Final report on Project 299600 (1MoleculeNearPlasmon)

Scientist in Charge: Prof. Dr. Michel Orrit

Name of Researcher: Dr. Mathias Müller

Full Title of the project: Single-molecule spectroscopy in the near field of plasmonic metal nanoparticles.

Reporting period: 01/04/2012 – 28/02/2013

In this project we aimed to combine single-molecule fluorescence spectroscopy and plasmonic nanomaterials at cryogenic temperatures. Plasmonic nanomaterials can be used to dramatically enhance the fluorescence of molecular emitters. On the other hand, single-molecule spectroscopy at low temperatures offers the possibility for spectral selection. That means that a large number of molecules (several thousands) can be addressed independently inside a diffraction-limited focal spot by tuning the excitation laser. This opens the possibility to probe the local field enhancement of single plasmonic antennas. Furthermore, measurements of linewidths and saturation curves of single molecules allow discriminating between fluorescence enhancement based on excitation and emission enhancement. In the long run, the local-field maps obtained by the above introduced method could potentially be used to optimize antennas which in turn allow enhancing light-matter interaction.

Since the existing low-temperature confocal microscope in the group was already heavily used by two other projects, we decided to build up an additional low-temperature confocal microscope which shares only the excitation lasers. For the researcher and a PhD-student (Nico Verhart), who started on the same project during the course of the reporting period, this also offered the unique opportunity to get in-depth knowledge of the experimental techniques used in cryogenic single-molecule experiments. In detail, a beam-scanning confocal microscope which enables measurements at temperatures as low as 1.2 K (-271.95 ˚C) was build up. For single-molecule fluorescence experiments the set-up makes use of a single-frequency Ti:Sa laser, whereas for the characterization of plasmonic nanoparticles scattering of white-light in a bright-field geometry or photoluminescence (PL) excited with a 532 nm diode laser can be used.

After the set-up was completed, first test measurements were performed. To test single-molecule fluorescence, we used single-crystalline Anthracene flakes which were doped with a small concentration of Dibenzoterrylene molecules (DBT) by means of co-sublimation. Detection of single DBT molecules at low temperatures was proved to be possible and the results obtained were consistent with earlier experiments performed in the host's group.

Thereafter, we tested the capability of the set-up to detect single plasmonic nanoparticles. For this, we used gold nanorods (Au-NRs) which were first synthesized by wet-chemical synthesis and then spin-coated on glass substrates. In order to perform low-temperature experiments the microscope objective has to be immersed in liquid helium. Highly corrected microscope objectives with high numerical aperture (NA), typically used for these kind of experiments at room temperature, cannot be used at low temperatures due to their mechanical instability. To detect single Au-NRs using poor, but low-temperature compatible, optics turned out to be a challenging task on its own. We circumvented this problem by the use of relatively large Au-NRs (diameter=40 nm, length=84 nm) which could be detected in PL and scattering.

Further challenges occurred when we tried to combine single-molecule systems and gold nanorods. The difficulty was to establish a contact on the nanoscale between these two material systems. In order to solve this issue, it became necessary to investigate a number of new molecular host-guest systems for single-molecule spectroscopy, which are expected to be more feasible for the mechanical combination with gold nanorods. After exploring different possibilities, we found the combination of para-dichlorobenzene (pDCB) and Dibenzoterrylene (DBT) to be most promising. We could show that this system features stable, bright and narrow molecular lines as required for this project, while mechanical combination with other small objects, e.g. plasmonic structures or waveguides is easily doable.

During the end phase of this project, we combined this new molecular system with gold nanorods and tried to measure the fluorescence enhancement expected for molecules close to the tip of gold nanorods. So far, we were not able to observe any fluorescence enhancement. This is most likely caused by the limited solubility of the chromophore (DBT) in the matrix (pDCB) combined with the extremely small volume in which fluorescence enhancement can be expected.

However, we do not see any fundamental reason which prohibits the enhancement of fluorescence at low temperature. This line of research will hence be continued by Nico Verhart, the PhD student who was working together with the researcher in this project.