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Enhanced light extraction from emitters close to clusters of resonant plasmonic nanoantennas

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Abstract

We perform time-resolved fluorescence spectroscopy on clusters of plasmonic nanoantennas covered with a dye–polymer mixture. Dimer antenna structures were fabricated consisting of two interacting gold nanorods with varying lengths and interparticle separation. By combining four individual antennas into a cluster within a diffraction limited spot size, we can couple out half of the dye molecule fluorescence via antenna plasmons. Two-dimensional confocal fluorescence lifetime scans visualize the spontaneous emission enhancement of the molecular fluorescence around the antenna clusters.

Keywords: Plasmon enhanced; Fluorescence; Nanoantennas

Enhancement of the excitation and emission rates of fluorescent molecules and quantum dots by coupling to well-defined plasmonic nanosystems is currently seeing an enormous activity [1–7]. One can generally find applications in which the local enhancement of an optical pump is important, such as SERS, biosensing, and near-field optics (NSOM). On the other hand, enhancement of spontaneous emission rates via the plasmonic density of states is of importance for the improvement of light-emitting devices. In particular, the improvement of the quantum efficiency via modification of the branching ratio between radiative and nonradiative decay channels leads to more efficient light sources. Enhancement of radiative rates using plasmonic antennas may eventually lead to novel applications in quantum optics, strong coupling, and plasmonic nanolasers.

Here we present confocal fluorescence lifetime imaging experiments of fluorescence emission of a high efficiency dye around resonant metal nanostructures. We use dimer nanoantennas consisting of two adjacent gold nanorods, since these have shown large local field enhancements in the gap between the two nanorods [8]. These local field effects are strongly dependent on both the length of the nanorods and their separation, and are related to standing wave resonances of plasmon polariton modes in the rods [9]. In this study, the plasmon resonance position is tuned to the emission band of the dye molecules, in order to enhance their radiative decay rate and hence the quantum efficiency.

Arrays of nanoantennas have been fabricated using high-resolution e-beam lithography with a 40 kV electron beam lithography system (FEI Company). Fig. 1 shows a typical array, consisting of clusters of four antenna structures in a small submicrometer area. We have chosen for this configuration of four antennas to maximize the amount of dye molecules in a diffraction limited laser spot that will couple to plasmons. In the array, two antenna parameters, namely the antenna arm lengths and gap widths, are varied along the two directions, allowing for a fast exploration of a large parameter space in a single scan. In the SEM image, the metal nanostructures were already covered with a 10-nm layer of silica, which acts as a spacer between the metal and the dye. The first column on the left contains only single nanorods, with the length of the long axis varying from 70 nm (bottom left) to 150 nm (top left). The second to eight columns contain structures where the gap between two adjacent nanorods has not opened up; these were designed with too narrow gaps for the e-beam writing. The magnified part of the array shown in Fig. 1(b) shows the transition from interconnected nanorods to dimer antennas with a gap Δ of 20 nm. Columns 9–14 of Fig. 1(a)

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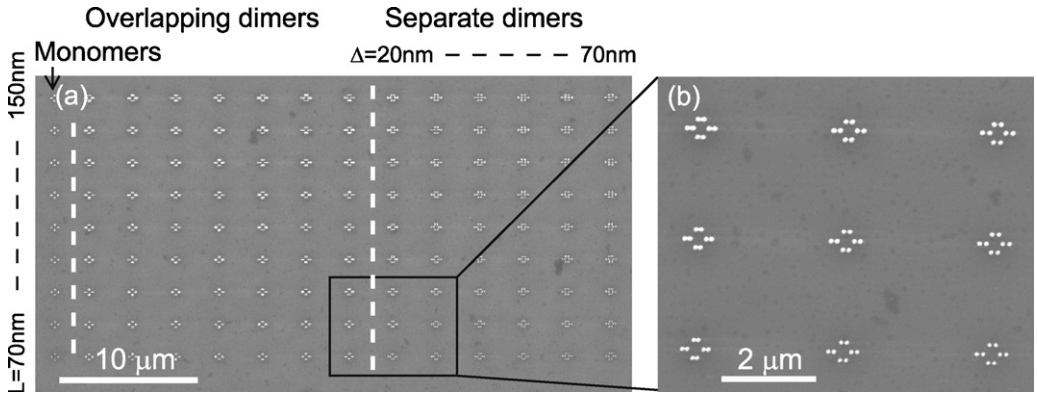

Fig. 1. SEM image of a nanoantenna array with varied antenna arm lengths (vertical) and antenna gaps (horizontal), with detailed images of several single nanorods and dimer antennas.

contain dimers with gap spacings varying from 20 nm up to 70 nm.

After deposition of the sol–gel silica spacer layer, a 10-nm layer of polymer–dye mixture was spincoated. As a dye we use Atto680 (Attotec GmbH), which is a highly photostable, water soluble dye with specified quantum efficiency in water of 30%, combined with a decay time of 1.8 ns, and values in ethanol of 40% and 3.4 ns, respectively. The decay time in the spin-coated thin-film was measured to be 3.3 ±0.1 ns, from which we estimate a corresponding quantum efficiency of 40%.

Fluorescence lifetime imaging (FLIM) was performed using an optical microscope equipped with laser-scanning confocal scanning head (Nikon) synchronized to a commercial picosecond FLIM system (Picoquant). In this configuration, both the pump and the detection foci are scanned synchronously over the sample using a galvanometric scanning mirror pair, as shown schematically in Fig. 2. [10] Fluorescence photons are detected, after confocal filtering, by means of a fast silicon avalanche photodetector. The arrival time of the photons is measured using a time-to-amplitude convertor. The confocal scanning microscope is optimized to work at high frame rates, limiting the pixel dwell time per pass to 64 μs. The FLIM acquisition system continuously synchronizes the arriving photons with the scanning system to allow a 2D image to be built up over subsequent confocal scans. Given the obtained fluorescence count rates of around 20 kcts/s, an integration time of 10 ms per pixel was sufficient for a lifetime analysis. As a pump we use ∼150 ps pulses from a pulsed diode laser operating at 5 MHz. The laser is polarized using a linear polarizer and focused using a 100 ×, N.A. = 0.9 microscope objective. Fluorescence photons are collected using the same objective; different polarizations of the emitted light are selected using a polarization filter before the detector. The time resolution is limited by the combination of pump laser and detection electronics to 0.3 ns. We did not use any deconvolution on the fluorescence decay curves, since this would only be reliable at very high signal-to-noise ratios above our current levels.

The collected lifetime images are analyzed using double-exponential decay fits, as shown in Fig. 2. We choose this approach since we found a considerable background of dye molecules in the diffraction limited volume that does not couple to the nanoantenna structures. This background component is

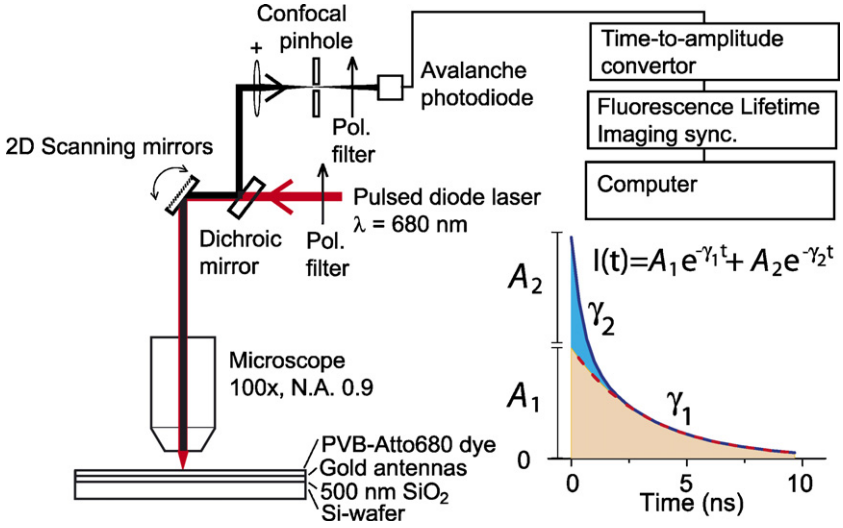

Fig. 2. Experimental setup for confocal fluorescence lifetime imaging, using a pulsed pump laser at λ = 660 nm, a picosecond time-to-amplitude convertor (Picoquant) synchronized with a laser-scanning confocal microscope (Nikon). Inset: illustration of the double-exponential analysis of the time-resolved fluorescence decay, shown amplitudes A_1, A_2 and decay rates γ_1, γ_2, for the slow and fast contributions, respectively.