UNIVERSITY OF AMSTERDAM

Plasmon Asssisted Fluorescence Emission: Far-Field Observables and Their Fluctuations

L.A. Langguth

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Summary:

Fluorescence describes the property of matter to absorb light and shortly after emit light of another color. Fluorescent materials are found in nature, e.g. in the jelly-fish *Aequorea victoria*, in some plants and mushrooms, and in minerals such as *Fluorite* in which this property was first scientifically described. For electric lighting in our homes and streets fluorescent materials are a key ingredient in every compact fluorescent lamp and white light LED. In the life sciences, fluorescent molecules have become indispensable to selectively mark functional parts of living cells or tissues, and fluorescence microscopy is of paramount importance for today's biological imaging. Which color is absorbed by the fluorophore, and how much time it takes until the fluorescence photon of lower frequency is emitted, are properties of the fluorescent molecule. Additionally, these parameters depend on the optical environment of the molecule. Metallic nano-structures can act as effective antennas for fluorophores, as they can increase the emission rate, determine the polarization, spectral shape and radiation pattern of the fluorescence emission. Therefore, metal nano-structures are pursued by many groups to improve fluorescence microscopy.

This thesis is divided into three parts and targets the question of how different fluorescence applications can benefit from metal nano-antennas.

The first part addresses the scenario of a plasmon-antenna enhanced fluorescence correlation spectroscopy (FCS) experiment. FCS allows to locally determine the mobility of fluorescent molecules in solution, via the analysis of fluctuations of the fluorescence intensity generated from a high numerical aperture focus. The fluorescence fluctuations originate from random motions of the fluorophores in and out of the detection volume. In 2003, Levene et al. performed FCS in round nano-apertures (ø~ 50 nm) in an optically thick aluminum film, to reduce the detection volumes by three orders of magnitude compared to a diffraction limited focus. In Chapter 2 we revisit conventional FCS where the detection volume is given by a diffraction limited focus in a bulk liquid. How the detection volume changes in the presence of a spherical nano-antenna is illustrated by exact calculations of antenna-enhanced FCS at a Mie sphere, which evidences two intense near-field lobes i.e. `hotspots'. In Chapter 3 a general model is developed which allows the efficient calculation of FCS measurements in the presence of arbitrarily complex detection volumes. The model is applied to a simple system of a diffraction limited focus with a superimposed hot-spot, which elucidates the requirements and limitations of a plasmon-enhanced FCS experiment. It is shown, how the fluorescence background originating from the diffraction limited focus, adversely affects the high correlation contrast provided by the hotspot.

The second part of the thesis describes how the position of a single molecule relative to a nano-antenna translates into far-field properties of the fluorescence emission, such as polarization, fluorescence lifetime or radiation pattern. In Chapter 4 we present a new method to localize single molecules close to a nano-antenna based on these different far-field observables. The proposed method uses simultaneous measurements of different far-field observables, which allow to reconstruct the coordinates with an accuracy of a few nanometers relative to the nano-antenna. Moreover, it allows localization rates in the kHz regime. Chapter 5 shows how diffusing emitters introduce fluctuations in non-intensity observables. Furthermore, we discuss how lifetime fluctuations can alleviate the problems of background signals which we encountered in Chapter 3. Additionally, Chapter 5 shows that lifetime and polarization fluctuations can be used to measure the near-field volume of plasmonic antennas.

As the calibration of a plasmon enhanced FCS experiments is intrinsically challenging, Chapter 6 presents a plasmonic design of a dual focus FCS experiment which allows the measurement of a diffusion coefficient without additional calibration.

Part three discusses two experiments which address the question of how to shape the angular distribution of the fluorescence emission of an incoherent ensemble of dye molecules. Chapter 7 presents an improvement to the nano-aperture enhanced FCS measurements. Typically, a large fraction of fluorescence photons is lost because the emitter does not radiate into the collection optics, but rather into surface plasmons, i.e., surface waves bound to the metal film. We show how the surface plasmons can be recuperated to contribute to the photon signal by using small periodic arrays of nano-apertures. These couple the surface plasmon polaritons into highly directional free space radiation right into collection optics. Chapter 8 combines the concept of metasurfaces with an ensemble of incoherent sources in a waveguide. Metasurfaces consist of nano-structured elements which are arranged on a periodic lattice in a plane. If the spacing between these elements is much smaller than the wavelength of an impinging electromagnetic wave, the wave perceives effective interface properties, which can modify the polarization and phasefront almost arbitrarily by design of the metasurface.

We show how the design of the periodic meta-surface allows to control the scattering amplitude of the reciprocal lattice, and how it translates into directional emission of the ensemble fluorescence into the far-field.