Advances in Nanophotonics: Ultrafast & Ultrasensitive

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Abstract: In this tutorial on **NanoPhotonics** recent advances are highlighted with focus on near field optical methods, ultra-fast probing of single molecules and ultra-sensitive detection of individual non-fluorescent nanoparticles.

OCIS codes: 180.5810 Scanning microscopy; 140.7090 Ultrafast lasers

1. Introduction

Rapid advances in *NanoPhotonics* now allow the exploration and manipulation of light in and around nanostructures, single molecules, molecular complexes, etc. Indeed by proper control on the nm-scale sub-wavelength light fields are being created and detected, where large (imaginary) wave vectors dominate, resulting in strong field confinement, sharp field gradients, photon tunneling, (plasmonic) resonances, extraordinary transmission, etc.

2. Near field probing

The main tool to create and visualize the nanoscale optical fields is near field scanning optical microscopy (NSOM). Two main NSOM approaches are pursued: the traditional aperture on top of a glass fiber, and scatter NSOM, where the field is locally enhanced by sharp metallic tip. For "aperture" NSOM throughput is a limiting factor: smaller apertures give a large decrease in output power density, limiting the response to about 75 nm (figure 1). For scatter NSOM the response can be local within 10 nm, however background from diffraction limited illumination is a problem.

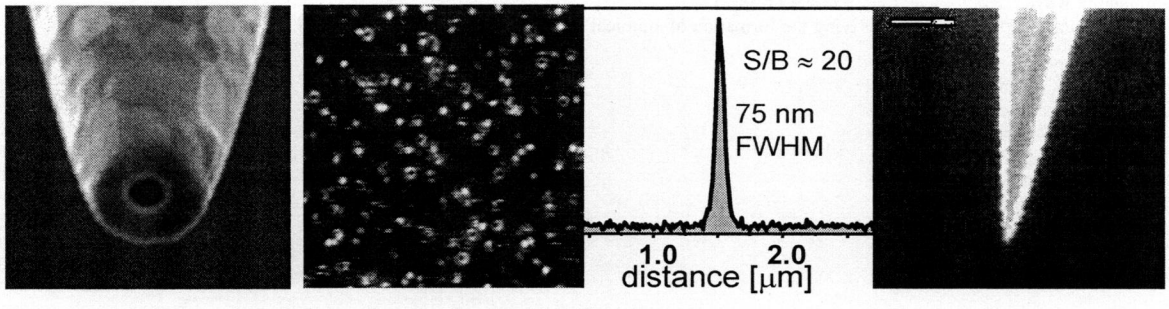

Figure 1. Aperture probe, response of individual fluorescent molecules and a scatter probe.

The current state-of-the-art in near field optical methods will be briefly reviewed, with the emphasis on the detection of single molecules and nanoparticles as the ideal detectors of the local optical field amplitude, the field direction, the mode density and any interaction with the environment.

Surprisingly enough ultrafast fs-ps laser-spectroscopy, one of the major advantages of photonics, has hardly been exploited at the nanometer scale, let alone on single molecules or nanoparticles. Indeed femtosecond nanophotonics is experimentally challenging, but once mastered full of novel promises. Here we will focus on ultra fast single molecule detection.

Detection of nanoparticles is generally restricted to single emitters, i.e. particles with efficient Stokes shifted emission, that allow background free detection. Here we will address new routes towards the background free detection of non-fluorescent nanoparticles.

3. Femtosecond single molecule detection

Single molecules are exquisite sensors for nanoscale chemical influences, conformational changes, photonic density of states etc. Single molecule studies reveal how changes in the local environment lead to wide variations, in both space and time. Whereas nanometric accuracy is obtained using local probes the time resolution is limited to submicroseconds due to the limited photon flux. Still ultrafast processes on femto-and picosecond timescale play a crucial role in the functioning of both natural and synthetic molecular assemblies, such as light harvesting complexes and conjugated polymers. Generally, advanced spectroscopic methods (hole-burning, photon-echo, pump-probe spectroscopy) are invoked to reach into the femtosecond domain.

Here, the first ultrafast experiments on the single molecule level are presented [1], using a novel approach that enhances the fluorescence in a double-pulse excitation scheme (figure 2). From molecule to molecule a wide range of ultrafast relaxation times is measured (from 20 fs up to over a ps, figure 3). A wide range of emitters is investigated: perylenes, carebocyanines, rhodamines, etc.

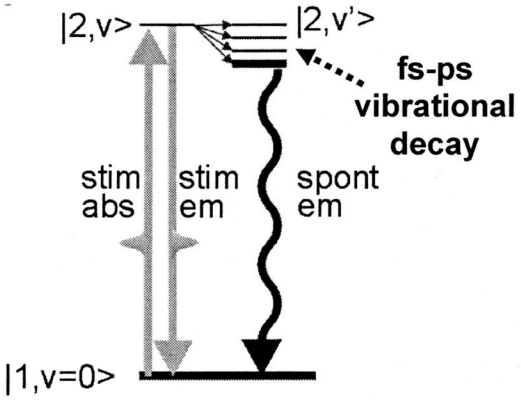

Figure 2.
Simplified three level scheme. The ground state |1, v=0> is coupled to a vibronic excited state (|2,v>) by saturation with a broad band laser pulse. In the absence of other states the balance between stimulated absorption and emission gives equal state probability for both states. However, the excited state |2,v> couples to other vibrational states |2,v'> with sub-picosecond decay time, reducing the stimulated emission by the laser pulse to the ground state, and therefore a new equilibrium between level |1, v=0> and |2,v > will be reached.

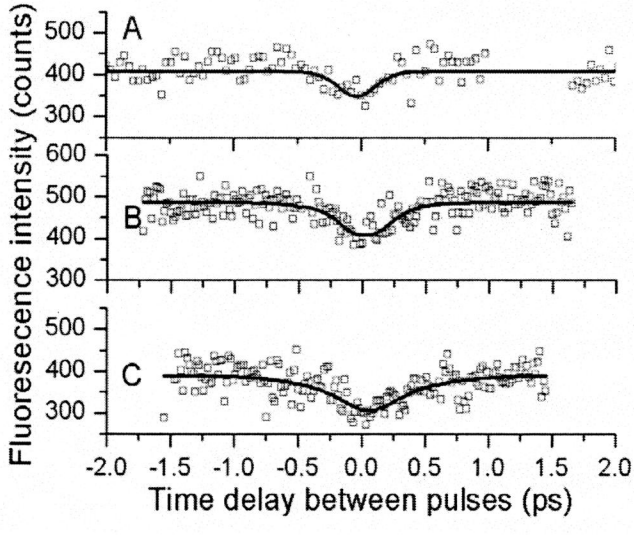

Figure 3.
First femtosecond response of individual molecules: delay traces for three different carbocyanine (DiD) molecules (A, B & C) in a polymer film (PMMA) when scanning the pump-probe delay.
From molecule to molecule different decay times are observed: fitting the data yields 95 ± 50, 160 ± 30 and 350 ± 25 fs, for the molecules A, B and C, respectively.

The main strength of our novel approach is towards ultrafast processes in extended multi-chromophoric molecular assemblies. As a first step in this direction, we have studied excitonically coupled systems consisting of 2 and 3 rigidly linked perylene-diimide units in a head to tail configuration. We observe superradiance and inhibited *intra*molecular decay and reveal discrete jumps in femtosecond response upon break-up of the strong coupling. Recent progress in this ultrafast direction will be discussed.

4. Single nanoparticle detection

The detection of non-fluorescent nanoparticles requires an alternative approach to reduce the enormous resonant background and provide sufficient sensitivity. It is well-known that sensitivity can be dramatically enhanced by heterodyning. The general idea now is that by suitable selection of the polarization states in respectively a signal and a reference branch mainly the signal from the object in the signal branch is amplified, leading to a shot noise limited sensitivity. Moreover both amplitude and phase response are obtained. We have integrated heterodyne detection in a confocal microscope to enable detection of individual particles. Simultaneously the fluorescence of individual particles can still be monitored.
Figure 4 shows a typical result for a sample with gold nano particles. The incident polarization is linear. The image on the left shows the amplitude of the detected signal and the image on the right shows the phase of this signal. It is clear that each gold bead generates the same pattern which is characteristic for a dipole source under given polarization conditions. The amplitude of the signal is comparable for all the features indicating that this is indeed the response of individual particles.

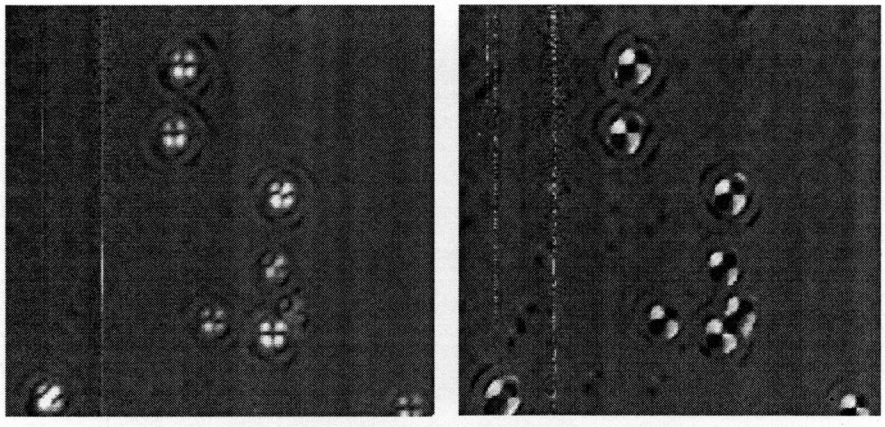

Figure 4. Amplitude (left) and phase(right) reponse of single gold nano particles, Scan range 20 x 20 μm

[1] E.M.P.H. van Dijk, J. Hernando, *et al.* Single-Molecule Pump-Probe Detection Resolves Ultrafast Pathways in Individual and Coupled Quantum Systems, Submitted.