article, we describe a simple multilayer metal–dielectric structure that allows excitation with light that is perpendicular (normal) to the plane and provides emission within a narrow angular distribution that is normal to the plane. This structure consists of a thin silver film on top of a multilayer dielectric Bragg grating, with no nanoscale features except for the metal or dielectric layer thicknesses. Our structure is designed to support optical Tamm states, which are trapped electromagnetic modes between the metal film and the underlying Bragg grating. We used simulations with the transfer matrix method to understand the optical properties of Tamm states and localization of the modes or electric fields in the structure. Tamm states can exist with zero in-plane wavevector components and can be created without the use of a coupling prism. We show that fluorophores on top of the metal film can interact with the Tamm state under the metal film and display Tamm state-coupled emission (TSCE). In contrast to SPCE, the Tamm states can display either S or P polarization. The TSCE angle is highly sensitive to wavelength, which suggests the use of Tamm structures to provide both directional emission and wavelength dispersion. Metallic structures can modify fluorophore decay rates but also have high losses. Photonic crystals have low losses but may lack the enhanced light-induced fields near metals. The combination of plasmonic and photonic structures offers the opportunity for radiative decay engineering to design new formats for clinical testing and other fluorescence-based applications.

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Fluorescence detection is one of the most widely used tools in the biosciences, with applications to cell imaging, medical diagnostics, biophysics, DNA sequencing, and protein arrays. Beginning with the initial applications of fluorescence to biochemistry during the 1960s, there have been continual improvements in probe chemistry, light sources, optics, and detectors. Currently, probes have high quantum yields and detectors have reached maximum quantum efficiencies. As a result of these advances, there are only limited opportunities to increase the observed brightness of fluorophores using classical far-field free space optics. Because of these limitations, we began an investigation of the effects of metallic particles and surfaces on fluorescence. We took this approach because there was an opportunity to increase the brightness of fluorophores by coupling both excitation and emission to surface plasmons [1–3], which can result in metal-enhanced fluorescence [4,5]. In addition, we saw the opportunity to convert the usual omnidirectional fluorescence to directional emission by using wavevector matching at the metal surfaces [6,7]. This phenomenon

* Corresponding author. Fax: +1 410 706 8408.
E-mail address: jlakowicz@umaryland.edu (J.R. Lakowicz).

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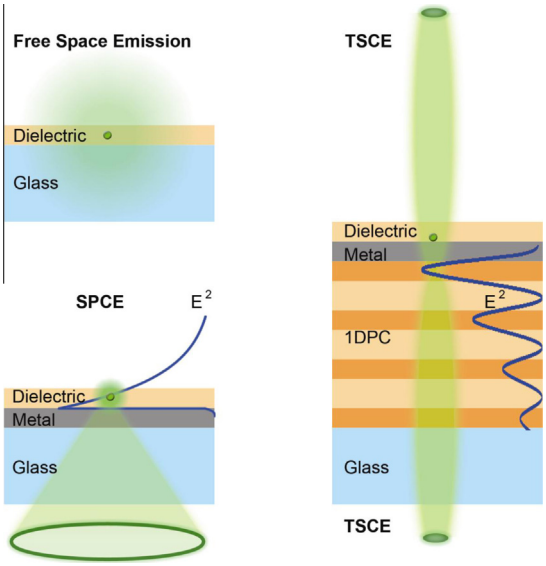
is called surface plasmon-coupled emission (SPCE).[1] We refer to these general approaches as radiative decay engineering (RDE) to emphasize the distinction from classical fluorescence with unrestricted free space emission. The interaction of fluorophores with metals is now an active area of research.

Many laboratories have reported that metallic particles of Ag, Au, and Al can enhance the emission intensities in both ensemble and single-molecule experiments [8–14] at wavelengths from the ultraviolet (UV) to the near infrared (NIR) [15–17]. Novel plasmon-coupled probes, which are composite structures of fluorophores with metal particles or fluorophores contained in nanoshells, have been reported. These probes display single-particle intensities that are comparable to quantum dots [18–24]. One of the most remarkable aspects of RDE is its ability to design the desired directional and wavelength distribution of the emission using nanostructured metal surfaces [25–27]. All of these effects are based on the same phenomenon, which is the interaction of fluorophores (dipoles) with resonant or nonresonant plasmons on the metal nanoparticles or surfaces [28–31]. These interactions can occur both during excitation, via the high light-induced fields, and during emission, by changes in the radiative decay rate [32–35]. Fluorophore–plasmon coupling offers the opportunity to combine fluorescence with the rapidly developing field of plasmonics [36–39].

Photonic crystals (PCs) offer another approach for modification of fluorescence. PCs are composed of dielectrics rather than metals. PCs typically contain repeated structural features that are comparable in size to 0.25 to 1.0 wavelengths. PCs can have features in one, two, or three dimensions [40,41]. In the current article, we deal only with one-dimensional PCs (1DPCs), which consist of alternative layers of high and low dielectrics of appropriate thickness. These structures are sometimes referred to as Bragg gratings (BGs). PCs and BGs display the remarkable phenomenon of photonic band gaps (PBGs). A PBG is a range of wavelengths of light that cannot propagate in the structure. These wavelengths are almost completely reflected. Reflection by a PC with a PBG is different from reflection by a metal. In the case of metals, the electrons in the metal oscillate in response to the incident light so that the electric field direction is reversed. In a PC with a PBG, the incident light penetrates a short distance into the PC as an attenuated wave, which is then reflected out of the PC. Reflection at a PBG is analogous to total internal reflection (TIR) at a dielectric–air interface. Because PBGs often exist over a narrow range of wavelengths, PCs often display bright colors that are determined by which wavelengths are accepted or repelled by the structure. These colors exist without chromophores and are sometimes called structural colors [42,43]. Typically, the optical constants of dielectrics vary slowly with wavelength. As a result, the optical properties usually scale with the physical dimensions of the structure. An important difference between PCs and metals is that the dielectrics in PCs have low losses at visible wavelengths. Hence, the quality factors for a mode can be high, and there is less quenching or fewer energy losses than with metals.

The high scientific interest in PCs gives the impression of a long scientific history. However, PBGs were first predicted rather recently in 1987 [44,45]. Most experimental results on PCs are focused on the physics or their application to fiber-optic communications, where they are referred to as distributed BGs [46]. There have been a limited number of publications on the effects of PCs on fluorescence, mostly using three-dimensional colloidal dielectric crystals [47,48]. Recently, we reported on properties of fluorophores on 1DPCs [49,50]. We found that fluorophores located within the strong fields of Bloch surface waves (BSWs) or internal modes of the 1DPC efficiently emit into the radiation modes, yielding sharp angular distribution of emission in and through the substrate. We refer to this phenomenon as Bragg grating-coupled emission (BGCE). However, BGCE and SPCE share the same disadvantage. In both cases, the emission appears at large angles relative to the surface normal (Scheme 1). These angles are above the critical angle (outside the light cone), which in turn requires immersion objectives for efficient collection of the emission. In addition, incident light from the air cannot interact with these resonances. A prism or grating coupler is needed to increase the wavevector of the incident light [50–52].

In the current article, we extend our previous work on fluorescence using plasmonic or photonic structures to a structure that contains features of both plasmonic and photonic components. We chose this approach because it offers the opportunity to allow both excitation and emission to occur within the light zone at angles less than the critical angle. In fact, depending on dimensions



Scheme 1. Comparison of a free space emission and a surface plasmon-coupled emission (SPCE) with a Tamm state-coupled emission (TSCE).

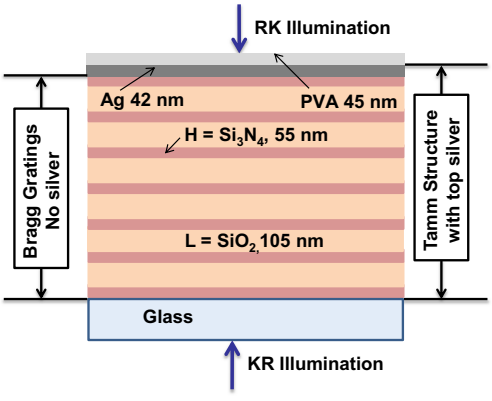


Fig.1. Schematic for the Tamm structure and Bragg grating (BG).

[1] *Abbreviations used:* SPCE, surface plasmon-coupled emission; RDE, radiative decay engineering; PC, photonic crystal; 1DPC, one-dimensional PC; BG, Bragg grating; PBG, photonic band gap; BGCE, Bragg grating-coupled emission; SPR, surface plasmon resonance; OTS, optical Tamm state; PVA, polyvinyl alcohol; S101, sulforhodamine 101; RhB, rhodamine B; Rh6G, rhodamine 6G; FL, fluorescein; PECVD, plasma-enhanced chemical vapor deposition; L, low; H, high; KR, Kretschmann; RK, reverse Kretschmann; TSCE, Tamm state-coupled emission; NPM, nanoporous metal.