7. Summary and Outlook

The results of this work can be separated in two parts – the experimental and theoretical assessment of the fluorescence in the vicinity of a flat gold interface, and the surface modification and synthesis of gold nanoparticles and gold nanowires. At the end first steps to a more complex study on the fluorescence intensity near more complex objects as gold nanoparticles were done.

A defined multilayer architecture at the nanometer scale for the study of the fluorescence in the presence of a metal interface was designed and precisely experimentally implemented. An ultrasmooth gold film was used in combination with self-assembled monolayers and layer-by-layer deposition of polyelectrolytes allowing for the separation of fluorescing dyes from a gold interface in a controlled and precise manner. The characteristics (thickness, roughness, optical constants) of the layers were fully analysed by a variety of techniques (Small Angle X-ray Reflectivity, Atomic Force Microscopy, Surface Plasmon Spectroscopy).

In Chapter 4 the behaviour of fluorescing dyes at a planar metal-dielectric interface was investigated in Kretschmann configuration. The fluorescence intensity, angular distribution of the emission, and photobleaching rate of fluorescing molecules placed at different separation distance to the gold interface were experimentally and theoretically evaluated. A perfect correlation between theory and experiment was found for a separation distance larger than 15 nm. Surprisingly, a clear discrepancy between measurement and experiment was determined at very close proximity to the gold layer, though experiments on the excitation lifetime of europium complex conducted by other researchers showed very good correlation to the theory. In order to clarify that, the problem was addressed on single molecule level which confirmed the results with an ensemble of molecules. One speculation on the reason for the discrepancy between the results described here and others results may imply that this is due to the stronger oscillator strength of fluorophore used in the current study (compared to the Europium complex which is phosphorescent) which leads to stronger interaction with the gold interface. Another reason could be the ultrasmooth gold interface used in experiments described here, since it is known that rough metal surfaces can lead to enhancement of the fluorescence. Moreover, it is known that the very elegant Langmuir-Blodgett deposition technique used in the experiments before, often leads to films with pinholes, defects and domains which will be a reason for inhomogeneous distribution of the dye in vertical direction. Although, the complete understanding of the effects described above might need further experimental and theoretical
attention, this study is a significant contribution to the application of Surface Plasmon Fluorescence Spectroscopy as an analytical tool for detection of surface recognition reactions as well as in all processes were a fluorescing dye is used with a metal interface.

The second part of this work was dedicated to gold nanoparticles and gold nanowires (Chapter 5). Firstly, the undefined shell of physically adsorbed ions on the surface of citrate reduced gold nanoparticles was exchanged by a self-assembled monolayer of 2-mercaptosuccinic acid. Series of comparative tests unambiguously proved a successful surface modification expressed in a better pH stability and cyanide dissolution resistance. Then a new route for the synthesis of monolayer protected gold nanoparticles with size above 10 nm was established. The syntheses were conducted in aqueous medium as only HAuCl₄ and 2-MSA were used, without employing any additional reduction agent. This new synthesis can be very useful in cell imaging, DNA labels, catalysts or optical sensors, applications where narrow size distribution is not required. At a particular molar ratio between the reagents this new synthesis resulted in gold nanowires. The synthetic procedure is simple, one step, conducted in aqueous medium and without the use of any additional surfactants. The length of the gold wires is in the order of micrometers and the cross section down to 15 nm. Surface analytical techniques such as SEM, TEM and AFM were used in order to clarify the structure and morphology of the wires. Conductivity measurements of a single wire proved its metallic properties. The suitability of the wires for nanomanipulation as well as the very high current density suggests their usefulness for application in nanoelectronic devises. The synthesis of nanowires in solution is also interesting from a point of view to reaching the gram scale production and their use as fillers, since the production of a composite conducting material will require 10 times less material if metal particles are exchanged with wires.

Pursuing the ultimate goal, or the behaviour of fluorescing dyes near more complex metal objects, a multilayered architecture involving a gold interface and gold nanoparticles, which were separated by a well defined polymer spacer was constructed. The properties of the system were fully characterized by surface and optical analytical techniques. The optical constants of the gold nanoparticles were found to be strongly dependent on the separation distance to the gold interface.

In an outlook, a next step of research involving the multilayered system described in Chapter 6 could be the deposition of fluorescing dyes around the gold nanoparticles. The plasmon field of the gold nanoparticles, excited by the surface plasmon field of the flat gold interface could lead to a modification of the emission rate of the fluorophore expressed in an enhanced emission. The direct consequence of that could be an improved sensitivity of the
instrument. Another possible variation could be the deposition of a polymer spacer around the gold nanoparticles. This could happen in solution or on surface. Then the influence of the separation distance between the curved interface of the gold nanoparticles and a fluorescing dye can be investigated. Another approach can be the deposition of fluorophore between two gold nanoparticles or a gold nanoparticle and a flat gold interface. In this case the enhanced electromagnetic field between the two metal surfaces will impact on the radiative emission of the dye.

This work is to be understood as a small step toward the understanding of the behaviour of fluorescing species in the vicinity of a metal interface. For complete revealing of the corresponding phenomena more work should be done in the future. Due to its complexity, the research should involve the efforts of interdisciplinary teams composed of scientists with diverse background.